STABILITY AND ELECTRONIC PROPERTIES OF LOW-DIMENSIONAL NANOSTRUCTURES

by

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ABSTRACT

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As the devices used in daily life become smaller and more concentrated, traditional threedimensional (3D) bulk materials have reached their limit in size. Low-dimensional nanomaterials have been attracting more attention in research and getting widely applied in many industrial fields because of their atomic-level size, unique advanced properties, and varied nanostructures. In this thesis, I have studied the stability and mechanical and electronic properties of zerodimensional (0D) structures including carbon fullerenes, nanotori, metallofullerenes and phosphorus fullerenes, one-dimensional (1D) structures including carbon nanotubes and phosphorus nanotubes, as well as two-dimensional (2D) structures including layered transition metal dichalcogenides (TMDs), phosphorene and phosphorus carbide (PC).

I first briefly introduce the scientific background and the motivation of all the work in this thesis. Then the computational techniques, mainly density functional theory (DFT), are reviewed in Chapter 2.

In Chapter 3, I investigate the stability and electronic structure of endohedral rare-earth metallofullerene La@C₆₀ and the trifluoromethylized La@C₆₀(CF₃)_n with $n \leq 5$. Odd n is preferred due to the closed-shell electronic configuration or large HOMO-LUMO gap, which is also meaningful for the separation of C₆₀-based metallofullerenes.

Mechanical and electronic properties of layered materials including TMDs and black phosphorus are studied in Chapter 4 and 5. In Chapter 4, a metallic NbSe₂/semiconducting WSe₂ bilayer is investigated and besides a rigid band shift associated with charge transfer, the presence of NbSe₂ does not modify the electronic structure of WSe₂. Structural similarity and small lattice mismatch results in the heterojunction being capable of efficiently transferring charge across the interface. In Chapter 5, I investigate the dependence of stability and electronic band structure on the in-layer strain in bulk black phosphorus.

In Chapters 6, 7 and 8, novel 2D structures are predicted theoretically. In Chapter 6, I propose two new stable structural phases of layered phosphorus besides the layered α -P (black) and β -P (blue) phosphorus allotropes. A metal-insulator transition caused by inlayer strain or changing the number of layers is found in the new γ -P phase. An unforeseen benefit is the possibility to connect different structural phases at no energy cost, which further leads to a paradigm of constructing very stable, faceted phosphorus nanotube and fullerene structures by laterally joining nanoribbons or patches of different planar phosphorene phases, which is discussed in Chapter 7. In Chapter 8, I propose previously unknown allotropes of PC in the stable shape of an atomically thin layer. Different stable geometries, which result from the competition between *sp*² bonding found in graphitic C and *sp*³ bonding found in black P, display different electronic properties including metallic, semi-metallic with an anisotropic Dirac cone, and direct-gap semiconductors with their gap tunable by in-layer strain.

In Chapter 9, I propose a fast method to determine the local curvature in 2D systems with arbitrary shape. The curvature information, combined with elastic constants obtained for a planar system, provides an accurate estimate of the local stability in the framework of continuum elasticity theory. This approach can be applied to all 2D structures.

Finally, I present general conclusions from the PhD Thesis work in Chapter 10.

To my parents.

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Chapter 1

Introduction

In this thesis, I have studied four different topics related to low-dimensional nanostructures and their associated with stability and electronic properties: stable and extractable metallofullerenes, electronic properties and applications of layered materials, novel two-dimensional (2D) structures, as well as curvature and stability for 2D systems. All these topics are studied to explore the advanced properties of existing nanomaterials and to discover unknown promising nanomaterials, and finally to lead to applications in different fields.

1.1 Stable and extractable metallofullerenes

The discovery of C_{60} in 1985 [1] started the nanotechnology revolution. In the mean time, metallofullerene La C_{60} was also observed in a mass spectrum of the products from laser vaporization of a LaCl₃ impregnated graphite rod [2]. As more endohedral metallofullerens were successfully synthesized [3–6], there have emerged wide applications in different fields, such as solar cells [7,8] and biomedicine [9,10]. However, unlike hollow fullerenes, it is not easy to separate the metallofullerenes except M@C₈₂ from the raw soot containing both hollow fullerenes and metallofullerenes with different sizes [3, 11–14]. The extraction of small metallofullerenes especially for most abundant M@C₆₀, has become a big challenge due to their insolubility in normal fullerene solvents such as toluene and CS₂ [11, 15, 16]. These metallofullerenes are chemically reactive due to their open-shell electronic configurations or small HOMO-LUMO gaps and consequent tendency to form insoluble polymerized solids [17]. Recently, Shinohara's group at Nagoya University reported a new strategy to open the HOMO-LUMO gaps of small metallofullerenes including $M@C_{60}$ and $M@C_{70}$ by trifluoromethylation [18, 19], and a number of trifluoromethylated metallofullerenes have been purified.

In this thesis I investigated the stability and electronic structure of the endohedral rareearth metallofullerene La@C₆₀ and trifluoromethylized La@C₆₀(CF₃)_n with $n \leq 5$. Unlike the trifluoromethyl derivatives of C₆₀, La@C₆₀(CF₃)_n prefers odd numbers of n, due to the 3 extra valence electrons from the encapsuled metal atom La. Calculated electronic eigenstates of molecular orbitals further confirmed that with an odd number n La@C₆₀(CF₃)_n is more stable by forming a closed-shell electronic configuration or large HOMO-LUMO gap, which is also significant for the separation of C₆₀-based metallofullerenes.

1.2 Electronic properties and applications of layered materials

2D materials have been attracting the electronics community's research interest since the successful exfoliation of single-layer graphene from bulk layered graphite [20]. Applications in 2D electronics are limited for graphene due to its zero band gap. Layered transition-metal dichalcogenides (TMDs) have been considered as promising candidates for 2D electronics in the post-graphene era, since the isolation of single-layer molybdenum disulfide (MoS_2) and its application in field-effect transistors [21, 22]. One of the biggest challenges for the fabrication of high-performance electronic devices is the poor contact between metal and the TMD surface [23–26].

In this thesis, in search of an improved strategy to form low-resistance contacts to semiconducting TMDs, I propose to use metallic TMD as 2D/2D drain/source contacts. A metallic NbSe₂/semiconducting WSe₂ bilayer is investigated. Very different from traditional contacts with relatively thick depletion layer, I found that the electronic structure of WSe₂ is not modified by the NbSe₂ layer besides a rigid band shift associated with charge transfer. Since the two TMDs are structurally similar and display only a small lattice mismatch, they form a heterojunction capable of efficiently transferring charge across the interface, thus improving current injection into WSe₂.

Layered black phosphorus has been another promising 2D material since the successful applications of few-layer phosphorene in electronic devices [27, 28]. Bulk black phosphorus has been known for a century [29] and displays an interesting change in its electronic and topological properties under compression [30–32]. Similar to bulk black phosphorus, its band gap displays a strong and anisotropic response to in-layer strain in phosphorene monolayers and few-layer systems [27, 28, 33–38], which is now well established. However, no dependable data are available for the corresponding response in the bulk system.

In this thesis, I investigate the dependence of stability and electronic band structure on the in-layer strain in bulk black phosphorus and found that the strain energy and interlayer spacing display a strong anisotropy with respect to the uniaxial strain direction. The band gap depends sensitively on the in-layer strain and even vanishes at compressive strain values exceeding $\approx 2\%$, thus suggesting a possible application of black P in strain-controlled infrared devices.

1.3 Novel 2D structures

Even though interest in 2D electronics and the family of 2D semiconductors is growing fast, a consensus has not been reached regarding the optimum candidate for channel materials. Semi-metallic graphene, with an excellent carrier mobility, has received the most attention so far, but all attempts to open up a sizeable, robust, and reproducible band gap have failed due to the negative side effects of the different modifications [39–42]. The TMD family, such as MoS₂ [22, 43] has sizeable fundamental band gaps, but lower carrier mobility. Recently isolated few-layer films of black phosphorus, including phosphorene monolayers, combine high carrier mobility with a sizeable and tunable fundamental band gap [27, 28], but have limited stability in air [44]. Novel low-dimensional structures and materials with advanced properties are still desirable.

In this thesis, I propose two new stable structural phases of layered phosphorus besides the layered α -P (black) and β -P (blue) phosphorus [33] allotropes. The possibility to connect these different structural phases at no energy cost further leads to the paradigm of constructing very stable, faceted phosphorus nanotube and fullerene structures by laterally joining nanoribbons or patches of different planar phosphorene phases. I also propose previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer. Different stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, display different electronic properties including metallic, semi-metallic with an anisotropic Dirac cone, and direct-gap semiconductors with their gap tunable by in-layer strain.

1.4 Curvature and stability for 2D systems

One of the most important advantages of 2D systems is mechanical flexibility, which allows tuning of the morphology of the 2D surface. The most prominent example, graphitic carbon, is the structural basis not only of graphene [45], but also fullerenes, nanotubes, tori and schwarzites [46–50]. Even though the structural motif in all of these systems may be the same, their mechanical and electronic properties depend sensitively on the local morphology [51– 53]. On the other hand, *ab initio* calculations are impractical to estimate the global or local stability for very large structures. Empirical rules or parameterized force fields, including the Tersoff potential and molecular mechanics [54–57], have often been used to estimate stability but are sometimes unsatisfactory. Application of continuum elasticity theory, which can describe stability changes due to deviation from planarity, has been successful, but it is limited to systems with a well-defined, constant curvature [58, 59].

Since strain energy is dominated by local geometry and independent of the global morphology, here I propose a fast method to determine the local curvature in 2D systems with arbitrary shape. The curvature information, combined with elastic constants obtained for a planar system, provides an accurate estimate of the local stability in the framework of continuum elasticity theory. This approach can be applied to all 2D structures.

1.5 Outline of the dissertation

This PhD thesis contains 9 chapters, including Chapter 1 as an introductory chapter and Chapter 2 to describe the computational methods used throughout this thesis.

In Chapter 3, I investigated stability and electronic structure of endohedral rare-earth metallofullerene La@C₆₀ and the trifluoromethylized La@C₆₀(CF₃)_n with $n \leq 5$. Preferred

odd number of n are found benefits from the close-shell electronic configuration or large HOMO-LUMO gap, which is also meaningful for the separation of C_{60} -based metallo-fullerenes.

Mechanical and electronic properties of layered materials including TMDs and black phosphorus are studied in Chapter 4 and 5. In Chapter 4, a metallic NbSe₂/semiconducting WSe₂ bilayer is investigated and besides a rigid band shift associated with charge transfer, the presence of NbSe₂ will not modify the electronic structure of WSe₂. Structurally similar and small lattice mismatch result in the heterojunction being capable of efficiently transferring charge across the interface. In Chapter 5, I investigate the dependence of stability and electronic band structure on the in-layer strain in bulk black phosphorus.

In Chapters 6, 7 and 8, novel 2D structures are predicted theoretically. In Chaper 6, I propose two new stable structural phases of layered phosphorus besides the layered α -P (black) and β -P (blue) phosphorus allotropes. Metal-insulator transition caused by in-layer strain or changing the number of layers are found in the new γ -P phase. An unforeseen benefit is the possibility to connect different structural phases at no energy cost, which further leads to a new paradigm in constructing very stable, faceted phosphorus nanotube and fullerene structures by laterally joining nanoribbons or patches of different planar phosphorene phases, which is discussed in Chapter 7. In Chapter 8, I propose previously unknown allotropes of PC in the stable shape of an atomically thin layer. Different stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, display different electronic properties including metallic, semi-metallic with an anisotropic Dirac cone and direct-gap semiconductors with their gap tunable by in-layer strain.

In Chapter 9, I propose a fast method to determine the local curvature in 2D systems

with arbitrary shape. The curvature information, combined with elastic constants obtained for a planar system, provides an accurate estimate of the local stability in the framework of continuum elasticity theory. This approach can be applied to all 2D structures.

Finally in Chapter 10, I provide my conclusions for the whole work of my PhD study.

Chapter 2

Introduction to Density Functional Theory

In this chapter, I will start with the Hartree-Fock (HF) approximation and show the disadvantage of this single-particle approximation. Then I will introduce density functional theory (DFT) which is better method for many materials. I will talk about the Hohenberg-Kohn (HK) theorem, Kohn-Sham (KS) equations, as well as the approximations and methods used in the application of DFT.

2.1 Hartree-Fock approximation

In a complex nanostructure including many atoms and electrons, the Hamiltonian operator of the whole system can be written as:

$$\hat{H} = \sum_{I} -\frac{\hbar^2}{2M} \nabla_{I}^2 + \sum_{i} -\frac{\hbar^2}{2m} \nabla_{i}^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{J}}|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_{\mathbf{i}} - \mathbf{r}_{\mathbf{j}}|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{r}_{\mathbf{i}} - \mathbf{R}_{\mathbf{I}}|}$$
(2.1)

Here, the uppercase indices describe the ions and the lowercase indices describe electrons. The first two terms represent the kinetic energy of the ions and the electrons. The last three terms are, respectively, ion-ion, electron-electron and the electron-ion interactions. $\mathbf{R}_{\mathbf{I}}$ and $\mathbf{R}_{\mathbf{J}}$ denote the ion positions and $\mathbf{r}_{\mathbf{i}}$ and $\mathbf{r}_{\mathbf{j}}$ denote the electron positions. As the nucleus is thousands of times heavier than the electron, the ion motion and the electron motion can be separated by the Born-Oppenheimer approximation [60]. Based on this approximation, the ions can be seen as fixed when considering the electron system. In this case, the Hamiltonian of electrons can be written as

$$\hat{H} = \sum_{i} -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}.$$
(2.2)

To get the states of electrons we need to solve the Schrödinger's equation

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \tag{2.3}$$

In a system including N electrons, the HF approximation assumes that the wave function of the whole system can be written as a Slater determinant

$$\Psi(\mathbf{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(\mathbf{r_1}) & \Phi_1(\mathbf{r_2}) & \cdots & \Phi_1(\mathbf{r_N}) \\ \Phi_2(\mathbf{r_1}) & \Phi_2(\mathbf{r_2}) & \cdots & \Phi_2(\mathbf{r_N}) \\ \vdots & \vdots & \vdots \\ \Phi_N(\mathbf{r_1}) & \Phi_N(\mathbf{r_2}) & \cdots & \Phi_N(\mathbf{r_N}) \end{vmatrix}$$

Here the $\Phi_i(\mathbf{r_j})$ represents the electron orbital *i* at position $\mathbf{r_j}$, and they are orthonormal

$$\int \Phi_i^*(\mathbf{r}) \Phi_j(\mathbf{r}) = \delta_{ij}.$$
(2.4)

.

The last term in Eq. (2.2) represents the periodic potential in a crystal and can be written as

$$V(\mathbf{r}) = \sum_{I} v(\mathbf{r} - \mathbf{R}_{\mathbf{I}}) = -\sum_{I} \frac{Z_{I} e^{2}}{|\mathbf{r} - \mathbf{R}_{\mathbf{I}}|}.$$
(2.5)

The total energy of the system is

$$E = \int \Psi^*(\mathbf{r}) \hat{H} \Psi(\mathbf{r}) d\mathbf{r}.$$
 (2.6)

By substituting the Hamiltonian and wave function into Eq. (2.6), we can get the average energy

$$E = \sum_{i} \int d\mathbf{r} \Phi_{i}^{*}(\mathbf{r}) \left[-\frac{\hbar^{2}}{2m} \nabla^{2} + V(\mathbf{r}) \right] \Phi_{i}(\mathbf{r}) + \frac{1}{2} \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' |\Phi_{i}(\mathbf{r})|^{2} \frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} |\Phi_{j}(\mathbf{r}')|^{2} - \frac{1}{2} \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \Phi_{i}^{*}(\mathbf{r}) \Phi_{j}^{*}(\mathbf{r}') \frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} \Phi_{j}(\mathbf{r}) \Phi_{i}(\mathbf{r}').$$
(2.7)

We can see that if the electrons in the system do not interact with each other, then the energy will only include the first term. Obviously this is not the truth. The second term is the Coulomb interaction between different electrons. The third term describes the exchange interaction between electrons with the same spin. To find the ground state of the system we need to minimize the total energy. We can use the variational principle to do it and find that $\Phi_i(\mathbf{r})$ should satisfy the following equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + \sum_j \int d\mathbf{r}' |\Phi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Phi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \frac{e^2 \Phi_j^*(\mathbf{r}') \Phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \Phi_j(\mathbf{r}) = \epsilon_i \Phi_i(\mathbf{r}).$$
(2.8)

Here we obtained the famous HF equation. Notice that in the second term of the left hand side of the equation the operator is related to the wave function for the electron we consider, so the equation can only be solved in a self consistent way.

The HF method is only an approximation and sometimes does not give a satisfactory result. This is because in HF we assume that the electron wave function can be written as a single Slater determinant, which is wrong. In this way we assume that each electron interacts with an average charge distribution due to the other electrons. This introduces an error in the wave function and the energy of the electrons. The energy error here ignored in HF is called the electron correlation energy. The error sometimes can be rather big and give wrong results.

2.2 Hohenberg-Kohn theorem

Although the HF method has been applied for a long time in solid state physics, it is not a strict theoretical basis for the single-particle approximation of the many-body system. Density functional theory based on the Hohenberg-Kohn theorem [61] and the subsequent Kohn-Sham equations [62] gives strict evidence that the ground state problem of a manybody system can be transformed to a ground state problem of a single quasi-particle problem in an effective external potential. The essential idea of the Hohenberg-Kohn theorem is that in a many-body system, the electron density $\rho(\mathbf{r})$ is the basic variable that determines the physical quantities. In 1964, Hohenberg and Kohn first proved a basic lemma which states that one external potential $V(\mathbf{r})$ on a many-electron system only corresponds to one ground state electronic density $\rho(\mathbf{r})$. With a known $V(\mathbf{r})$, both the ground state wave function and the total energy of the system are decided. In this way, we reach the first Hohenberg-Kohn theorem, which states that the ground-state properties of a many-electron system depend only on the electronic density $\rho(\mathbf{r})$. Thus, in the ground state, it turns out that the total electronic energy of the system can be expressed by a functional of the electronic density $\rho(\mathbf{r})$, including the kinetic energy of electrons $T[\rho]$, the interaction between electrons $V_{ee}[\rho]$, and the interaction with the external potential $V(\mathbf{r})$ as

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \mathrm{d}\mathbf{r} V(\mathbf{r})\rho(\mathbf{r}).$$
(2.9)

The second Hohenberg-Kohn theorem states that the correct ground state density for a system is the one that minimizes the total energy through the functional $E[\rho]$. Once the expression for the kinetic energy $T[\rho]$ and electron-electron interaction energy V_{ee} are known, the ground state electron density ρ and total energy $E[\rho]$ can be calculated based on the variational principle, which minimizes the total energy while keeping the total number of electrons N constant.

2.3 Kohn-Sham equations

The Hohenberg-Kohn theorems justify that the ground-state properties of the system are determined by the functional of the ground state electron density $\rho(\mathbf{r})$. However, as exact expressions for the kinetic energy $T[\rho]$ and electron-electron interaction $V_{ee}[\rho]$ are unknown, it is still unclear how to obtain $E[\rho]$.

Kohn and Sham introduced the idea that the ground state electron density of a manyelectron system can be approximated using contributed by N independent orbitals:

$$\rho(\mathbf{r}) = \sum_{i} \psi_{i}^{*}(\mathbf{r})\psi_{i}(\mathbf{r}).$$
(2.10)

Here $\{\psi_i(\mathbf{r})\}\ (i = 1, 2, \dots, N)$ is a supposedly noninteracting quasi-electron system, which just happens to have the same ground state electron density $\rho(\mathbf{r})$ as the interacting system we are considering here. Since the Hohenberg-Kohn theorem tells us that the ground state properties only depend on $\rho(\mathbf{r})$, we can obtain the ground state properties from this equivalent noninteracting quasi-electron system.

Using the noninteracting quasi-electron wave functions $\psi_i(\mathbf{r})$, we can write down the Coulomb energy (Hartree energy) as

$$V_{H}[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}')$$
$$= \frac{1}{2} \sum_{i,j} \langle \psi_{i} \psi_{j} | \frac{e^{2}}{r_{12}} | \psi_{i} \psi_{j} \rangle, \qquad (2.11)$$

and the kinetic energy for the noninteracting quasi-electron system as

$$T_0[\rho] = \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2\right) \psi_i(\mathbf{r})$$
$$= \sum_i \langle \psi_i | -\frac{\hbar^2}{2m} \nabla^2 | \psi_i \rangle.$$
(2.12)

Then, the ground state energy as a functional of $\rho(\mathbf{r})$ for the system can be rewritten as

$$E_{KS}[\rho, V] = T_0[\rho] + V_H[\rho] + E_{xc}[\rho] + \int \mathrm{d}\mathbf{r} V(\mathbf{r})\rho(\mathbf{r}).$$
(2.13)

Here $E_{xc}[\rho]$ is the term for electron exchange and correlation, which is defined as

$$E_{xc}[\rho] = (T[\rho] - T_0[\rho]) + (V_{ee}[\rho] - V_H[\rho]).$$
(2.14)

It describes the energy caused by the exchange interaction and electron correlation in the electron-electron interaction energy $V_{ee}[\rho]$ after subtracting the Hartree energy; and the difference in the kinetic energy between the interacting electrons and the non-interacting quasi-electrons.

We can use variational method to minimize $E_{KS}[\rho, V]$ by keeping the total number of electrons N unchanged as the constraint condition:

$$N = \int \mathrm{d}\mathbf{r}\rho(\mathbf{r}) = \sum_{i} \langle \psi_{i} | \psi_{i} \rangle.$$
(2.15)

The quasi-electron wave functions $\langle \psi_i | \psi_j \rangle$ are orthonormal. The ground state energy and electron density are decided by the variational extremum of $E_{KS}[\rho, V] - \sum_i (\epsilon_i \langle \psi_i | \psi_i \rangle - 1)$, where ϵ_i are the Lagrange multipliers. Substituting Eq. (2.13) into the variational term and doing the variation with respect to $\langle \psi_i |$, we get

$$<\delta\psi_{i}\left|\frac{\delta T_{0}[\rho]}{\delta\rho} + \frac{\delta V_{H}[\rho]}{\delta\rho} + \frac{\delta E_{xc}[\rho]}{\delta\rho} + V(\mathbf{r}) - \epsilon_{i}\right|\psi_{i} >= 0.$$
(2.16)

The equation is satisfied for arbitrary $\langle \delta \psi_i |$, so the coefficient of $\langle \delta \psi_i |$ should be zero. Then we get

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}).$$
(2.17)

It is very similar to the single-electron equation except V_{eff} is the effective potential and has the form

$$V_{eff}(\mathbf{r}) = \frac{\delta V_H[\rho]}{\delta \rho} + \frac{\delta E_{xc}}{\delta \rho} + V(\mathbf{r}) = V_C(\mathbf{r}) + V_{xc}(\mathbf{r}) + V(\mathbf{r}), \qquad (2.18)$$

$$V_C(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}.$$
(2.19)

Eq. (2.17) describes the motion of a quasi-electron under the effective potential $V_{eff}(\mathbf{r})$. However, this effective potential depends on the ground-state electronic density

$$\rho(\mathbf{r}) = \sum_{i} |\psi_i(\mathbf{r})|^2.$$
(2.20)

Eqs. (2.17) and (2.20) are called Kohn-Sham equations and they need to be solved in a self-consistent way.

This is an important theoretical result because it demonstrates that the ground state problem can be solved by Kohn-Sham self-consistent equations, which describe the motion of single quasi-electrons. However, the electron exchange and correlation part $E_{xc}[\rho]$ and corresponding $V_{xc}[\rho]$ are unknown, and solving the Kohn-Sham equations is still a challenge. Another thing that must be noticed is that the Lagrange multipliers ϵ_i are not the singleelectron energies in the many-body system.

2.4 Exchange-correlation functionals

The application of DFT depends on the choice of the exchange-correlation functional $E_{xc}[\rho]$. To construct suitable forms of the exchange-correlation functionals, approximations at different levels have been made.

The local density approximation (LDA) [62, 63], which is applied for most of the carbon systems in this thesis, is the most straightforward approximation of the exchange-correlation functional where the exchange-correlation energy is a function of the local electron density ρ . The exchange-correlation energy can be written as

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho).$$
(2.21)

Here, $\epsilon_{xc}(\rho)$ is the exchange and correlation energy density of a homogenous electron gas with density ρ . $\epsilon_{xc}(\rho)$ can be further separated into an exchange term and a correlation term

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho). \tag{2.22}$$

In a uniform electron gas, the exchange part is known:

$$\epsilon_x(\rho) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho(\mathbf{r})^{\frac{1}{3}}.$$
(2.23)

The remaining part of ϵ_{xc} , the correlation energy ϵ_c , has been determined by Ceperley and

Alder [63] using quantum Monte Carlo calculations of a uniform electron gas with different densities.

LDA is exact for the uniform electron gas. However, the electron density is not homogenous in real systems. Application of LDA is based on the assumption that the exchangecorrelation energy of the nonuniform system can be obtained approximately by separating the system into infinitely many small portions with constant electron density and by treating these as a locally uniform electron gas of the same density.

LDA provides a good approximation to the exchange-correlation energy when the charge density does not change dramatically. However, ignoring the variation of the electron density will lead to errors especially for systems with significant variations in the electron density. To correct this error, E_{xc} can be considered as a functional of not only the local electron density but also the electron density gradient, which is the essential idea of the so-called generalized gradient approximation (GGA). In GGA, the exchange-correlation energy can be written as

$$E_{xc}^{GGA}[\rho] = \int \mathrm{d}\mathbf{r} f(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})).$$
(2.24)

Here the function $f(\rho, \nabla \rho)$ can have different choices and there are many different GGAs depending on different $f(\rho, \nabla \rho)$. The GGA functional used in this thesis applied to most layered structures is the PBE [64] functional proposed by Perdew, Burke and Ernzerhof in 1996, which is currently the most popular GGA functional.

Although GGAs are sometimes called "nonlocal" functionals, the density and its gradient still supply only local information. Neither LDA and GGA can give a good description for long-range dispersion (or van der Waals (vdW) interaction), which is important layered structures. Various functionals including vdW interaction corrections have been developed recently. In this thesis, the optB86b-vdW [65,66] functional has been used to describe the inter-layer interaction of the layered structures studied. However, the results using vdW-corrected functionals have been shown to depend sensitively on the choice of functionals and cannot compared to quantum Monte Carlo calculations [67] in their ability to correctly describe the physics of the inter-layer interaction.

As discussed above, in the Kohn-Sham equations Eq. (2.17), ϵ_i are Lagrange multipliers and have no particular physical meanings. However, it turns out that while this is strictly approximate, the energy spectrum of ϵ_i often resembles the eigenvalues of electronic states. In addition, there is usually an underestimation of the electronic band gap of semiconductors in both LDA and GGA. Although DFT is not designed to reproduce the band gap in solids, efforts have been made to correct the underestimation of the band gap in LDA and GGA. Hybrid functional methods, which combine partial Hartree-Fock exact exchange with the partial exchange-correlation energy of DFT, have been applied to correctly reproduce the band gap in solids. The mixture of HF, which typically overestimates the band gap, with DFT, which typically underestimates the band gap, usually predicts a reasonable electronic band gap value. In this thesis, the HSE06 hybrid functional approximation introduced by Heyd, Scuseria, and Ernzerhof [68] are used to predict the band gap values of certain systems.

2.5 Basis sets and pseudopotentials

In order to solve the Kohn-Sham equations Eq. (2.17), a preselected basis set $\{\chi_{\nu}(\mathbf{r})\}$ needs to be chosen and then the single quasi-electron wave function $\psi_i(\mathbf{r})$ can be projected to the basis functions:

$$\psi_i(\mathbf{r}) = \sum_{\nu} c_{\nu i} \chi_{\nu}(\mathbf{r}). \tag{2.25}$$

Here $c_{\nu i}$ are the coefficients. Defining

$$f(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}), \qquad (2.26)$$

Eq. (2.17) can be rewritten as

$$f(\mathbf{r})\sum_{\nu}c_{\nu i}\chi_{\nu}(\mathbf{r}) = \epsilon_{i}\sum_{\nu}c_{\nu i}\chi_{\nu}(\mathbf{r}).$$
(2.27)

As the basis functions $\{\chi_{\nu}(\mathbf{r})\}\$ are known, what we need now are just the coefficients $c_{\nu i}$. In this way, the problem can be transformed to a matrix problem, which is much easier to deal with by a computer.

In quantum chemistry, atomic orbitals are usually used as the basis for the molecular orbitals, based on the LCAO-MO approximation, which assumes that the molecular orbitals (MO) are a linear combination of atomic orbitals (LCAO). In physics, plane wave basis sets are also often used in solids. In this thesis, atomic-orbital basis sets are used in DFT as implemented in the SIESTA code [69]. Plane wave basis sets are used in DFT as implemented in the VASP code [70–73].

Since the chemical properties are decided by the valence electrons of each atom, the core electrons have little effect on the properties of solids. Therefore, their effects on the valence electrons can be represented by a pseudopotential, which simplifies the complicated real allelectron potential and reduces the computational effort substantially. There are many different formulas to construct pseudopotentials. In this thesis, norm-conserving pseudopotentials are used in the SIESTA code and projector augmented wave (PAW) pseudopotentials [73,74] are used in the VASP code.
Chapter 3

Stability and electronic structure of $La@C_{60}$ functionalized by CF_3 radicals

This study is a collaboration with Prof. Hisanori Shinohara's group at Nagoya University, Japan.

3.1 Introduction

At the same time as the famous fullerene C_{60} was observed experimentally in 1985 [1], the complexes LaC_{60} and other LaC_{2n} were also found by laser vaporization of a $LaCl_3$ impregnated graphite rod [2]. Later on, more metal and nonmetal atoms encapsuled by fullerenes were synthesised with different methods [3–6,75–78]. Unlike previous expectations, only M@C₈₂-type metallofullerenes were separated from the raw soot containing hollow fullerenes and other metallofullerenes with different sizes [3,11–14]. It has been difficult to extract the most abundant M@C₆₀ and M@C₇₀ metallofullerenes due to their insolubility in normal fullerene solvents such as toluene and CS₂ [11,15,16]. Although several M@C₆₀ metallofullerenes have been extracted by solvents such as pyridine and aniline [16,79–81], purification and isolation of the M@C₆₀ metallofullerenes is still a big challenge since pyridine and aniline are not suitable solvents for HPLC (high-performance liquid chromatography) separation methods [15]. Right now it is still not clear why the M@C60 metallofullerenes behave so differently from M@C82, which is easy to extract and isolate.

Recently, Wang et al. reported a new strategy to isolate small metallofullerenes including $M@C_{60}$ and $M@C_{70}$ by trifluoromethylation [18, 19]. The key point here is that the small metallofullerenes with open-shell electronic configurations are chemically unstable [17] and this can be solved by trifluoromethylation.

In this chapter I investigated stability and electronic structure of endohedral rare-earth metallofullerene La@C₆₀ and the trifluoromethylized La@C₆₀(CF₃)_n. Isomers with trifluoromethyls at different sites on the C₆₀ are calculated by *ab initio* Density Functional Theory and the most stable isomers for $2 \le n \le 5$ are identified. Unlike the trifluoromethyl derivatives of C₆₀, La@C₆₀(CF₃)_n prefers odd numbers of n, due to the 3 extra valence electrons from the encapsuled metal La. Calculated electronic eigenstates of molecular orbitals further confirmed that with an odd number $n \text{ La}@C_{60}(CF_3)_n$ is more stable by forming a close-shell electronic configuration or large gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which is also relevant for the separation of C₆₀-based metallofullerenes.

3.2 Computational methods

I utilize *ab initio* density functional theory (DFT) as implemented in the VASP code [70–72] to obtain the optimized structure and energy of the endohedral metallofullerene, as well as the electronic structure. I used projector-augmented-wave (PAW) pseudopotentials [82] and the Perdew-Burke-Ernzerhof (PBE) [64] exchange-correlation functionals. All isolated structures have been represented using periodic boundary conditions and separated by a 12 Å thick vacuum region. I used 500 eV as the electronic kinetic energy cutoff for the plane-wave basis



Figure 3.1: Ball-and-stick model of the optimized structure of the most stable isomers of La@C₆₀(CF₃)_n for (a) n = 0, (b) n = 1, (c) n = 2, (d) n = 3, (e) n = 4, (f) n = 5.

and a total energy difference between subsequent iterations below 10^{-5} eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method [83] until none of the residual Hellmann-Feynman forces exceeded 10^{-2} eV/Å.

3.3 Results and discussion

The equilibrium geometry of La@C₆₀ and La@C₆₀(CF₃)_n for $n \leq 5$ as determined by DFT-PBE calculation are shown in Fig. 3.1. For $n \geq 2$, the trifluoromethyls can have more than one configuration on the C₆₀ surface. Many different isomers for n from 2 to 5 are calculated and the detailed results are discussed in Appendix A. Here I show the most stable isomers for n from 2 to 5 in Fig. 3.1(c)-(f). I can see that for n = 2 and n = 3, the trifluoromethyls prefer to be close to each other with a separation distance of para-position in one hexagon (third nearest neighbor) on the surface of fullerene. For n = 4 the trifluoromethyls are separated into two para-(CF₃)₂ pairs, and for n = 5 it prefers one CF₃ separated from the



Figure 3.2: Energy change ΔE^t based on DFT-PBE for attaching one trifluoromethyl of different La@C₆₀(CF₃)_n isomers. Here ΔE^t is defined as $\Delta E^t(n) = E_{tot}(n) - E_{tot}^{min}(n-1) - 1/2E_{tot}((CF_3)_2)$. $E_{tot}^{min}(n)$ is the total energy for the most stable isomer of La@C₆₀(CF₃)_n, which are indicated by the larger symbols in green.

other para- $(CF_3)_4$ group. I also noticed that for n = 3 and n = 4, the most stable isomers have C_{2v} symmetry, as shown in Fig. 3.1(d) and (e).

The Bader charge analysis [84–87] is performed and about 1.8 electrons are found to be transferred from the La atom to the cage for all the molecules shown in Fig. 3.1. An average off-center distance of about 1.2 Å for the La atom is found, and an average energy of about 3.3 eV is gained by moving the La atom from the center to the optimized position. This can be simply interpreted as the electrostatic polarization energy of the model with a point charge inside a thin metallic spherical shell, which has been successfully applied for metallofullerenes before [88,89]. Using the 3.5 Å radius of C₆₀ as the radius of the shell, I obtained an energy gain of 1.7 eV, which is the same order as the value obtained by DFT calculation.

To find out the preferential number of trifluoromethyls attached on the La@C₆₀, I calculated the energy change ΔE^t for attaching one trifluoromethyl of La@C₆₀(CF₃)_n by DFT-



Figure 3.3: Hydrogenated La@C₆₀(CF₃)_n for (a) n = 0, n = 1 with hydrogen and trifluoromethyl at (b) para-position and (c) ortho-position in a hexagon. The first row is the ball-and-stick model of the structures without La atom inside the cage and the second row is the structures with La atom inside the cage. The last row is the corresponding Schlegel diagram of C₆₀ with hydrogen site indicated by blue dot and trifluoromethyl site by red. ΔE^H here is defined as $\Delta E^H = E_{tot}(\text{La@C}_{60}(\text{CF}_3)_n-\text{H}) - E_{tot}(\text{La@C}_{60}(\text{CF}_3)_n) - 1/2E_{tot}(\text{H}_2)$, or $\Delta E^H = E_{tot}(\text{C}_{60}(\text{CF}_3)_n-\text{H}) - E_{tot}(\text{C}_{60}(\text{CF}_3)_n) - 1/2E_{tot}(\text{H}_2)$ for that without La atom inside.

PBE. The specific definition for ΔE^t as a function of n is $\Delta E^t(n) = E_{tot}(n) - E_{tot}^{min}(n-1) - 1/2E_{tot}((CF_3)_2)$. Here $E_{tot}^{min}(n)$ is the total energy for the most stable isomer of La@C₆₀(CF₃)_n. The negative value of ΔE^t indicates an exothermic reaction for adsorbing one CF₃ radical from a hexafluoroethane molecule. The lower ΔE^t is, the more stable the structure would be. According to the results plotted in Fig. 3.2, I find that there can be an energy difference of as much as 3 eV for different isomers with the same n. Comparing the most stable isomers, I see that, in general, La@C₆₀ molecules prefer to have an odd number

of CF₃s. Three is the indicated best number of attached CF₃s on La@C₆₀, which has the lowest ΔE of -0.44 eV. n = 4 has the highest ΔE of -0.11. eV, 0.33 eV higher than n = 3. This result is consistent with previous work on M@C₇₀ molecules [18, 19]. However, this is contrary to the hollow fullerenes, which prefer even number of attached CF₃s [90, 91]. It is easy to understand that on a hollow fullerene, when adding CF₃s, the C-C double bonds of the fullerene need to be broken and the C atom where CF₃ is attached will change to a sp³ bonding from the original sp² bonding. In that case, an odd number of CF₃ radicals attached must produce one C radical on the fullerene surface, which is unstable. This difference is caused by the encapsuled metal atom La, which has three valence electrons. The odd number of extra free electrons will try to transfer to the cage and modify the electronic environment of the surface, which consequently results in a preference for an odd number of attached CF₃s.

To further investigate the influence of the encapsulated La atom in La@C₆₀(CF₃)_n molecules on the cage surface, I calculated the hydrogenation process of La@C₆₀(CF₃)_n molecules with and without La inside for n = 0 and n = 1. The energy change ΔE^H for adsorbing one hydrogen atom from a hydrogen molecule on La@C₆₀(CF₃)_n was calculated. The results are shown in Fig. 3.3. The specific definition for ΔE^H here is $\Delta E^H = E_{tot}(\text{La@C}_{60}(\text{CF}_3)_n\text{-H}) - E_{tot}(\text{La@C}_{60}(\text{CF}_3)_n) - 1/2E_{tot}(\text{H}_2)$ for molecules with La encaplsuled or $\Delta E^H = E_{tot}(\text{C}_{60}(\text{CF}_3)_n\text{-H}) - E_{tot}(\text{C}_{60}(\text{CF}_3)_n) - 1/2E_{tot}(\text{H}_2)$ for those without La atom. From the first row of Fig. 3.3 I can see that for the hollow fullerene C₆₀-H, I obtained a positive value of 0.205 eV for ΔE^H , which indicates a endothermic process. Similar as previously discussed for trifluoromethyls, the attached H atom must break one double bond on C₆₀ and change the original sp² C atom where H is attached to sp³. Then the C atom on the other end of the original double bond will have an unpaired electron left and cause instability. This is consistent with previous work on hydrogenation of carbon nanotubes and fullerenes [92,93]. However, for the $C_{60}(CF_3)$ -H molecule, the attached H atom and CF₃ radical can fill the two unstable sites with unpaired electrons caused by breaking one double bond. I got negative values for both the H and CF₃ in a para arrangement (-0.807 eV) and an ortho arrangement (-1.083 eV) on the C₆₀ surface. A lower value of ΔE^H is obtained for the ortho arrangement where H and CF₃ are attached to the two ends of a double bond on C₆₀, which can easily be seen in the Schlegel diagram shown in the last row of Fig. 3.3.

The situation will be totally different when a La atom is encapsulated. As shown in the second row of Fig. 3.3, I always get negative ΔE^H regardless of whether or where the CF₃ is attached. The extra three free electrons coming from the valence electrons of La change the electronic environment on the surface of the whole molecule and make it always favorable to adsorb H atoms. The difference of ΔE^H for La@C₆₀(CF₃)-H and La@C₆₀-H is about 0.1 eV (from -0.485 eV to -0.592 eV and -0.332 eV), which is much smaller than the ≥ 1.0 eV change (from 0.205 eV to -0.807 eV and -1.083 eV) in the absence of encapsulated La. Moreover, for La@C₆₀(CF₃)-H, the H and CF₃ no longer like the ortho arrangement on the ends of a broken double bond but prefer the para arrangement, which is the optimized arrangement for La@C₆₀(CF₃)₂ as shown in Fig. 3.1(c). The result of the comparison of hydrogenation for the metallofullerenes with La encapsuled and hollow fullerenes confirms that the La atom is the key factor for why La@C₆₀(CF₃)_n prefers an odd number n rather than the even n, which is preferred for hollow C₆₀. The three valence electrons of La also agree well with three being the best number n.

Since the electronic strucures will significantly affect the chemical stability of the metallofullerene molecules, I calculated the electronic eigenstates of C_{60} and $La@C_{60}(CF_3)_n$



Figure 3.4: Electronic eigenstates for molecular orbitals based on DFT-PBE of (a) C_{60} and $La@C_{60}(CF_3)_n$ with (b) n = 0,(c) n = 1, (d) n = 2, (e) n = 3, (f) n = 4, (g) n = 5. The LUMO and HOMO of C_{60} and the corresponding states in $La@C_{60}$ are indicated in red and orange squares, respectively, in (a) and (b).

molecules with *n* from 0 to 5 at the DFT-PBE level and show the results in Fig. 3.4. In Fig. 3.4(a), I show the molecular states of C_{60} . It has a wide gap of 1.6 eV. The HOMO (in orange dashed square) is five-fold degenerate, and the LUMO (in red dashed square) is three-fold degenerate due to the high symmetry of C_{60} . In comparison, in Fig. 3.4(b) I see that for La@C₆₀, since the symmetry of C₆₀ is broken by the encapsulated La atom, the five-fold degenerate HOMO in C₆₀ splits into two doubly degenerate states and one separate state, which are very close to each other (shown in orange square). The three-fold degenerate LUMO in C₆₀ splits into a doubly degenerate state and a separate state about 0.2 eV higher in energy (shown in the red square). La@C₆₀ displays metallic character with the Fermi level lying on the doubly degenerate state which used to be the LUMO in C₆₀. This is due to the three valence electrons from La partly occupying the doubly degenerate state.

For La@C₆₀(CF₃)_n when $n \ge 1$, the eigenstates change a lot due to the attached CF₃s and I cannot distinguish the original HOMO and LUMO in C₆₀ any more. The most important thing I find is that for even n I always get a metallic character with the Fermi level on a partly filled state, as shown in Fig. 3.4(b), (d), and (f). On the other hand, for odd n I always get a non-zero gap, as shown in Fig. 3.4(c), (e), and (g). This also agrees with previous discussions that odd n is preferred, since structures with a non-zero gap are chemically more stable than those with no gap. I also found that La@C₆₀(CF₃)_n molecules with larger n will have a larger gap. Therefore for odd number of n, n = 5 with a gap of 1.0 eV should be the most chemically stable, followed by n = 3 with a gap of 0.7 eV. n = 1 will be relatively the least stable with a narrow gap of 0.1 eV. I expect that La@C₆₀(CF₃)_n molecules with n = 3 and 5 will be easy to separate in experiment since they have relatively large gaps.

3.4 Summary

In summary, I investigated the stability and electronic structure of endohedral rare-earth metallofullerene La@C₆₀ and the trifluoromethylized La@C₆₀(CF₃)_n. Isomers with trifluoromethyls at different sites on the C₆₀ are calculated using *ab initio* Density Functional Theory, and the most stable isomers for $2 \le n \le 5$ are identified. Unlike the trifluoromethyl derivatives of C₆₀, La@C₆₀(CF₃)_n prefers odd n, due to the 3 extra valence electrons from the encapsuled metal La. Calculated electronic eigenstates of molecular orbitals further confirmed that with an odd n La@C₆₀(CF₃)_n is more stable due to formation of a closed-shell electronic configuration or large HOMO-LUMO gap, which is also relevant for the separation of C₆₀-based metallofullerenes.

Chapter 4

Electronic structure and charge injection across transition metal dichalcogenide heterojunctions

This study is a collaboration with Prof. Zhixian Zhou's group at Wayne State University.

4.1 Introduction

Since the successful isolation of single-layer molybdenum disulfide (MoS₂) and its application in field-effect transistors [21,22], layered transition-metal dichalcogenides (TMDs) have been considered as promising candidates for two-dimensional (2D) electronics and optoelectronics applications [94–112]. Even though much effort has been devoted to the fabrication of highperformance electronic devices, the device performance typically suffers from inadequate electrical contacts caused by significant Schottky barriers (SB) between the contact metal and the TMD [23–26]. Local doping near the metal-semiconductor interface, which has been successfully used in traditional three-dimensional (3D) silicon-based devices, cannot be easily realized in 2D cases [113–117]. Metal electrodes with a proper work function and Fermi level close to the conduction band minimum (CBM) or valence band maximum (VBM) are expected to have a lower Schottky barrier height (SBH) and to decrease the contact resistance [118–121]. However, the complex Fermi level pinning at the electrodesemiconductor interface makes Ohmic contacts rather difficult to achieve [122–124]. The metal-TMD interface and thus the extent of Fermi level pinning is highly sensitive to the processing environment and the crystalline order in TMDs [125,126]. Several other strategies to reduce the contact resistance have been proposed and used, such as in-layer junctions obtained by phase engineering [127,128] and 2D/2D inter-layer junctions with weak Fermilevel pinning [129], including hexagonal boron nitride (hBN) [130], graphene [131–134] and doped TMDs [135].

In search of an improved strategy to form low-resistance contacts to semiconducting TMDs, I propose to use metallic TMDs as drain/source contacts. I find the Schottky/tunneling barrier between metallic and semiconducting TMDs is fundamentally different from a conventional metal-semiconductor Schottky barrier for the following important reasons. First, the formation of interface states is suppressed in TMD heterojunctions due to the lack of dangling bonds on TMD surfaces similar to graphene/TMD junctions. Second, an abrupt potential drop, rather than a relatively thick depletion layer, forms across the van der Waals gap of TMD heterojunctions. As a result of these differences, Fermi level pinning is expected to be significantly reduced at metallic and semiconducting TMD interfaces. To validate this behavior, I perform *ab initio* density functional calculations of a NbSe₂/WSe₂ bilayer, consisting of semiconducting WSe₂ and metallic NbSe₂ monolayers. Besides a rigid band shift associated with charge transfer, I find that presence of NbSe₂ does not modify the electronic structure of WSe₂. Since the two transition metal dichalcogenides are structurally similar and display only a small lattice mismatch, they form a heterojunction capable of efficiently transferring charge across the interface, thus improving current injection into WSe₂.

4.2 Computational Methods

Same DFT method as the former chapter is utilized to obtain the optimized structure and electronic properties of WSe₂ and NbSe₂ monolayers, the NbSe₂/WSe₂ bilayer, and the corresponding bulk structures with AB stacking of layers. The two-dimensional (2D) structures are represented by a periodic array of slabs separated by a vacuum region in excess of 15 Å. Besides the Perdew-Burke-Ernzerhof (PBE) [64] exchange-correlation functionals, the optB86b-vdW [65, 66] functional is used to address the weak interlayer interactions. The Brillouin zone of the primitive unit cell of the 2D structures was sampled by $8 \times 8 \times 1 k$ -points and that of bulk structures by $8 \times 8 \times 2$ [136]. A total energy difference between subsequent self-consistency iterations below 10^{-6} eV as the criterion for reaching self-consistency. The other parameters are the same as used before.

4.3 **Results and discussions**

I first optimized the bulk structures of WSe₂ and NbSe₂ in the stable 2H phase. Results of my DFT-optB86b calculations show that the AB layer stacking is energetically favorable compared to the AA stacking in both systems. For bulk NbSe₂, I found that my calculated in-plane lattice constant $a_{theor} = 3.46$ Å lies close to the observed value [137] $a_{expt} = 3.44$ Å and the out-of-plane lattice constant, covering two interlayer distances, is $c_{theor} = 12.74$ Å, close to the observed value [137] $c_{expt} = 12.48$ Å. For bulk WSe₂, I also obtained very good agreement with experiment [138]: $a_{theor} = 3.30$ Å and $a_{expt} = 3.28$ Å for the in-layer lattice constant and $c_{theor} = 13.10$ Å and $c_{expt} = 12.96$ Å for the out-of-plane lattice constant. I notice that the in-layer lattice constant of NbSe₂ is only 5% larger than that of WSe₂ in the bulk, suggesting the likelihood of epitaxial stacking especially in few-layer systems.



Figure 4.1: Ball-and-stick model of the AB-stacked NbSe₂/WSe₂ bilayer in (a) top view and (b) side view. The unit cell is indicated by yellow shading in the top view. $\mathbf{a_1}$ and $\mathbf{a_2}$ are the lattice constants spanning the layers and d is the inter-layer distance.

I also found a preferential AB stacking for the 2H-NbSe₂/2H-WSe₂ bilayer, depicted in Fig. 4.1. The bilayer forms a honeycomb lattice with 6 atoms per unit cell, 3 of which are in the NbSe₂ and the other 3 in the WSe₂ layer. The optimum in-layer lattice constant $a_{theor} =$ 3.37 Å, which lies in-between the values for the individual bulk components. Also the value $d_{theor} = 6.41$ Å for the optimum inter-layer distance lies in-between the corresponding values in bulk NbSe₂ and WSe₂. The binding energy of the two layers is 0.19 eV per unit cell based on DFT-optB86b, indicating a weak interlayer coupling.

Electronic band structure results for the NbSe₂/WSe₂ bilayer and its monolayer components are shown in Fig. 4.2. As seen in Fig. 4.2(a), the NbSe₂/WSe₂ bilayer is metallic. To interpret the band structure of the bilayer, I calculated separately the band structure of isolated NbSe₂ and WSe₂ monolayers and displayed it in Fig. 4.2(b). These results indicate that the NbSe₂ monolayer is metallic, whereas the WSe₂ monolayer is semiconducting with a direct gap of about 1.35 eV at the K point. Even though the absolute value of the band



Figure 4.2: Electronic structure of an $NbSe_2/WSe_2$ bilayer and its decomposition. The band structure of the bilayer in (a) is compared in (b) to a superposition of individual monolayers of $NbSe_2$ (solid red lines) and WSe_2 (dashed green lines). The band structure in (c) is obtained from (b) by shifting the bands of semiconducting WSe_2 rigidly up by 0.293 eV. The resulting band structure is superimposed on that of (a) representing the bilayer.

gap is typically underestimated in DFT calculations, the dispersion of individual bands is typically in good agreement with more adequate self-energy calculations. I found that individual bands in isolated NbSe₂ and WSe₂ monolayers in Fig. 4.2(b) can be identified in the band structure of the bilayer. To prove this point, I superposed the band structure of the two constituent parts, shifting rigidly the bands of WSe₂ up by 0.293 eV. The resulting band structure, presented in Fig. 4.2(c), is finally superposed with that of the bilayer of Fig. 4.2(a). The agreement between the band structure of the bilayer and the superposition of monolayers is near-perfect, suggesting the applicability of a rigid-band model and a small charge transfer between otherwise unaffected NbSe₂ and WSe₂ monolayers.

To better understand the inter-layer interaction in the NbSe₂/WSe₂ bilayer, I calculated the charge density difference $\Delta \rho = \rho_{tot}$ (bilayer) $-\sum \rho_{tot}$ (monolayers) associated with the assembly of the bilayer from isolated monolayers. This charge density difference is visualized by contour plots in Fig. 4.3(a). I find that the charge redistribution is very small, with



Figure 4.3: Charge redistribution $\Delta\rho(\mathbf{r})$ and spatial variation of the electron potential associated with assembling the NbSe₂/WSe₂ bilayer from isolated monolayers. (a) Charge density difference $\Delta\rho = \rho(\text{NbSe}_2/\text{WSe}_2) - \rho(\text{NbSe}_2) - \rho(\text{WSe}_2) \cdot \Delta\rho$ is shown by isosurfaces bounding regions of electron excess (yellow) at $+2.5 \times 10^{-4} \text{ e/Å}^3$ and electron deficiency (blue) at $-2.5 \times 10^{-4} \text{ e/Å}^3$. (b) $\langle \Delta\rho(z/c) \rangle$ averaged across the x - y plane of the layers. The raw data, shown by the red solid line, have been convoluted by a Gaussian with a full-width at half-maximum $\Delta(z/c) = 0.17$, shown by the blue dashed line. (c) Electrostatic potential $\langle V(z/c) \rangle$ averaged across the x - y plane of the layers. z/c indicates the relative position of the plane within the unit cell.

electrons transferring mainly from the WSe₂ layer to the inter-layer region and to the NbSe₂ layer. To further elucidate the charge redistribution, I averaged the charge density difference in planes with constant z that are parallel to the NbSe₂ and WSe₂ layers. The averaged quantity $\langle \Delta \rho(z/c) \rangle$, shown by the solid line in Fig. 4.3(b), displays many oscillations even in individual TMD layers. To better understand the net charge flow, I convoluted the raw data by a Gaussian with a full-width at half-maximum of 0.17. The resulting function, displayed by the blue dashed line in Fig. 4.3(b), indicates a very small net flow of electrons from the WSe₂ layer to the NbSe₂ layer. This result is consistent with the upward shift of WSe₂ bands discussed in relation to Fig. 4.2(c). What I found here agreed with previous work on the VS₂/MoS₂ bilayer system [129]. As a more quantitative measure of the charge redistribution, I performed a Bader charge analysis [84-87] in the NbSe₂/WSe₂ bilayer and found that 0.017 electrons per unit cell are transferred from the WSe₂ to the NbSe₂ layer.

Since charge injection across the interface is modulated by potential barriers, which appear as tunnel or Schottky barriers, I also investigated the local electrostatic potential Vin the whole NbSe₂/WSe₂ bilayer region. For easy interpretation, I averaged V in constant z planes, similar to $\Delta \rho(z/c)$ in Fig. 4.3(b), and present results for $\langle V(z/c) \rangle$ in Fig. 4.3(c). The difference between the electrostatic potential in the vacuum region and the Fermi level, observed at $V(vac.) - E_F \approx 5.6$ eV, corresponds to the work function. I also observe a narrow Schottky barrier characterized by $\Delta(z) \approx 3.4$ Å and $\Delta V \approx 14$ eV when measured from the bottom of the closest potential well. For electrons at the Fermi level, the effective barrier to tunnel through reduces to one third of ΔV and the barrier thickness reduces $\Delta(z)$ by more than half, thus significantly increasing the probability of tunneling across the interface [119].

4.4 Summary

In summary, I performed *ab initio* density functional calculations of a NbSe₂/WSe₂ bilayer, consisting of semiconducting WSe₂ and metallic NbSe₂ monolayers. This system can be considered a heterojunction between two related materials and may be viewed as a new paradigm for high-transparency metal contacts to transition metal dichalcogenides. Besides a rigid band shift associated with a small electron transfer from NbSe₂ to WSe₂, I find that the presence of NbSe₂ does not modify the electronic structure of the semiconducting channel. Since the two transition metal dichalcogenides are structurally similar and display only a small lattice mismatch, their heterojunction is capable of efficiently transferring charge across the interface, thus improving on current metal contacts to WSe₂.

Chapter 5

Structure and electronic properties of strained bulk black phosphorus

The following discussion is my original contribution to the related publication by Jie Guan, Wenshen Song, Li Yang and David Tománek, Phys. Rev. B **94**, 045414 (2016) [139]. This study is a collaboration with Prof. Li Yang's group at Washington University in St.Louis.

5.1 Introduction

Layered bulk black phosphorus (BP), discovered only one century ago [29, 140], is a directgap semiconductor with an observed fundamental band gap [141–144] of 0.31 - 0.36 eV. The electronic response distinguishes BP as favorable from other well-studied layered systems including semimetallic graphite and transition metal dichalcogenides (TMDs) such as MoS₂, which are indirect-gap semiconductors. Under compression, bulk BP displays an interesting change in its electronic and topological properties [30–32]. Similar to bulk BP but a much wider direct fundamental band gap is found in phosphorene monolayers and few-layer systems, suggesting promising applications in 2D semiconductor electronics [27,28,33]. Whereas it is now well established that the gap displays a strong and anisotropic response to in-layer strain in phosphorene monolayers and few-layer systems [27,28,33–38], no dependable data are available for the corresponding response in the bulk system. To fill in this missing information, I study theoretically the structural and electronic response of layered bulk black phosphorus to in-layer strain. My *ab initio* density functional theory (DFT) calculations reveal that the strain energy and interlayer spacing display a strong anisotropy with respect to the uniaxial strain direction. To correctly describe the dependence of the fundamental band gap on strain, I combined my DFT results with the computationally more involved GW quasiparticle approach, performed by Li Yang's group, which is free of parameters and superior to DFT studies, which are known to underestimate gap energies. I find that the band gap depends sensitively on the in-layer strain and even vanishes at compressive strain values exceeding $\approx 2\%$, thus suggesting a possible application of black P in strain-controlled infrared devices.

5.2 Computational methods

I utilized *ab initio* density functional theory (DFT) as implemented in the SIESTA [69] code to optimize the structure and to determine the structural response to in-plane strain. I used the Perdew-Burke-Ernzerhof (PBE) [64] exchange-correlation functional, norm-conserving Troullier-Martins pseudopotentials [145], and a double- ζ basis including polarization orbitals. Reciprocal space was sampled by a fine grid [136] of $8 \times 8 \times 4$ k-points in the first Brillouin zone of the primitive unit cell containing 8 atoms. I used a mesh cutoff energy of 180 Ry to determine the self-consistent charge density, which provided us with a precision in total energy of ≤ 2 meV/atom. The same conjugate gradient method [83] as former chapters is used in a same accuracy.

DFT calculations are not designed to reproduce the electronic band structure correctly. Even though DFT band structure usually resembles observed results, the fundamental band



Figure 5.1: (a) Ball-and-stick model of the structure of bulk black phosphorus in top and side views. (b) Fractional change of the interlayer distance a_3 as a function of the in-layer strain ϵ along the a_1 and a_2 directions. (c) Dependence of the strain energy ΔE per unit cell on the in-layer strain along the a_1 and a_2 directions.

gap is usually underestimated. The proper way to calculate the band structure without adjustable parameters involves solving the self-energy equation. My collaborators from Washington University in St.Louis perform such calculations using the GW approximation [146] as implemented in the BerkeleyGW package [147], where the dynamical electronic screening is captured by the general plasmon pole model. [146] We chose this state-of-the-art approach to computationally less involved hybrid DFT functionals such as HSE06 [68], which mix Hartree-Fock and DFT-PBE exchange-correlation energies using an adjustable parameter. They use single-shot G_0W_0 calculations with a $14 \times 10 \times 4$ k-point grid, which provides converged results for the self-energies and quasiparticle energy gaps in strained bulk black phosphorus.

5.3 Results and discussion

The optimum structure of bulk black phosphorus, as obtained by DFT-PBE calculations, is shown in Fig. 5.1(a). As seen in the bottom panel, individual layers in the layered structure are not flat due to the non-planar sp^3 hybridization of the P atoms. The AB stacking is caused by displacing every other layer along the \vec{a}_2 -direction, yielding an orthorhombic lattice spanned by the orthogonal lattice vectors \vec{a}_1 , \vec{a}_2 and \vec{a}_3 , with \vec{a}_3 extending over two inter-layer distances. The covalent in-plane bonding is adequately described by DFT-PBE, as suggested by the agreement between the calculated lattice constants, $a_1(\text{PBE}) =$ 4.53 Å and $a_2(\text{PBE}) = 3.36$ Å, and the experimental values [148] $a_1(\text{expt}) = 4.38$ Å and $a_2(\text{expt}) = 3.31$ Å. As indicated by recent Quantum Monte Carlo studies [67], the nature of the weak inter-layer interaction in bulk black phosphorus differs in a non-trivial manner from a van der Waals interaction. In view of this fact, the calculated value of the out-ofplane lattice constant $a_3(\text{PBE}) = 11.15$ Å agrees rather well with the observed value [148] $a_3(\text{expt}) = 10.50$ Å.

As a result of the weak inter-layer interaction contrasting the strong in-layer covalent bonding, I do not expect the interlayer distance to change much when the lattice is subjected to in-layer strain. I considered both tensile and compressive in-layer strain ϵ up to 2%. Results for the fractional change $\Delta a_3/a_3$ for different strain combinations $\epsilon(a_1), \epsilon(a_2)$ are presented in Fig. 5.1(b). The continuous contour plot is based on a cubic spline interpolation of a 5×5 grid of data points for different strain value combinations. These results, as well as my findings, suggest that the interlayer spacing changes much less than 1% for the strain range considered here. Such small changes in the interlayer distance are unlikely to be affected by the choice of the total energy functional, which plays only a minor role in the interlayer separation [67] and are consistent with very weakly coupled layers.

My results in Fig. 5.1(b) indicate a trend that the inter-layer distance increases by stretching and decreases by compressing the crystal along the soft, accordion-like a_1 direction. In contrast, both stretching and compression along the stiffer a_2 direction cause a reduction of the inter-layer spacing. Even though these effects are small, they clearly reflect the anisotropy of the system. They translate to a very small negative Poisson ratio between the soft $\vec{a_1}$ in-layer direction and the $\vec{a_3}$ direction normal to the layers. The Poisson ratio between the hard $\vec{a_2}$ in-layer direction and the $\vec{a_3}$ direction is also very small in magnitude, but changes sign near $a_2 = 0$. This definition of the Poisson ratio in the bulk differs from the "Poisson ratio" in a phosphorene monolayer, which relates the monolayer thickness to the in-layer strain and finds a negative value for that quantity [149].

With the optimum value of the inter-layer spacing $a_{3,opt}(a_1, a_2)$ for the different strain combinations at hand, I have calculated the strain energy ΔE as a function of $\epsilon(a_1)$ and $\epsilon(a_2)$ and present the results in Fig. 5.1(c). The prominently elliptical shape of the isoenergetic contours is another manifestation of the elastic anisotropy in the system. The observed tilt of the elliptical axes from the horizontal and vertical direction indicates a positive Poisson ratio $\nu_{21} = -d\epsilon(a_2)/d\epsilon(a_1) = 0.19$ within the phosphorene plane, indicating that stretching in one (in-plane) direction results in a lattice contraction in the normal (in-plane) direction. I find the lattice to be rather soft with respect to in-plane compression, since stretching by 2% even along the stiffer a_2 direction requires an energy investment of only ≈ 0.06 eV per unit cell.

Results of my calculations for the electronic band structure and density of states (DOS) of unstrained and strained bulk black phosphorus are shown in Fig. 5.2. The DFT-PBE results, represented by the dashed red lines in Fig. 5.2(a), predict an extremely small direct



Figure 5.2: Electronic band structure (left panels) and density of states (right panels) of bulk black phosphorus (a) without strain, (b) when stretched by 1% along the a_1 direction, and (c) when stretched by 2% along the a_1 direction. GW results are shown by the solid black lines. DFT-PBE results, which underestimate the band gap, are shown by the dashed red lines.

fundamental band gap value $E_g(PBE)\approx 0.05$ eV for unstrained bulk black phosphorus. The band gap becomes larger as the structures are stretched along the a_1 direction. As mentioned before, the DFT results are known to substantially underestimate the band gap in semiconductors. Band structure results obtained using the more proper GW approach by my collaborators are represented by the solid black lines in Fig. 5.2(a). These data suggest a larger quasiparticle band gap of $E_g(qp)\approx 0.35$ eV in unstrained bulk black phosphorus, very close to the published value based on GW calculations [150, 151] and to the observed value [141] of ≈ 0.33 eV.

Differences between quasi-particle spectra, $E_{\rm qp}$, and DFT band structure results, $E_{\rm PBE}$, are summarized in Fig. 5.3(a). As shown previously [146,152], the self-energy (or GW) correction is roughly represented by a "scissor operator", which would shift DFT-based valence states rigidly down and conduction states rigidly up by ≤ 0.2 eV in bulk black phosphorus, thus opening up the fundamental band gap.

A more precise comparison between the quasiparticle spectra and DFT eigenvalues reveals that the difference $E_{qp} - E_{PBE}$ does depend on the energy, but is independent of the



Figure 5.3: (a) Correlation between quasiparticle (GW) energies $E_{\rm qp}$ and Kohn-Sham energy values $E_{\rm PBE}$, obtained using the DFT-PBE functional, for states along high symmetry lines in the Brillouin zone. The straight lines in the valence and conduction band regions are drawn to guide the eye. The results represent bulk black phosphorus subject to strain values $\epsilon(a_1) = 1\%$ and $\epsilon(a_2) = 0$. The Fermi level is at zero energy. (b) Dependence of the quasiparticle (GW) electronic band gap E_g on the in-layer strain applied along the a_1 and a_2 directions.

crystal momentum **k**. I considered black phosphorus stretched by 1% along the soft a_1 direction, which has a nonzero band gap in DFT-PBE, and displayed the correlation between quasiparticle energies $E_{\rm qp}$ and corresponding DFT eigenvalues $E_{\rm PBE}$ at selected high symmetry points in the Brillouin zone in Fig. 5.3(a). Besides the discontinuity at the Fermi level, I found that the quasiparticle energies display a linear relationship with DFT eigenvalues, given by

$$E_{\rm qp}({\rm CB}) = 1.10 \times E_{\rm PBE}({\rm CB}) + 0.11 \text{ eV}$$
 (5.1)

$$E_{\rm qp}(\rm VB) = 1.07 \times E_{\rm PBE}(\rm VB) - 0.18 \ eV$$
 . (5.2)

Assuming that the Fermi level defines zero energy, the linear relationship between E_{qp} and E_{PBE} is slightly different in the conduction band (CB) region, identified by $E_{qp} > 0$, and the valence band region, identified by $E_{qp} < 0$. Since GW energies have been calculated

only at a few k-points, I have used expressions (5.1) and (5.2) to generate the continuous GW band structure shown in Fig. 5.2.

Comparing DFT and GW values at different strains, I found that the modulation of the band gap $\Delta E_g(\text{PBE}) \approx \Delta E_g(\text{qp})$ is the same up to $\leq 0.01 \text{ eV}$ in the strain range studied here. With the quasiparticle band gap of unstrained black phosphorus at hand, I thus can deduce the quasiparticle band gap in phosphorus subject to different strain values $\epsilon(a_1)$ and $\epsilon(a_2)$ by combining the DFT band gap values $E_g(\text{PBE})$ with Eqs. (5.1) and (5.2). My results, based on a cubic spline interpolation of a 5×5 grid of data points, are shown in Fig. 5.3(b).

My results indicate that, within the range $|\epsilon| \lesssim 2\%$ of strain applied along the a_1 and a_2 direction, the band gap E_g of bulk black phosphorus varies smoothly between 0.05 eV and 0.70 eV. Independent of the strain direction, E_g increases upon stretching and decreases upon compression. Noticing the nearly equidistant spacing between the contour lines in Fig. 5.3(b), I can extrapolate to larger strains and expect the band gap to close at compressive strains along both a_1 and a_2 directions exceeding 2%.

So far, much less attention has been paid to the moderate 0.3 eV band gap of bulk BP than to the 2 eV wide direct band gap of a phosphorene monolayer [28]. The inter-layer coupling in bulk BP, which is responsible for the large difference in the band gap, displays a nontrivial character [67]. Therefore, it has not been clear *a priori* if previously reached conclusions for the band gap dependence on uniaxial in-layer strain in a phosphorene monolayer will also be applicable for the bulk system. There is an independent, more practical concern about band gap modulation in BP systems by strain. Pristine phosphorene monolayers and few-layer systems are very unstable under ambient conditions [153–155] and must be capped, typically by sandwiching in-between inert h-BN layers to remain useful [156]. It is unclear if applying in-layer strain will not destroy the rigid capping layer before reaching desirable strain values in the enclosed phosphorene. This limitation applies to a much lesser degree to bulk black phosphorus, which is chemically much more stable and thus can be handled more easily in the experiment.

The sensitivity of the band gap to the in-layer strain suggests the use of bulk or multilayer black phosphorus in infrared devices tunable by strain. Optical measurements should be able to reveal the band gap value discussed here, since observed optical spectra should not be modified by excitonic states due to the negligibly small exciton binding energy in bulk black phosphorus [150].

5.4 Summary

In summary, I have studied theoretically the structural and electronic response of layered bulk black phosphorus to in-layer strain. Ab initio density functional theory (DFT) calculations reveal that the strain energy and interlayer spacing display a strong anisotropy with respect to the uniaxial strain direction. To correctly describe the dependence of the fundamental band gap on strain, I combined the computationally more involved GW quasiparticle approach performed by my collaborators from Washington University in St.Louis that is free of parameters and superior to DFT studies, which are known to underestimate gap energies. I found that the main difference between GW quasiparticle energies $E_{\rm qp}$ and DFT eigenvalues $E_{\rm PBE}$ is a discontinuity at the Fermi level and have identified the relationship between $E_{\rm qp}$ and $E_{\rm PBE}$ in the valence and conduction band regions. Similar to a phosphorene monolayer, I found that the band gap depends sensitively on the in-layer strain and even vanishes at compressive strain values exceeding $\approx 2\%$, thus suggesting a possible application of black P in strain-controlled infrared devices.

Chapter 6

Various phases of few-layer phosphorene

The following discussion is my original contribution to the related publication by Jie Guan, Zhen Zhu and David Tománek, Phys. Rev. Lett. **113**, 046804 (2014) [157].

6.1 Introduction

Layered black phosphorus is considered as a viable contender in the competitive field of twodimensional (2D) semiconductors [158, 159]. Unlike the popular semi-metallic graphene, it displays a significant band gap while still maintaining a high carrier mobility [27,28,160]. The band gap in few-layer phosphorus, dubbed phosphorene, is believed to depend sensitively on the number of layers and in-layer strain [28, 33, 116, 161]. Layered blue phosphorus, previously described as the A7 phase [162, 163], has been predicted to be equally stable as black phosphorus but to have a different electronic structure [33]. It is intriguing to find out, whether there are more than these two stable layered phosphorus allotropes, and to what degree their dielectric response may be modified from semiconducting to metallic.

Here I introduce γ -P and δ -P as two additional stable structural phases of layered phosphorus besides the layered α -P (black) and β -P (blue) phosphorus allotropes. Based on my *ab initio* density functional calculations, I find these new structures, shown in Fig. 6.1, to



Figure 6.1: Equilibrium structure of (a) an α -P (black), (b) β -P (blue), (c) γ -P and (d) δ -P monolayer in both top and side views. Atoms at the top and bottom of the non-planar layers are distinguished by color and shading and the Wigner-Seitz cells are shown by the shaded regions.

be almost as stable as the other layered allotropes. Monolayers of some of these allotropes have a wide band gap, whereas others, including γ -P, show a metal-semiconductor transition caused by in-layer strain or changing the number of layers. An unforeseen benefit is the possibility to connect different structural phases at no energy cost. This becomes particularly valuable in assembling heterostructures with well-defined metallic and semiconducting regions in one contiguous layer.

6.2 Computational techniques

The DFT method used to obtain insight into the equilibrium structure, stability and electronic properties of γ -P and δ -P is the same as last chapter. Reciprocal space was sampled by a fine grid [136] of $8 \times 8 \times 1$ k-points in the Brillouin zone of the primitive unit cell or its equivalent in supercells. Equilibrium structures and energies based on SIESTA were checked against values based on the VASP [70] code. The OptB86b-vdW functional [65,66], same as used in Chapter 4, is used to estimate the effect of van der Waals interactions on the inter-layer distances and interactions in the layered systems. For selected systems, I performed GW self-energy calculations using VASP.

6.3 Results and discussions

Referring to the well-established black phosphorus structure as α -P and to blue phosphorus [33] as β -P, I present the optimized structure of these two and two additional layered phosphorus allotropes, called γ -P and δ -P, in Fig. 6.1. All share the threefold coordination of all atoms and a nonzero intrinsic thickness of the layers, caused by the preference of phosphorus for a tetrahedral arrangement of its nearest neighbors. In fact, the differences among these structures arise from the different ways to connect tetrahedrally coordinated P atoms in a 2D lattice. There are 4 atoms in the rectangular Wigner-Seitz cell of γ -P and 8 atoms in that of δ -P. The ridge structure of these phases is analogous to that of the anisotropic α -P, but differs from the isotropic β -P with a hexagonal Wigner-Seitz cell containing only two atoms. The optimum structural parameters are summarized in Table 6.1.

Results of my total energy calculations in Table 6.1 indicate that all layered structures are nearly equally stable, with cohesive energy differences below 0.1 eV. This comes as no surprise, since the local environment of the atoms is very similar, resulting in all bond lengths being close to 2.29 Å. Due to the well-known overbinding in density functional calculations, my DFT-PBE cohesive energies are larger than the experimental value.

Independent of its cohesive energy, a structure may only be considered stable if it does not spontaneously change. A tendency for spontaneous structural change is indicated by the presence of soft modes (or imaginary frequency values) in the vibrational spectrum. To demonstrate the stability and structural rigidity of γ - and δ -P, I present the vibrational

Table 6.1: Observed and calculated properties of the four layered bulk phosphorus allotropes. $|\vec{a_1}|$ and $|\vec{a_2}|$ are the in-plane lattice constants defined in Fig. 6.1. d is the inter-layer separation and E_{il} is the inter-layer separation energy per atom. E_{coh} is the cohesive energy with respect to isolated atoms. $\Delta E_{coh} = E_{coh} - E_{coh}(\alpha$ -P) is the relative stability of the layered allotropes with respect to the most stable black phosphorene (or α -P) phase.

Phase	<i>α</i> -P	<i>α</i> -P	<i>β</i> -P	γ -P	<i>δ</i> -P
	(expt.)	(calc.)	(calc.)	(calc.)	(calc.)
$ \vec{a}_1 $ (Å)	4.38^{1}	4.53^{2}	3.33 ^b	3.41 ^b	5.56^{b}
$ \vec{a}_2 $ (Å)	3.31 ^a	3.36^{b}	3.33^{b}	5.34^{b}	5.46^{b}
d (Å)	5.25^{a}	5.55^{b}	5.63^{b}	4.24^{b}	5.78^{b}
	_	5.30^{3}	4.20^{c}	4.21^{c}	5.47^{c}
E_{il} (eV/atom)	_	0.02^{b}	$0.01^{\rm b}$	0.03^{b}	0.02^{b}
	_	0.12^{c}	0.10^{c}	0.13^{c}	0.11 ^c
$E_{coh}(\text{eV/atom})$	3.43^{4}	3.30^{b}	3.29^{b}	3.22^{b}	3.23^{b}
$\Delta E_{coh}(\text{eV/atom})$	_	0.00^{b}	-0.01^{b}	-0.08^{b}	-0.07^{b}
	_	0.00^{c}	-0.04^{c}	$-0.09^{\rm c}$	-0.08^{c}

spectra of these phases in Figs. 6.2(a) and 6.2(b). Absence of soft modes in these spectra indicates that γ - and δ -P are stable. I compare the vibrational spectra with those of α -P and β -P monolayers in a previous study [33] and find them to be rather similar, reflecting similar bonding character in all four phosphorene allotropes. The hardest optical mode frequency in γ -P near 500 cm⁻¹ at Γ lies very close to that of β -P due to the close relationship of the two structures. Similar to β -P, the vibration spectrum of γ -P is nearly isotropic. This can be explained by a close inspection of the structural differences, which indicate that the level of buckling in γ -P is much smaller than in α -P and δ -P. The vibrational spectrum of δ -P best matches that of α -P in terms of the hardest mode frequency and the anisotropy of the longitudinal acoustic modes. The differences in the vibrational spectra offer a promising route to identify the presence of γ -P and δ -P using Raman or infrared spectroscopy.

Structural stability at T = 0, evidenced in the vibrational spectra, says little about stability at high temperatures, where thermally activated structural changes may take place. α -P, β -P, γ -P and δ -P are structurally related by different ways to connect tetrahedrally coordinated P atoms in a 2D lattice. Local structural changes may be achieved by flipping bonds in a bi-stable configuration at an energy cost of ≤ 0.5 eV/atom, identified in the α -P $\rightarrow \beta$ -P transition [33]. The relatively high activation energy value suggests that structural changes will only rarely occur before the system melts.

A more direct way to probe the stability of γ -P and δ -P at high temperatures is by performing molecular dynamics (MD) simulations. Results of my canonical MD simulations are presented as structural snap shots of infinite γ -P and δ -P monolayers at T = 300 K and T = 1,000 K in Fig. 6.3. To avoid artifacts associated with constraints imposed by finite-size unit cells, I used very large supercells containing 96 atoms for γ -P and 128 atoms for δ -P. Due to the large unit cell size, I needed to limit the simulation time to 1.6 ps for γ -P and 0.6 ps for δ -P when using 1 fs time steps. This simulation time still covers about 10 vibrational periods of the optical modes and thus should indicate the propensity towards structural changes.

At room temperature, I find the structural changes in the layers to be minimal. More significant changes are expected at T = 1,000 K, which lies well above $T_M = 863$ K, the melting point of red phosphorus [165]. Even though the changes are larger in this case, they resemble more the onset of a melting process than a concerted structural change. I also expect that few-layer structures may convert to an amorphous structure resembling red phosphorus above the melting point.

The high-temperature MD simulations suggest that γ -P and δ -P should display similar thermal stability as previously found [33] for α -P and β -P. In view of cohesive energy differences between the structures not exceeding 0.1 eV per atom, I expect the four phosphorene allotropes to coexists under experimental conditions.

My results for the optimum inter-layer separation d ($d = |\vec{a_3}|$ for the AA layer stacking)



Figure 6.2: Vibrational band structure $\omega(\vec{k})$ of a monolayer of (a) γ -P and (b) δ -P. High-symmetry lines are shown in the insets.

and inter-layer interaction energy E_{il} in the four phases are summarized in Table 6.1. By not taking proper account of the van der Waals interactions [166, 167], DFT-PBE calculations tend to underestimate E_{il} and overestimate d [28, 33]. Probably the best, albeit computationally extremely demanding way to correct this deficiency is the Quantum Monte Carlo (QMC) approach [168]. QMC results for α -P indicate $E_{il}\approx40$ meV/atom [169], twice the 20 meV/atom value based on DFT-PBE, as cited in Table 6.1. I also list the value obtained for α -P using van der Waals-corrected OptB86b-vdW functional, $E_{il}\approx120$ meV/atom, which is significantly larger than the more reliable QMC value. Very similar corrections to the interlayer interaction of ≤ 0.1 eV and a reduction of the inter-layer distance are also obtained for the other layered allotropes. In spite of these minor differences, I find the inter-layer interactions and distances to be rather similar in all these allotropes and in reasonable agreement with observed data in the only previously known allotrope black phosphorus (α -P).

The calculated energy differences between the AA, AB and ABC stacking of layers of few meV/atom represent only a fraction of the inter-layer interaction E_{il} . Since the inter-layer distances are large and inter-layer interactions are small in all four phases, the optimized



Figure 6.3: Snap shots of canonical molecular dynamics simulations depicting structural changes in γ -P at (a) T = 300 K and (b) T = 1,000 K. Corresponding snap shots of δ -P are shown in (c) for T = 300 K and (d) for T = 1,000 K. For better comparison, both top and side views are presented for all structures. The unit cell of the lattice contains 96 atoms in γ -P and 128 atoms in δ -P.

layer structures of the bulk system and the monolayer are nearly indistinguishable. The fact that the inter-layer interaction is similarly small in all phases indicates the possibility of layer-by-layer exfoliation not only of black phosphorus [28], but also the other layered allotropes.

I present results of DFT-PBE electronic band structure calculations for γ -P and δ -P monolayers in Fig. 6.4. As can also be inferred from the numerical results in the related

Table 6.2: The fundamental band gap E_g in monolayers of α -P, β -P, γ -P and δ -P, based on DFT-PBE calculations.

Phase	<i>α</i> -Ρ	β -P	γ -P	<i>δ</i> -P
$E_g (eV)$	0.90	1.98	0.50	0.45



Figure 6.4: Electronic band structure and density of states (DOS) of (a) γ -P and (b) δ -P monolayers. Results for bilayer and bulk systems are shown for comparison in the DOS plots only. Top and side views of the electron density ρ_{vc} near the top of the valence and the bottom of the conduction bands of (c) γ -P and (d) δ -P. Only states in the energy range $E_F - 0.4 \text{ eV} < E < E_F + 0.4 \text{ eV}$ are considered, as indicated by the green shaded region in (a) and (b). ρ_{vc} is represented at the isosurface value $\rho_{vc} = 1.1 \times 10^{-3} \text{ e/Å}^3$ for γ -P and δ -P and superposed with a ball-and-stick model of the structure.

Table 6.2, the fundamental band gaps in γ -P and δ -P are somewhat smaller than those of α -P and β -P monolayers, but still significant. Since my GW self-energy calculations indicate that these DFT-PBE band gap values are underestimated by ≈ 1 eV, as expected for DFT calculations, all four phases should display a fundamental band gap in excess of 1 eV in the monolayer. Whereas γ -P has an indirect band gap, δ -P is a direct band gap semiconductor. Besides the electronic band structure of the monolayers, I present the associated density of states of a monolayer and of the bulk system in Figs. 6.4(a) and 6.4(b). As already noticed for the α -P and β -P structures in previous works [28, 33], the electronic structure near E_F including the band gap depends sensitively on the number of layers in all phosphorene allotropes, including γ -P and δ -P. The most notable difference in the density of states of γ -P



Figure 6.5: (a) Dependence of the fundamental band gap E_g on the slab thickness in N-layer slabs of α -P (black), β -P (blue), γ -P, and δ -P. Dependence of the fundamental band gap on in-layer strain σ is presented in (b) for γ -P and in (c) for δ -P. The strain direction is defined in Fig. 6.1. The shaded regions in (a) and (b) highlight conditions, under which γ -P becomes metallic. Dashed vertical lines in (b) and (c) indicate a direct-to-indirect band gap transition.

in Fig. 6.4(a) is between a semiconductor for N = 1 and a metal for $N \ge 2$.

Whereas DFT calculations typically underestimate the fundamental band gap, they are believed to correctly represent the electronic structure in the valence and the conduction band region. To get a better impression about the nature of the conducting states in doped γ -P and δ -P, I display the charge distribution associated with states near the Fermi level in Figs. 6.4(c) and 6.4(d), superposed with the atomic structure. These states and their hybrids with electronic states of the contact electrodes will play a crucial role in the carrier injection and quantum transport. I find these conduction states to have the character of *p*-states normal to the layers, similar to graphene. In multi-layer systems, these states hybridize between adjacent layers, causing a band dispersion normal to the slab. This causes a change in the density of states in the gap region between a monolayer and the bulk structure.

To judge how the fundamental band gap depends on the slab thickness, I present my DFT-PBE band gap results for α -P, β -P, γ -P and δ -P as a function of the number of layers N in Fig. 6.5(a). My most important finding is that the band gap vanishes for $N \ge 2$ in γ -P,



Figure 6.6: Energetically favorable in-layer connections between (a) α -P and β -P, (b) β -P and γ -P, and (c) γ -P and δ -P, shown in perspective and side view. l represents the edge length at the interface and φ is the connection angle. The color scheme for the different allotropes is the same as in Fig. 6.1.

turning bilayers and thicker slabs metallic.

A similarly intriguing picture emerges when studying the dependence of the fundamental band gap on the in-layer strain. Results for strain applied in two orthogonal directions are shown in Fig. 6.5(b) for γ -P and in Fig. 6.5(c) for δ -P. Again, my most significant finding is that stretching beyond 4% should turn a γ -P monolayer metallic.

As already reported for α -P and β -P [28,33,116,161], applying even relatively low levels of in-layer strain causes drastic changes in the band gap, and may even change its character from direct to indirect. The latter fact results from the presence of several valleys in the conduction band, which may change their relative depth due to lattice distortions. Strain of up to a few percent may be accomplished when phosphorene is grown epitaxially on a particular substrate. We may even consider the possibility of in-layer band gap engineering by substrate patterning.

Even richer possibilities for band structure engineering should arise by in-layer connections between the different phases. In-layer connections, which have been observed in hybrid systems of graphene and hexagonal BN [170], suffer from large interface energy penalties

Table 6.3: Energy cost per edge length $\Delta E_c/l$ and connection angle φ , defined in Fig. 6.6, associated with connecting two semi-infinite phosphorene monolayers.

Phase connection	α - β	eta - γ	γ - δ
$\Delta E_c/l$	< 1 meV/Å	$< 17 \text{ meV/\AA}$	< 6 meV/Å
Angle φ	142°	160°	145°

due to the lack of commensurability. The situation is very different in phosphorene, since the four layered allotropes share the same structural motif of threefold coordinated P atoms surrounded by nearest neighbors in a tetrahedral arrangement. I find that this tetrahedral arrangement can be maintained even within specific in-layer connections of the different structures, resulting in an extremely low energy penalty.

I have optimized the structure of in-layer connections between α -P and β -P, between β -P and γ -P, and between γ -P and δ -P. My results, depicted in Fig. 6.6, indicate that an optimum connection involves different orientations of the joined planes. The optimization calculations, performed in a supercell geometry with varying cell sizes, allowed us to determine the energy cost per edge length $\Delta E_c/l$ to connect two structural phases. To obtain this quantity for a connection between phases 1 and 2, I considered N_1 atoms of phase 1 and N_2 atoms of phase 2 per unit cell and varied the N_1/N_2 ratio while keeping the same length of the interface boundary. For a reliable estimate of the energy penalty associated with forming an interface between the two phases, I compared total energies of optimized structures with coexisting phases to those of pure, defect-free phases. My results for $\Delta E_c/l$ for the connection shown in Fig. 6.6 are listed in Table 6.3, along with the optimum values of the connection angle φ .

The energy results in Table 6.3 indicate that the energy cost to connect stable, but different, structural phases is negligible in comparison to the cohesive energy. The implication that coexistence of several phases within one layer is not energetically penalized is extremely uncommon in nature. I can envisage the possibility of forming such multi-phase structures
by depositing phosphorene monolayers on a substrate with a specific step structure, such as a vicinal surface, using Chemical Vapor Deposition. The domain wall boundaries between different phases may also move to optimize adhesion to an inhomogeneous or non-planar substrate. The electronic properties of a heterostructure within one layer will depend not only on the electronic structure of the pure phases, but also their finite width or size and the defect bands associated with the interfaces. In principle, it should be possible to form a complex device structure by a judicious arrangement of different structural phases within one phosphorene monolayer.

Monolayers containing the four layered phosphorene phases are expected to be not only stable, but also flexible. Consequently, the non-planarity of multi-phase structures does not pose a real problem. It may even provide an advantage in formation of complex foam structures, similar to graphitic carbon foams, with unusual electronic properties [171, 172].

6.4 Summary

In conclusion, based on *ab initio* density functional calculations, I have proposed γ -P and δ -P as two additional stable structural phases of layered phosphorus besides the layered α -P (black) and β -P (blue) phosphorus allotropes. Monolayers of some of these allotropes have a wide band gap, whereas others, including γ -P, show a metal-insulator transition caused by in-layer strain or changing the number of layers. An unforeseen benefit is the possibility to connect different structural phases at no energy cost. This becomes particularly valuable in assembling heterostructures with well-defined metallic and semiconducting regions in one contiguous layer.

Chapter 7

Faceted nanotubes and fullerenes of multi-phase phosphorene

The following discussion is my original contribution to the related publication by Jie Guan, Zhen Zhu and David Tománek, Phys. Rev. Lett. **113**, 226801 (2014) [173].

7.1 Introduction

One reason for the unprecedented interest in graphitic carbon is its ability to form not only self-supporting graphene layers [174,175], but also single- and multi-wall nanotubes [47] and fullerenes [46]. Similar to graphite, which is the parent compound of these carbon allotropes, the stable black phosphorus allotrope is a layered compound that can be exfoliated to phosphorene monolayers [27,28]. Phosphorus nanotubes [176,177] and fullerenes [178–180] have been postulated to form in analogy to their carbon counterparts by deforming a phosphorene monolayer, typically at significant energy cost. In contrast to the unique structure of planar graphene, at least four equally stable phases with different properties, α -P, β -P, γ -P and δ -P, can be distinguished in the puckered structure of a phosphorene monolayer [33,163,181]. The ability of the different phases to form non-planar in-layer connections at essentially zero energy cost suggests the possibility to form faceted nanotube and fullerene structures that are as stable as planar phosphorene. The possibility to mix different phases within each wall of spherical and cylindrical single- and multi-wall structures would offer unprecedented richness not only of form but also the associated electronic properties. Bulk quantities of carbon nanotubes and fibers are currently used as a performance-enhancing additive to graphite in Li-ion batteries (LIBs) [182]. Since black phosphorus is considered superior to graphite for LIB applications [183,184], a similar benefit could be derived from the presence of phosphorene nanotubes and related structures.

Here I present a new paradigm in constructing very stable, faceted nanotube and fullerene structures by laterally joining nanoribbons or patches of different planar phosphorene phases. My *ab initio* density functional calculations indicate that these phases may connect laterally at an angle. Unlike fullerenes and nanotubes obtained by deforming a single-phase planar monolayer at substantial energy penalty, I find faceted fullerenes and nanotubes to be nearly as stable as planar single-phase monolayers. The resulting rich variety of polymorphs allows one to tune the electronic properties of phosphorene nanotubes and fullerenes not only by the chiral index but also by the combination of different phosphorene phases. In selected PNTs, a metal-insulator transition may be induced by strain or by changing the number of walls.

7.2 Computational techniques

The same method as last chapter is used to obtain insights into the equilibrium structure, stability and electronic properties of nanotubes and fullerenes based on different layered phosphorus allotropes. I use periodic boundary conditions throughout the study, with nanotubes and fullerenes separated by a vacuum region exceeding 15 Å. I sample reciprocal space by a fine grid [136] of 8 k-points for the 1D Brillouin zone of nanotubes and only 1 k-point



Figure 7.1: (a) Atomic structure of α -, β -, γ - and δ -P in top view and the side view of zigzag and armchair edges. The orthogonal lattice vectors \vec{a}_1 and \vec{a}_2 define the unit cells or supercells used in this study. Schematic and atomic structure of (b) an armchair and (d) a zigzag PNT, with the different structural phases distinguished by color and shading. The cross-sections of (c) an armchair and (e) a zigzag nanotube illustrate the symmetry and the distribution of phases along the perimeter.

for the small Brillouin zone of isolated fullerenes.

7.3 Results and discussions

The nanotube and fullerene structures presented in this study are formed by laterally connecting the different stable allotropes of layered phosphorus, namely α -, β -, γ - and δ -P, which are shown in Fig. 7.1(a). Whereas α - and β -P are the most stable allotropes with $E_{coh} = 3.28 \text{ eV/atom}$ in the monolayer, the stability of γ - and δ -P are lower only by < 0.1 eV/atom [181]. All these structures share the underlying honeycomb lattice with graphene but – in contrast to graphene – are not flat. In analogy to graphene, I define the armchair and zigzag edges of the different phosphorene phases in Fig. 7.1(a). The vectors \vec{a}_1 and \vec{a}_2 , which span these lattices, may also be used to identify the edges of phosphorene



Figure 7.2: Geometric cross-section of selected (a) a-PNTs and (b) z-PNTs. Different structural phases are distinguished by color.



Figure 7.3: Source of ambiguity in the nomenclature of faceted nanotubes. In two identical junctions of phases α and β , atoms along the connection line, indicated by the dotted ellipse, may be assigned to the phase on either side.

nanoribbons (PNRs). Considering the equilibrium non-planar connections between α -, β -, γ -P along zigzag edges and γ -, δ -P along armchair edges [181], I can design two types of faceted nanotubes.

The exact morphology of the more common carbon nanotubes (CNTs) is defined by the chiral index (n_1, n_2) , which is associated with the chiral vector $\vec{C}_h = n_1 \vec{a}_1 + n_2 \vec{a}_2$ on a graphene monolayer. This vector defines the wrapping into a nanotube and identifies its edge. There is a common distinction between armchair nanotubes (a-NTs) with an armchair edge and zigzag nanotubes (z-NTs) with a zigzag edge. A similar convention can be used when bending monolayers of α -, β -, γ - and δ -P into corresponding nanotubes.

The nanotubes I consider here are very different, as they are formed by connecting narrow planar nanoribbons of different phosphorene allotropes. Armchair nanotubes (a-PNTs), shown in Fig. 7.1(b) and 7.1(c), form by connecting laterally α -PNRs with β - and γ -PNRs along their zigzag edges. Virtually no deformation is required to form a nanotube with C_3 symmetry and a polygonal cross-section like that shown in Fig. 7.1(c). The three identical 120° segments in the cross-section of this a-PNT contain, in this sequence, an α -PNR connected to a β -PNR, γ -PNR, and β -PNR. The width of each individual PNR may be zero or nonzero, giving rise to many different morphologies. Since the two β -PNRs in this segment may also have different widths, I distinguish them by a subscript. Next, I imagine joining laterally all nanoribbons of a given phase ϵ to a wider ribbon of width $W_{\epsilon} = n_{\epsilon} |\vec{a}_1|$. Obtaining in this way the values n_{α} , n_{β_1} , n_{γ} and n_{β_2} , I may characterize an armchair nanotube as a-PNT($n_{\alpha}, n_{\beta_1}, n_{\gamma}, n_{\beta_2}$) and identify the nanotube in Fig. 7.1(c) as a-PNT(6,3,3,3).

In analogy to a-PNTs, zigzag nanotubes (z-PNTs), as shown in Fig. 7.1(d) and 7.1(e), form by connecting laterally γ - and δ -PNRs along their armchair edges. Virtually no deformation is required to form a nanotube with C_2 symmetry and a polygonal cross-section, shown in Fig. 7.1(e). The two identical 180° segments in the cross-section of this z-PNT contain, in this sequence, a γ -PNR connected to a δ -PNR, γ -PNR, and δ -PNR. The width of each individual PNR may be zero or nonzero, giving rise to many different morphologies. Since the two γ - and the two δ -PNRs in this segment may also have different widths, I distinguish them by a subscript. Next, I imagine joining laterally all nanoribbons of the same phase ϵ to a wider ribbon of width $W_{\epsilon} = n_{\epsilon} |\vec{a}_2|$. Obtaining in this way the values n_{γ_1} , n_{δ_1} , n_{γ_2} and n_{δ_2} , I may characterize a zigzag nanotube as z-PNT($n_{\gamma_1}, n_{\delta_1}, n_{\gamma_2}, n_{\delta_2}$) and identify the nanotube in Fig. 7.1(e) as z-PNT(5,2,5,4). I do not discuss here the narrowest z-PNT(1,0,1,0) with a P_4 square in the cross-section, which is in reality a nanowire. Additional examples of narrow armchair nanotubes are shown in Fig. 7.2(a) and of zigzag nanotubes in Fig. 7.2(b). Even though these nanotubes have a small average radius, they are unusually stable as I will discuss later.

I also wish to point out that the faceted nanotubes described here are not completely free of strain. Assuming that the optimum connection angles between narrow strips are the same as between semi-infinite planes provided in Reference [181], I do find that narrow strips of the different phases, connected at the optimum angle, would not form a perfect tube. Specifically, constituents of an armchair nanotube would ideally connect at 348° instead of 360°, requiring a small amount of additional bending to form a armchair nanotube. Similarly, constituents of a zigzag nanotube would connect at 280° instead of 360°, requiring a larger amount of additional bending to form a zigzag nanotube. While this residual strain is very small, it is not negligible. As stated before, the stability of a particular nanotube is mainly determined by the different stabilities of the constituent phases and, to a much smaller degree, by this residual strain.

Whereas the designation a-PNT $(n_{\alpha}, n_{\beta_1}, n_{\gamma}, n_{\beta_2})$ defines the way to construct a unique armchair nanotube from PNRs, a given nanotube may be characterized by different sets of chiral indices. Ambiguity arises from assigning atoms along the connection line to either the phase on the one or on the other side of the connection line. As shown in Fig. 7.3, the same structure could be described by (n_{α}, n_{β}) and $(n_{\alpha} + 1, n_{\beta} - 1)$. This would lead to different values of n_{α} in the same a-PNT and different values of n_{γ_1} and n_{γ_2} in the same z-PNT. This ambiguity can be avoided by selecting $n_{\alpha} = max$. A similar ambiguity in the nomenclature of z-PNTs can be avoided by selecting n_{γ_1} to be maximum and n_{γ_2} to be maximum.

Similar to the construction of nanotubes by connecting nanoribbons of different phases,



Figure 7.4: Phosphorene-based fullerene structures with (a-c) octahedral and (d-f) icosahedral symmetry. The structural models in (a) and (d) indicate how triangular facets of β -P are connected by γ -P along the edges. The stick models of P₇₂ in (b), P₂₀₀ in (c), P₈₀ in (e) and P₁₈₀ in (f) depict the relaxed atomic structures of octahedral and icosahedral fullerenes.

fullerenes, too, may be constructed by connecting planar triangular segments of β -P monolayers by narrow γ -P strips at the edges, as shown in Fig. 7.4. I have considered octahedral fullerenes, illustrated schematically in Fig. 7.4(a), and icosahedral fullerenes, illustrated schematically in Fig. 7.4(d). Ideal P_n octahedral fullerenes contain $n = 8m^2$ atoms and icosahedral fullerenes contain $n = 20m^2$ atoms, where m is an integer. Two examples of octahedral fullerenes are presented in Figs. 7.4(b) and 7.4(c), and two examples of icosahedral fullerenes in Figs. 7.4(e) and 7.4(f). Since these structures do not require significant deformation of the planar monolayer structure, but rather result from an optimum connection between β -P and γ -P, they also are expected to be nearly as stable as the planar single-phase allotropes.

My results for the relative stability of phosphorene nanotubes are presented in Fig. 7.5(a)



Figure 7.5: (a) Average strain energy per atom $\Delta E/n$ in PNTs of different radius R with respect to a planar β -P monolayer. The shaded region indicates the range of stabilities of different planar phases. I also present data points for pure-phase PNTs obtained by rolling up β - and γ -P to a tube. (b) Strain energy per atom in octahedral (o) and icosahedral (i) fullerenes of radius R. The dashed lines in (a) and (b) represent the $1/R^2$ behavior based on continuum elasticity theory for pure-phase nanostructures. (c) Band gaps E_g in faceted a-PNTs and z-PNTs. The horizontal lines depict E_g values in pure planar phosphorene monolayers. (d) HOMO-LUMO gaps in o- and i-fullerenes. The red and blue shaded regions indicate the range of values for a-PNTs and z-PNTs.

and those for fullerenes in Fig. 7.5(b). In both sub-figures, the dashed lines display the expected $1/R^2$ behavior of the strain energy per atom $\Delta E/n$ on the radius R that energetically penalizes structures with small radii.

As seen in Fig. 7.5(a), this projected behavior, based on continuum elasticity theory [58], agrees closely with my results for pure β - and γ -P nanotubes and previously published results for β -P nanotubes, calculated by density functional based tight-binding (DFTB) method [177]. As anticipated originally, the faceted multi-component nanotubes are much



Figure 7.6: Snap shots of canonical molecular dynamics simulations at T = 300 K and T = 1000 K depicting structural changes in phosphorus nanotubes and fullerenes. Nanotubes are represented by (a) the armchair a-PNT(3,3,0,0) and (b) the zigzag z-PNT(5,0,5,0). Fullerenes are represented by (c) P₇₂ and (d) P₈₀. The nanotubes are shown in end-on view.

more stable than these. I find that (i) their strain energies are nearly independent of the radius and (ii) their relative stabilities lie in the range delimited by the stabilities of the pure planar components, indicated by the shaded region. Since z-PNTs contain the least stable γ and δ phases, they are also the least stable among the faceted nanotubes. The presence of the more stable α and β phases, on the other hand, makes a-PNTs consistently more stable than z-PNTs.

Stability enhancement caused by the coexistence of multiple phases can also be observed in my results for fullerenes in Fig. 7.5(b). As in the nanotubes, I find most strain energies within the value range delimited by the pure planar β - and γ -P phases. The stability enhancement is most visible in very small fullerenes. Interestingly, I find the small fullerene structures more stable than P₄, the building block of the (most reactive) bulk phosphorus allotrope.

Structural stability at T = 0 says little about stability at high temperatures, where



Figure 7.7: Electronic band structure of (a) the z-PNT(3,0,3,0) and (c) the z-PNT(5,0,5,0) nanotube. The region associated with frontier orbitals is highlighted by the green shading in the energy range $E_F - 0.1 \text{ eV} < E < E_F + 0.1 \text{ eV}$ in (a) and $E_F - 0.2 \text{ eV} < E < E_F + 0.2 \text{ eV}$ in (c). Electron density ρ_f associated with frontier states in (b) the z-PNT(3,0,3,0) and (d) the z-PNT(5,0,5,0) nanotube, superposed with ball-and-stick models of the structures. ρ_f is represented by the isosurface value $8 \times 10^{-4} \text{ e/Å}^3$.

thermally activated structural changes may take place. A direct way to probe the stability of faceted phosphorus nanotubes and fullerenes at high temperatures is by performing molecular dynamics (MD) simulations. Results of my canonical MD simulations are presented in Fig. 7.6 as structural snap shots of the a-PNT(3,3,0,0) and the z-PNT(5,0,5,0) nanotube and the P₇₂ as well as the P₈₀ fullerene at T = 300 K and T = 1,000 K. To avoid artifacts associated with constraints imposed on nanotubes by finite-size unit cells, I used supercells containing 3 primitive unit cells. I used 1 fs time steps to cover 0.8-3 ps, depending on system and temperature. I found structural changes to be minimal at room temperature. I observed larger atomic motion at T = 1,000 K, which lies slightly above $T_M = 863$ K, the melting point of red phosphorus [165], but no indication of concerted structural changes to a different allotrope. I thus conclude that faceted nanotubes and fullerenes display a similar thermal stability as monolayers of α -, β -, γ - and δ -phosphorene discussed previously [33,181] and also in earlier chapters. Since the cohesive energies of faceted nanotubes and fullerenes are at most 0.2 eV/atom lower than bulk black phosphorus, I expect these nanostructures



Figure 7.8: (a) Cross-section and (b) DOS of the double-wall z-PNT (5,0,5,0)@(9,0,9,0). The solid line in (b) shows the total DOS and the dashed line depicts the superposition of the densities of states of the isolated nanotube components. The Fermi level E_F is set at 0. (c) Perspective view of the a-PNT(3,0,9,0) and (d) dependence of the gap energy E_g on axial strain.

to coexist with the bulk structure under experimental conditions.

In carbon nanotubes and fullerenes, the occurrence of a fundamental band gap is a signature of quantum confinement in the underlying semi-metallic graphene structure. The advantage of phosphorene over graphene is the presence of a fundamental band gap in all layered allotropes discussed here. I thus expect the fundamental band gaps, E_g , of nanotubes and fullerenes to approximately span the value range of the pure components of planar structures, indicated by the shaded regions in Figs. 7.5(c) and 7.5(d). Even though additional corrections are expected due to quantum confinement and structural relaxation, such corrections are apparently not as important, since most of my data points lie in the range delimited by the pure components. At this point, I wish to point out that my electronic structure results in Figs. 7.5(c) and 7.5(d), obtained by DFT-PBE, are expected to underestimate the fundamental band gaps [28,33].

As seen in Fig. 7.5(c), I find larger band gap values in armchair PNTs containing α -, β and γ -P, since each of the pure planar components has a band gap in excess of 0.5 eV in the monolayer. Since γ - and δ -P have the smallest band gaps among the phosphorene allotropes, I also see the smallest band gaps in z-PNTs, which contain these two pases.

Only the narrowest z-PNT(3,0,3,0) is metallic, with two bands crossing the Fermi level, as seen from its band structure in Fig. 7.7(a). Wider z-PNTs are all narrow-gap semiconductors, as seen in the representative band structure of the z-PNT(5,0,5,0) shown in Fig. 7.7(c). To find the reason for the anomalous electronic structure of the z-PNT(3,0,3,0), I examined the charge distribution in the frontier orbitals and display it in Fig. 7.7(b). For the sake of comparison, I display the analogous charge distribution in the wider z-PNT(5,0,5,0) in Fig. 7.7(d). I used a somewhat arbitrary definition of frontier orbitals as corresponding to the energy range $E_F - 0.1 \text{ eV} < E < E_F + 0.1 \text{ eV}$ in the metallic nanotube in Figs. 7.7(a) and 7.7(b). Since no states are found in this energy range in the semiconducting z-PNT(5,0,5,0), I expanded the energy range associated with the frontier orbitals to $E_F - 0.2 \text{ eV} < E < E_F + 0.2 \text{ eV} < E$ 0.2 eV in Figs. 7.7(c) and 7.7(d). I find the frontier orbitals to display a dominant p character with a small s admixture, causing them to point radially in or out. Whereas there is no overlap between such orbitals on neighboring sites in the wider z-PNT(5,0,5,0) in Fig. 7.7(d), I observe a significant overlap between third-neighbor sites along the inner perimeter, which come closer to each other in the narrow z-PNT(3,0,3,0), shown in Fig. 7.7(b). The origin of conduction in the narrow z-PNT(3,0,3,0) is the conduction channels formed by these rehybridized states. One beneficial effect of the rehybridization across the diameter is an improved rigidity of the nanotubes.

In finite-size fullerenes, E_g represents the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). My results in Fig. 7.5(d) suggest that the HOMO-LUMO gaps in icosahedral fullerenes are larger than in octahedral fullerenes. Even though the values are similar to those of nanotubes in Fig. 7.5(c), I can not easily rationalize the value range for o- and i-fullerenes, since both structures consist of the same β -P and γ -P allotropes.

As reported previously [28, 33, 116, 161, 181], the fundamental band gap in phosphorene depends sensitively on the number of layers and on in-layer strain. My results in Fig. 7.8 indicate that the same behavior occurs also in PNTs. I find multi-wall PNTs to be stabilized by an inter-wall interaction of \leq 50 meV/atom, roughly the same as in the layered compounds [168, 169]. Due to a large fraction of γ -P in the wall, which has been shown to undergo a metal-semiconductor transition, I investigated the (5,0,5,0)@(9,0,9,0) double-wall z-PNT, shown in Fig. 7.8(a). The density of states (DOS) of this double-wall PNT, shown in Fig. 7.8(b), indicates that the inter-wall interaction may turn two semiconducting nanotubes metallic upon being combined to form a double-wall nanotube. As seen in Figs. 7.8(c) and 7.8(d) for the single-wall a-PNT(3,0,9,0), even a modest 5% stretch may turn a semiconducting nanotube containing a significant fraction of γ -P metallic. This low level of strain may be applied externally or induced by epitaxy, including structural changes induced in multi-wall nanotubes.

The most important implication of my claim that faceted nanotubes and fullerenes are as stable as planar phosphorene is that they should exist in nature and will be observed eventually, as was the case with boron nanostructures [185,186]. Phosphorus nanotubes and fullerenes may form during ball milling of black phosphorus [184] under inert, oxygen-free atmosphere. This process may also produce structures with a large accessible surface area for phosphorus-based LIB applications [183, 184].

7.4 Summary

In conclusion, I have presented a new paradigm in constructing very stable, faceted nanotube and fullerene structures by laterally joining nanoribbons or patches of different planar phosphorene phases. My *ab initio* density functional calculations indicate that these phases may form very stable, non-planar joints. Unlike fullerenes and nanotubes obtained by deforming a single-phase planar monolayer at substantial energy penalty, I find faceted fullerenes and nanotubes to be nearly as stable as the planar single-phase monolayers. The resulting rich variety of polymorphs allows one to tune the electronic properties of phosphorene nanotubes and fullerenes not only by their chiral index but also by the combination of different phosphorene phases. In selected PNTs, a metal-insulator transition may be induced by strain or changing the number of walls.

Chapter 8

Combination of sp^2 and sp^3 bonding: two-dimensional phosphorus carbide

The following discussion is my original contribution to the related publication by Jie Guan, Dan Liu, Zhen Zhu and David Tománek, Nano Lett. **16**, 3247-3252 (2016) [187].

8.1 Introduction

There is growing interest in 2D semiconductors, both for fundamental reasons and as potential components in flexible, low-power electronic circuitry. A large number of substances with unique advantages and limitations has been studied in this respect, but consensus has not been reached regarding the optimum candidate. Semi-metallic graphene with an excellent carrier mobility has received the most attention so far, but all attempts to open up a sizeable, robust, and reproducible band gap have failed due to the negative side effects of the different modifications [39–42]. Transition metal dichalchogenides (TMDs) such as MoS_2 [22,43] or TcS_2 [188] do have a sizeable fundamental band gap, but they also have lower carrier mobilities. Recently isolated few-layer films of black phosphorus, including phosphorene monolayers, combine high carrier mobility with a sizeable and tunable fundamental band gap [27,28], but they have limited stability in air [44].

Since both elemental carbon and phosphorus form stable 2D monolayers, which have been



Figure 8.1: Possible stable structures of an atomically thin PC monolayer, represented by (a-c) a tiling pattern and (d-i) by ball-and-stick models in both top and side view. The number of like nearest neighbors defines the structural category N. There are two stable allotropes, α and β , for each N. The primitive unit cells are highlighted and the lattice vectors are shown by red arrows. Two inequivalent P sites are distinguished by a subscript in (d).

studied extensively, it is intriguing to find out whether the compound phosphorus carbide (PC), also called carbon phosphide, may also be stable as a monolayer and display properties that may even be superior to both constituents. The plausibility of a 2D structure of PC derives from the same three-fold coordination found both in graphene and phosphorene. On the other hand, the 2D structure will likely suffer from a competition between the planar sp^2 bonding characteristic of graphene and the significantly different non-planar sp^3 bonding found in phosphorene. The postulated 2D structure of PC with 1:1 stoichiometry is fundamentally different from the amorphous structure observed in deposited thin solid films [189], the postulated foam-like 3D structure [190], or the postulated GaSe-like multi-layer struc-

tures of PC containing C and P with the same sp^3 hybridization [191, 192]. On the other hand, 2D allotropes of PC are related to postulated and observed fullerene-like structures of CP_x [193, 194] and CN_x [195–198], and to g-C₃N₄, called graphitic carbon nitride. [199]

In this Letter, based on *ab initio* density functional calculations, I propose previously unknown allotropes of phosphorus carbide in the stable shape of an atomically thin layer. I find that different stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. I introduce the structural category N, defined by the number of like nearest neighbors, and find that N correlates with the stability and the electronic structure characteristic. Depending on the category, I identify 2D-PC structures that can be metallic, semi-metallic with an anisotropic Dirac cone, or direct-gap semiconductors with their gap tunable by in-layer strain.

8.2 Computational methods

Insight into the equilibrium structure, stability and electronic properties of 2D-PC allotropes reported in this chapter is obtained by the same method as used in last chapter. Reciprocal space is sampled by a fine grid [136] of $8 \times 12 \times 1$ k-points in the Brillouin zone of the primitive unit cell of 4 atoms or its equivalent in supercells. Since the fundamental band gap is usually underestimated in DFT-PBE calculations, I have resorted to the HSE06 [68, 200] hybrid exchange-correlation functional, as implemented in the VASP [70–73] code, to get a different (possibly superior) description of the band structure. I use 500 eV as the energy cutoff and the default mixing parameter value $\alpha = 0.25$ in these studies. DFT-PBE and DFT-HSE06 band structure results are compared.



Figure 8.2: Bonding configuration in (a) N = 1, (b) N = 2, and (c-e) N = 0 category 2D-PC allotropes. Green-shaded regions indicate sites that satisfy the octet rule discussed in the text. Bonding in β_0 -PC is characterized by panel (d) and bonding in α_0 -PC is described by panel (e).

8.3 Results and discussions

As mentioned above, all atoms in the 2D-PC allotropes are threefold coordinated, similar to the planar honeycomb lattice of graphene. Thus, the structure can be topologically mapped onto a 2D lattice with sites occupied either by P or C atoms. Bisecting all nearest-neighbor bonds by lines yields a 2D tiling pattern, where each triangular tile with a characteristic color represents either a P or a C atom. Next, I define a structural category N for each allotrope, with N given by the number of like nearest neighbors. For N = 0, none of the atoms are connected to any like neighbors. Each C or P atom has only one like (C or P) neighbor for N = 1, and two like neighbors for N = 2. There is no N = 3 structure, which would imply a pure carbon or phosphorus lattice. The tiling patterns for different 2D-PC allotropes are shown in Fig. 8.1(a)-8.1(c). A similar categorization scheme has been used previously to distinguish between different allotropes of 2D phosphorene [201], where N was the number of "like" neighbors either in the upper or lower position within the lattice.

Whereas the tiling pattern is useful for simple categorization, it does not provide infor-

mation about the nontrivial optimum structure shown in Fig. 8.1(d)-8.1(i), which results from a competition between the favored planar sp^2 hybridization of C and non-planar sp^3 hybridization of P. The side view of structures displayed in Fig. 8.1 best illustrates that allotropes with the same value of N may be structurally different. In analogy to the different postulated phosphorene allotropes [33, 157], I distinguish α_N , which display a black-P-like armchair structure in side view, from β_N phases of PC, which display a blue-P-like (or grey-As-like) zigzag structure in side view, and use the index N to identify the structural category.

I start my discussion with the N = 1 allotropes α_1 -PC and β_1 -PC, shown in the middle column in Fig. 8.1. According to the definition of N, each atom has one neighbor of the same species and two of the other species, forming isolated P-P and C-C dimers, as seen in the tiling pattern and the atomic structures. As seen in Fig. 8.2(a), the chemical octet rule [202] is satisfied both on C sites in the graphitic sp^2 configuration and on P sites, containing a lone electron pair, in sp^3 configuration, indicating stability. Both allotropes have rectangular unit cells consisting of distorted hexagons. The unit cell of α_1 -PC with 8 atoms is larger than that of β_1 -PC with four atoms.

In the N = 2 allotropes α_2 -PC and β_2 -PC, shown in the right column of Fig. 8.1, each atom has two like neighbors and one unlike neighbor. In the side view, these allotropes look very similar to those of the N = 1 category. The main difference becomes apparent in the top view. Whereas N = 1 structures contain ethylene-like C₂ units that are interconnected by P₂ dimers, N = 2 systems contain contiguous trans-polyacetylene-like all-carbon chains that are separated by P-chains. Due to the difference between the locally planar sp^2 bonding of C atoms and locally non-planar sp^3 bonding of P atoms, and due to the difference between equilibrium C-C and P-P bond lengths, the hexagons found in N = 1 structures change to

Table 8.1: Calculated properties of different 2D-PC allotropes. $\langle E_{coh} \rangle$ is the cohesive energy per "average" atom with respect to isolated atoms. $\langle \Delta E \rangle = \langle E_{coh} \rangle - \langle E_{coh,max} \rangle$ describes the relative stability of a system with respect to the most stable structure. $|\vec{a_1}|$ and $|\vec{a_2}|$ are the in-plane lattice constants defined in Fig. 8.1. d_{P-P} , d_{P-C} and d_{C-C} are the equilibrium bond lengths between the respective species. In α_0 -PC, the P₁-C bonds differ from the P₂-C bonds in length.

Structure	α_0 -PC	β_0 -PC	α_1 -PC	β_1 -PC	α_2 -PC	β_2 -PC
$< E_{coh} > (eV/atom)$	4.80	4.75	5.05	5.06	5.20	5.20
$<\Delta E > (eV/atom)$	-0.40	-0.45	-0.15	-0.14	0.00	0.00
$ \vec{a}_{1} $ (Å)	8.41	5.12	8.73	4.76	9.84	10.59
$ \vec{a}_2 $ (Å)	2.94	2.95	2.95	2.95	5.11	5.11
d_{P-P} (Å)	—	—	2.36	2.36	2.29	2.29
d_{P-C} (Å)	$1.86 (P_1)$	1.78	1.84	1.84	1.85	1.85
	$1.71 (P_2)$					
d_{C-C} (Å)	—	_	1.38	1.38	1.44	1.44

pentagon-heptagon pairs in the optimum N = 2 structure resembling the pentheptite or haeckelite structures of graphitic carbon. As seen in Fig. 8.2(b), similar to N = 1 structures, the chemical octet rule is satisfied on both C and P sites. The lattice of α_2 -PC and β_2 -PC allotropes contains rectangular unit cells with sixteen atoms.

In 2D PC compounds of category N = 0, shown in the left column of Fig. 8.1, each atom is surrounded by three unlike neighbors. There is no bonding configuration that would satisfy the octet rules on all sites. The bonding configuration depicted in Fig. 8.2(c) satisfies the octet rule only at the C sites, whereas the configuration in Fig. 8.2(d) favors only the P sites. The bonding configuration depicted in Fig. 8.2(e) contains alternating P-C chains containing P sites with lone electron pairs and C atoms in sp^2 configuration, which satisfy the octet rule, and P-C chains that do not satisfy it. In whatever bonding arrangement, the bonding configuration in N = 0 structures is frustrated. As a consequence, the α_0 -PC structure converts spontaneously from an initial armchair configuration, similar to α_1 -PC and α_2 -PC, to the zigzag structure depicted in Fig. 8.1(d).

The reconstruction process of α_0 -PC can be seen in the snap shots of the optimizing



Figure 8.3: Spontaneous structural transformation of α_0 -PC from its initial armchair profile in (a) to the final structure with a zigzag profile in (d). Snap shots of the intermediate structures, shown in side view in the upper panels, are accompanied by the corresponding band structure in the lower panels. Noteworthy is the transition from a metallic structure in (a) to a semiconductor in (d). The significance of the inequivalent P₁ and P₂ sites is discussed in the main text.

process shown in the upper panels of Fig. 8.3(a)-8.3(d). The changing band structure, calculated using the DFT-PBE functional, is presented below the structural snap shots in Fig. 8.3. These results allow us to follow the gradual transition from the initial metallic structure in (a) to a semiconductor with a 0.7 eV band gap in (d). The band gap opening comes along with a symmetry reduction, best seen in the transformation of the local environment at the P₁ and P₂ sites, which are equivalent in (a) and become significantly different in (d). The final α_0 -PC structure with inequivalent P₁ and P₂ sites reflects the bonding configuration in Fig. 8.2(e) containing P₁ sites with lone electron pairs and P₂ sites with lone electrons. The β_0 -PC structure, depicted in Fig. 8.1(g), remains locally stable in the electronic configuration shown in Fig. 8.2(d).

To make sure that the reconstruction process of α_0 -PC is unique and that all structures discussed in this chapter represent the true equilibrium configuration, rather than an artifact of unit cell limitations, I doubled the unit cells of all allotropes and found no further changes.



Figure 8.4: Phonon spectra of (a) β_0 -PC and (b) β_1 -PC monolayers.

I also found all structures resistant under arbitrary deformations, which is validated by showing that the phonon spectra of unsupported monolayers are free of imaginary frequencies that would indicate spontaneous collapse of the structure in a way dictated by the particular soft mode character. Computation of phonon spectra of 2D structures with low flexural rigidity is very demanding, since such calculations require very large supercells to yield converged results in particular for the flexural Z mode with an $\omega(k) \propto k^2$ dispersion near the Γ point. For the sake of illustration, I present the phonon spectra of β_0 -PC and β_1 -PC monolayers in Fig. 8.4. The soft out-of-plane acoustic Z modes can be clearly distinguished from the in-plane transverse acoustic and the in-plane longitudinal acoustic modes, which are the hardest of the three. Clearly, further structural stabilization that suppresses the Z modes will occur when PC is deposited on a substrate.

Structural characteristics and the binding energy of the different allotropes are summarized in Table 8.1. My energy results are obtained using the DFT-PBE functional (including spin polarization where required), which is known to overbind to some degree. I define the cohesive energy per atom, $\langle E_{coh} \rangle$, by dividing the total atomization energy by the total number of atoms, irrespective of species. The energy values in the first rows indicate that for given N, the α and β phases are almost equally stable, confirming that categorizing structures by the number of like neighbors at any site makes sense in terms of stability. Clearly, N = 2 systems are most stable, followed by N = 1 and N = 0 allotropes. In particular, the cohesive energy of N = 2 monolayers exceed the 5.14 eV/atom value of the postulated GaSe-like PC multi-layer structures [191, 192] by 0.06 eV/atom.

The lower stability of N = 0 systems has been anticipated above, since the octet rule can not be satisfied at all sites. I also note that the α_0 phase is slightly more stable than the β_0 phase of PC. The stability advantage of α_0 -PC derives from the larger variational freedom within the unit cell, which allows the distinction of two different P sites (P₁ and P₂), as shown in Fig. 8.1(d) and Fig. 8.2(e). The α_0 -PC structure consists of P₁(sp^3)-C(sp^2) chains, which obey the octet rule and form stable ridges, alternating with P₂-C chains, which do not obey the octet rule and form terraces.

Additional support for the plausibility of the bonding configuration depicted in Fig. 8.2 comes from the equilibrium bond lengths, which are listed in Table 8.1. With the exception of N = 0 structures, the bond lengths depend primarily on N and are rather insensitive to the phase (α or β). For N = 1 and N = 2 structures, the C-C bond lengths lie close to the 1.42 Å value in sp^2 bonded graphite (or graphene) and the P-P bond lengths are close to the 2.26 - 2.29 Å range found in layered black phosphorus (or phosphorene).

As seen in Fig. 8.2(a) and 8.2(b), P and C atoms are connected by a single-bond with $d_{P-C}\approx 1.85$ Å in N = 1 and N = 2 category structures. As suggested above, the bonding is frustrated at least in parts of N = 0 structures. In the significantly reconstructed α_0 -PC system, depicted in Fig. 8.1(d), I can distinguish P₁ sites at ridges from P₂ sites at terraces. The lengths of the three P-C bonds are very similar at each of the P sites of one type, but



Figure 8.5: Electronic band structure, density of states (DOS), and charge density ρ_{vc} associated with valence frontier states of α_N and β_N allotropes, where N is the structural category. The energy range associated with ρ_{vc} is indicated by the green shaded region in the band structure and DOS panels and extends from $E_F - 0.45$ eV< $E < E_F$ in (a), $E_F - 0.40$ eV< $E < E_F$ in (c) and (d), $E_F - 0.10$ eV< $E < E_F$ in (b), (e) and (f). Isosurface plots of ρ_{vc} are displayed in the right-side panels and superposed with ball-and-stick models of the structure in top and side view. The isosurface values of ρ_{vc} are 1.0×10^{-3} e/Å³ in (a), 2.0×10^{-3} e/Å³ in (b), 0.5×10^{-3} e/Å³ in (c) and (d), and 0.5×10^{-4} e/Å³ in (e) and (f).

they differ significantly between P₁ and P₂. At P₁ sites that satisfy the octet rule, as seen in Fig. 8.2(e), the P₁-C bond length of 1.86 Å is very similar to N = 1 and N = 2 structures. At P₂ sites, which do not satisfy the octet rule, the frustrated bonds are much shorter with $d_{P-C} = 1.71$ Å. As seen in Fig. 8.1(g), there is no reconstruction in the β_0 -PC structure. As seen in the corresponding Fig. 8.2(c) or 8.2(d), the octet rule is only satisfied at either the P or the C sites. The P-C bonds are frustrated and their length of 1.78 Å lies in-between the P₁-C and P₂-C bond lengths in α_0 -PC. Results of my DFT-PBE electronic band structure calculations for monolayers of the six proposed PC allotropes are presented in Fig. 8.5.

The electronic band structure and associated density of states (DOS) of N = 0 systems is shown in Fig. 8.5(a) and 8.5(b). My results in Fig. 8.5(a) suggest that α_0 -PC is an indirect-gap semiconductor with a band gap of ≈ 0.7 eV. In stark contrast, the structurally similar β_0 -PC allotrope is metallic according to Fig. 8.5(b). As suggested earlier, all bonds and electronic configurations are frustrated in β_0 -PC, with all C sites engaging only three valence electrons in sp^2 -like bonds, leaving one lone electron behind, and the angle at the P ridge being too large for typical sp^3 bonding. This finding, in particular the presence of a non-bonding electron in the C2 p_{\perp} orbital, is seen in the frontier states of β_0 -PC that are depicted in the right panel of Fig. 8.2(b).

 α_0 -PC is quite different from β_0 -PC, as it contains two inequivalent P and C sites. The P₁ site at the ridge displays the favored sp^3 bonding characteristic and its lone pair orbital is present in the frontier state displayed in the right-hand panel of Fig. 8.5(a). In contrast, the bonding is very different at the P₂ site, where the lone pair orbital does not contribute to the frontier state. The flat bonding geometry near this site is reminiscent of sp^2 bonding at the C sites. The added flexibility provided by a larger unit cell allows for additional stabilization of α_0 -PC due to the opening of a band gap, in rough analogy to the Peierls instability.

As seen in Fig. 8.5(c) and 8.5(d), both α_1 -PC and β_1 -PC have a direct band gap, which I attribute to the presence of isolated ethylene-like units mentioned above. The two allotropes display a very similar charge distribution in their valence frontier states, which contain lone pair orbitals on P sites and reflect sp^2 bonding between C sites. The main difference between the two structures is that the 0.4 eV wide gap in α_1 -PC is at the Γ point, whereas the 0.3 eV gap in β_1 -PC is at the X point. In both structures, the band dispersion is rather anisotropic near the top of the valence and bottom of the conduction band, which causes an anisotropy in the effective mass. I find the effective mass of both electrons and holes to be much smaller along x-direction than along the y-direction, which is reminiscent of the situation in black phosphorene [27, 28]. The effective mass anisotropy offers a significant advantage in transport, since it combines high mobility of carriers with a large DOS near the band edges.

According to Fig. 8.5(e) and 8.5(f), the two N = 2 allotropes, α_2 -PC and β_2 -PC, share very similar band structure, DOS, and frontier orbitals due to structural similarities. The electronic structure of these systems is nevertheless very different from the other two categories, chiefly due to the presence of trans-polyacetylene-like chains mentioned above. Both α_2 -PC and β_2 -PC display a Dirac cone at the Fermi level, at a crystal momentum between Γ and Y. As mentioned before, the distinguishing feature of N = 2 structures is the alternation between chains consisting of pure P or pure C atoms. Fig. 8.2(b) indicates that all P sites have occupied lone pair orbitals, which are also reflected in the frontier states. The P chains form ridges within the structure, with bond angles characteristic of the sp^3 bonding found in black phosphorus. The structure of the carbon chains, also illustrated in Fig. 8.2(b), resembles that of conjugated trans-polyacetylene or graphene with sp^2 bonding, and the presence of $C2p_{\perp}$ orbitals in the frontier states is clearly seen in the right-side panels of Fig. 8.5(e) and 8.5(f). Differences between equilibrium bond length and bond angles of the P and C chains are accommodated by introducing pentagon-heptagon pairs. The conjugation within C chains and their suppressed dimerization caused by their bonding to adjacent P chains lies behind the formation of the Dirac cone. Due to the strong anisotropy in the system, caused by the direction of the trans-polyacetylene-like chains, the Dirac cone is anisotropic in the plane of the layer.



Figure 8.6: Band structure of semi-metallic (a) α_2 -PC and (b) β_2 -PC near the Dirac point. (c) Definition of the high-symmetry points in the Brillouin zone of the structures in (a) and (b).

More information about the band structure of semi-metallic α_2 and β_2 allotropes of PC is displayed in Fig. 8.6(a) and 8.6(b). Each structure has a Dirac point at point A located in-between Γ and Y in the Brillouin zone shown in Fig. 8.6(c). The unusual location of the Dirac points inside the Brillouin zone differs from its location in Brillouin zone corners in graphene. Due to the strong structural anisotropy in the systems, the Dirac cone is anisotropic and thus not a true cone. The opening angle of the cone, given by the $E(\mathbf{k})$ dispersion near A, is largest along the A - B direction and the smallest along the $A - \Gamma$ or A - Y direction. I have found that uniaxial strain may be used to eliminate the anisotropy of the Dirac cone. At the same time, however, also the location of the Dirac point along $\Gamma - Y$ line in the Brillouin zone changes.

Even though DFT-PBE calculations notoriously underestimate the fundamental band gap between occupied and unoccupied states, the calculated dispersion $E(\mathbf{k})$ of individual bands is believed to closely resemble experimental values. For the sake of comparison, I have also performed DFT-HSE06 [68, 200] calculations with a hybrid exchange-correlation functional for the same structures. As seen in Fig. 8.7, my HSE06 studies use the default



Figure 8.7: Electronic band structure of (a) α_0 -PC, (b) α_1 -PC, (c) α_2 -PC, (d) β_0 -PC, (e) β_1 -PC, and (f) β_2 -PC monolayer obtained using DFT calculations with PBE and HSE06 exchange-correlation functionals.

value of 0.25 for the mixing parameter and, for the sake of fair comparison, the identical geometry that had been optimized by DFT-PBE. Band structure results in Fig. 8.7 indicate that for the semiconducting α_0 -PC, α_1 -PC and β_1 -PC structures, HSE06 shifts occupied states rigidly down and unoccupied states up with respect to the Fermi level, thus increasing the band gap value. As a result, HSE06 gives band gap values of 1.5 eV for α_0 -PC, 1.1 eV for α_1 -PC, and 0.8 eV for β_1 -PC. As a consequence of the increased band gap, the compressive in-layer strain required to close this gap in α_1 -PC and β_1 -PC will be larger than what was expected based on DFT-PBE results. HSE06 does not affect the metallic character of β_0 -PC and semi-metallic character of α_2 -PC and β_2 -PC predicted by DFT-PBE, but increases the band dispersion and thus the width of the valence and conduction bands.



Figure 8.8: Effect of uniaxial in-layer strain on (a) the relative binding energy ΔE_{tot} and (b) the fundamental band gap in different PC allotropes. Results for α_0 -PC, β_0 -PC, α_1 -PC, β_1 -PC, α_2 -PC and β_2 -PC are distinguished by color and symbols. Results for strain in the *x*-direction, defined in Fig. 8.1, are shown by solid lines and for strain in the *y*-direction by dashed lines.

Similar to other non-planar 2D systems like phosphorene, PC is susceptible to even minute in-plane stress, which can cause major distortions in the geometry, affecting the electronic structure and bonding. To quantify this effect, I have determined the effect of tensile and compressive strain on the stability and the fundamental band gap in the different PC allotropes and present the results in Fig. 8.8. I have considered uniaxial strain along the x- and the y-direction, defined in Fig. 8.1. Since all allotropes discussed here are nonplanar, applying in-layer strain changes the effective thickness of the layers and vice versa. As expected, layer thickness is reduced under tensile strain and increased under compressive strain. For strain values below 5%, I have observed changes in layer thickness of up to 10%. The distinct structural anisotropy, best seen in the side views, translates into a distinct anisotropy of the strain energy with respect to the strain direction, shown in Fig. 8.8(a). Similar to black phosphorene, the system appears soft when strained along the x-direction normal to the ridges and valleys, whereas it is much stiffer when distorted along the ydirection. I find the α phase to be particularly soft in the x-direction, with compressive or tensile strain requiring $\Delta E \lesssim 5$ meV/atom in strain energy.

The dependence of the fundamental band gap on the in-layer strain, as obtained by my DFT-PBE calculations, is shown in Fig. 8.8(b). I find that compression along the soft *x*-direction does not affect the band gap much, quite unlike what is expected to occur in black phosphorene [28]. This is quite different from my results for strain along the stiffer *y*-direction. There, I observe the fundamental band gap to disappear at compressive strain exceeding 4% for α_1 -PC and 3% for β_1 -PC. I also find that the metallic character of β_0 -PC and semi-metallic character of α_2 -PC and β_2 -PC are not affected by tensile or compressive strains up to 5% applied along the *x*- or the *y*-direction. Since vertical strain causing a 10% reduction of the layer thickness is equivalent to an effective tensile in-layer strain below 5%, I can judge its effect on the electronic structure based on the above findings.

Even though the cohesive energy of the 2D structures presented here exceeds that of previously discussed PC systems, the calculated cohesive energy per formula unit still falls 0.54 eV short of the sum of the cohesive energies of pure black phosphorene, 3.27 eV, and pure graphene, 7.67 eV according to DFT calculation. Even though the PC allotropes discussed here are all stable, the slight energetic preference for pure components over the PC compound should offer challenges in the synthesis. Recent advances in supramolecular assembly may solve this problem. Similar to my requirements, precisely designed structures including graphdiyne [203, 204], graphene nanoribbons [205] and carbon nanotubes [206] have been assembled using wet chemical processes from specific molecular precursors. In the same way, I expect that the postulated 2D-PC structures may be formed of proper molecular precursors that contain sp^2 bonded carbon and sp^3 bonded phosphorus.

8.4 Summary

In conclusion, I have performed *ab initio* density functional calculations and identified previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer. I found that different non-planar stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. I have introduced the structural category N, defined by the number of like nearest neighbors ranging from 0 to 2, and found that N correlates with the stability and the electronic structure characteristic. I found structures of the N = 0 category either to be metallic or to reconstruct spontaneously to a more stable structure with a larger unit cell and a sizeable fundamental gap. Systems of the N = 1 category are more stable than N = 0 systems and display a significant, direct band gap and a significant anisotropy of the effective mass of carriers. N = 2 systems are the most stable of all, are semi-metallic, and display an anisotropic Dirac cone at the Fermi level. Due to their non-planar character, all systems can sustain in-layer strain at little energy cost. The fundamental band gap is not very sensitive to strain in most systems with the exception of N = 1 allotropes, where it closes upon applying compressive strain of $\lesssim 5\%$ along the ridges and valleys.

Chapter 9

Curvature and stability for two-dimensional systems

The following discussion is my original contribution to the related publications by Jie Guan, Zhongqi Jin, Zhen Zhu, Chern Chuang, Bih-Yaw Jin and David Tománek, Phys. Rev. B **90**, 245403 (2014) [207], and by Chern Chuang, Jie Guan, David Witalka, Zhen Zhu, Bih-Yaw Jin and David Tománek, Phys. Rev. B **91**,165433 (2015) [208].

9.1 Introduction

Layered structures including graphite, hexagonal boron nitride, black phosphorus, transition metal dichalcogenides such as MoS_2 , and oxides including V_2O_5 are very common in Nature. The possibility to form stable two-dimensional (2D) structures by mechanical exfoliation of these structures appears very attractive for a variety of applications. [45, 209] The most prominent example of such 2D systems, graphitic carbon, is the structural basis not only of graphene, [45] but also fullerenes, nanotubes, tori, and schwarzites. [46–50] Even though the structural motif in all of these systems may be the same, their mechanical and electronic properties depend sensitively on the local morphology. [51–53] Not only does the natural abundance of structural allotropes and isomers reflect their net energetic stability, but also the relative chemical reactivity of specific sites in a given structure correlates well with the



Figure 9.1: Principal radii of curvature R_1, R_2 and the Gaussian curvature G on the surface of (a) a sphere and (b) a cylinder and (c) at a saddle point. (d) Determination of the local curvature at point P using the atomic lattice (grey dashed lines) and the dual lattice (blue solid lines). P is the center atom and F_i (i = 1 3) are three first neighbors. V_i (i = 1 3) are vertices of due lattice.

local curvature and local stability. [51-53] This relationship has been well established for the reactive sites in the C₅₀ fullerene, [51] used to induce structural collapse leading to chemical unzipping of carbon nanotubes, [93, 210, 211] and used to destroy collapsed carbon nanotubes. [53]

For very large structures, estimating the global or local stability using *ab initio* calculations has proven impracticable. Instead, in such structures the stability has often been estimated using empirical rules or parameterized force fields including the Tersoff potential and molecular mechanics, [54–57] with sometimes unsatisfactory results. Application of continuum elasticity theory, which can describe stability changes due to deviation from planarity, has been successful, but it is limited to systems with a well-defined, constant curvature. [58, 59] Since strain energy is dominated by local geometry and independent of the global morphology, it is intriguing to explore, whether the local deformation energy may be accurately determined from local morphology estimates using the atomic geometry. If so, then the local stability in even arbitrarily shaped structures could be estimated accurately.

Here I propose a fast method to determine the local curvature in 2D systems with a complex morphology using the local atomic geometry. Curvature information alone, combined with elastic constants obtained for a planar system, provides accurate stability estimates in the framework of continuum elasticity theory. I find that relative stabilities of graphitic structures including fullerenes, nanotori, nanotubes, and schwarzites, as well as phosphorene nanotubes, calculated using this approach, agree closely with *ab initio* density functional calculations. The continuum elasticity approach can be applied to all 2D structures and is particularly attractive in complex systems with known structure, where the quality of parameterized force fields has not been established.

9.2 Continuum elastic method

The local curvature at a particular location on a surface is given by the two principal radii of curvature R_1 and R_2 , as shown in Fig. 9.1. On a spherical surface, $R_1 = R_2$. On a cylindrical surface, R_1 is the cylinder radius and $R_2 \rightarrow \infty$. Finally, a saddle point on a surface is characterized by opposite signs of R_1 and R_2 . Knowing the principal radii of curvature everywhere, I may use continuum elasticity theory to determine the curvature energy ΔE_C with respect to a planar layer using [212]

$$\Delta E_C = \frac{1}{2} D \int_{surface} dA \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} + \frac{2\alpha}{R_1 R_2} \right) \,. \tag{9.1}$$

Here, the integral extends across the entire surface, D is the flexural rigidity and α is the Poisson ratio. Simple expressions for ΔE_C can be obtained for simple morphologies such as a sphere or a cylinder, where R_1 and R_2 are constant everywhere. [58] This is, however, not the case in general.

I find it convenient to introduce the local mean curvature

$$k = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{9.2}$$

and the local Gaussian curvature

$$G = \frac{1}{R_1 R_2} \,. \tag{9.3}$$

Using these quantities, I can rewrite Eq. (9.1) as

$$\Delta E_C = D \int_{surface} dA \left[2k^2 - (1 - \alpha)G \right] . \tag{9.4}$$

In the following, I will consider the equilibrium arrangement of atoms in a planar 2D structure as the reference structure and will determine the local curvature from changes in the local morphology. The discrete counterpart of Eq. (9.4) for the curvature energy ΔE_C is a sum over atomic sites i,

$$\Delta E_C \approx DA \sum_i \left[2k_i^2 - (1 - \alpha)G_i \right] , \qquad (9.5)$$
where A is the area per atom.

To use Eq. (9.5) for curvature energy estimates, I need to know the local curvatures k and G at all atomic sites. My approach to estimate these values at a given site P is illustrated in Fig. 9.1(d). According to Eq. (9.2), the local mean curvature k should be close to the average inverse radius of curvature at that point,

$$k \approx \left\langle \frac{1}{R} \right\rangle \ . \tag{9.6}$$

Since the atomic site P and its nearest three neighbors F_1 , F_2 and F_3 define the surface of a sphere of radius R, I take k = 1/R.

The positions of four atoms do not allow one to distinguish whether P is on a plane, a sphere or a cylinder or at a saddle point. I may obtain this additional information using the concept of an angular defect. On any surface that can be triangulated as in Fig. 9.1(d), the angular defect at a representative vertex V_1 is defined by $\Delta(V_1) = 2\pi - \sum_i \varphi_i$ in units of radians. The local Gaussian curvature at V_1 is then given by [213]

$$G(V_1) = \Delta(V_1)/A_t = \left(2\pi - \sum_i \varphi_i\right)/A_t , \qquad (9.7)$$

where A_t is the total area of the triangulated surface divided by the number of vertices.

For trivalent molecular graphs containing 5-, 6- and 7-membered rings found in fullerenes, carbon nanotubes, and schwarzites, a unique triangulation may be obtained by connecting the centers of adjacent polygons. This method is referred to as the dual graph in graph theory [214] and its use is illustrated in Fig. 9.1(d). Since P is not a vertex in the dual graph, but rather the center of the triangle $\Delta V_1 V_2 V_3$, I must infer the local Gaussian curvature at *P* from the angular defects at V_1 , V_2 and V_3 . If vertex V_j is surrounded by n_j triangles, I may assign to point *P* the angular defect $\Delta(P) = \Delta(V_1)/n_1 + \Delta(V_2)/n_2 + \Delta(V_3)/n_3$. Then, I can estimate the local Gaussian curvature at *P* as

$$G(P) = \Delta(P)/A , \qquad (9.8)$$

where A is the average area per atom. I use $A = 2.62 \text{ Å}^2$, the value found in the honeycomb lattice of graphene, for all graphitic structures.

The above definition of the local Gaussian curvature satisfies exactly the equality

$$A\sum_{atoms} G(P_j) = A_t \sum_{vertices} G(V_j) = 2\pi\chi .$$
(9.9)

Here, χ is the Euler characteristic of the surface, given by $\chi = 2 - 2g$, where g is the genus, meaning 'number of holes'. Of interest here is the fact that $\chi = 2$ for spherical objects like fullerenes and $\chi = 0$ for cylindrical objects such as nanotubes. Equation (9.9) is the discretized version of the Gauss-Bonnet theorem [215] regarding the integral of the Gaussian curvature over an entire closed surface, called the sum of the defect, which is usually formulated as $\int_{surface} GdA = 2\pi\chi$.

The variation of the local Gaussian curvature G and the local curvature energy $\Delta E_C/A$ across the surface of carbon polymorphs, including two fullerene isomers, a nanotube, and a schwarzite structure, is displayed in Fig. 9.2. The local curvature energy in these sp^2 -bonded structures has been evaluated using the elastic constants of graphene [58]: D = 1.41 eV and $\alpha = 0.165$. The higher stability of the C₃₈(17) isomer in Fig. 9.2(b) is reflected in a rather uniform curvature energy and Gaussian curvature distribution. The low stability of the



Figure 9.2: Local Gaussian curvature G (upper panels) and local curvature energy $\Delta E_C/A$ (lower panels) across the surface of (a) the least stable C₃₈ isomer, (b) the most stable C₃₈ isomer, (c) a (10,10) carbon nanotube, and (d) a schwarzite structure with 152 atoms per unit cell. The values of G and $\Delta E_C/A$ have been interpolated across the surface.

 $C_{38}(2)$ isomer in Fig. 9.2(a) is reflected in a large variation of curvature energy and Gaussian curvature, clearly indicating the most reactive sites. Cylindrical carbon nanotubes, such as the (10,10) nanotube displayed in Fig. 9.2(c), have zero Gaussian curvature and a constant curvature energy caused by the mean curvature. Schwarzites such as the C_{152} structure, displayed in Fig. 9.2(d), have only negative Gaussian curvature that may vary across the surface, causing variations in the local curvature energy.

9.3 Validation of the continuum elasticity approach

I will next test the accuracy of the continuum elasticity approach by calculating the relative stability of non-planar structures based on graphitic carbon. An infinite number of morphologies including nanotubes, fullerenes and schwarzites may be produced by deforming a segment of a graphene layer and reconnecting its edges so that all carbon atoms are



Figure 9.3: Strain energy ΔE in carbon nanostructures with respect to the graphene reference system. (a) DFT-based total strain energy ΔE_{tot}^{DFT} for selected fullerenes, with the most stable isomers indicated by the larger symbols. (b) Strain energy ΔE in different C₃₈ isomers. Total energy differences ΔE_{tot}^{DFT} based on DFT, $\Delta E_{tot}^{Tersoff}$ based on the Tersoff potential and $\Delta E_{tot}^{Keating}$ based on the Keating potential are compared to curvature energies $\Delta E_C^{Keating}$ based on Keating-optimized geometries. To further compare curvature energy based on different geometries, ΔE_{tot}^{DFT} are compared to curvature energies ΔE_C^{DFT} based on continuum elasticity theory for structures optimized by DFT, and $\Delta E_C^{Keating}$ in (c).

threefold coordinated. In many cases, the non-planar structures contain carbon pentagons and heptagons in the graphitic honeycomb arrangement of atoms as required by Euler's theorem. [215]

To validate the continuum elasticity theory results, I calculated the total energy of a graphene monolayer and selected graphitic structures using *ab initio* density functional theory (DFT) as implemented in the SIESTA code. [69] I used the Local Density Approximation (LDA) [216,217] and Perdew-Burke-Ernzerhof (PBE) [64] exchange-correlation functionals, norm-conserving Troullier-Martins pseudopotentials [145], and a double- ζ basis including polarization orbitals. The 1D Brillouin zone of nanotubes was sampled by 16 *k*-points and the 2D Brillouin zone of graphene by 16×16 *k*-points. [136] The small Brillouin zones of schwarzites with several hundred C atoms per unit cell were sampled by only 1 *k*-point. All the other parameters used here are the same as previous chapters.

My DFT-LDA results for the relative energy ΔE_{tot}^{DFT} of optimized C_n fullerenes [218]

with respect to graphene are shown in Fig. 9.3(a). The various data points for one size correspond to different structural isomers, which increase fast in number with increasing n. If all fullerenes were perfect spheres, Eq. (9.4) would simplify to [58] $\Delta E_C = 4\pi D(1 + \alpha)$. Using the proper elastic constants for graphene [58] D = 1.41 eV and $\alpha = 0.165$, I would estimate $\Delta E_C = 20.6$ eV for all fullerenes independent of size. The numerical values for the different optimized fullerene isomers in Fig. 9.3(a) are all larger, indicating that variations in the local curvature and bond lengths cause a significant energy penalty.

As I show in the following, considering only local curvature variations across the surface (and ignoring precise atomic positions) allows continuum elasticity theory to quantitatively predict the strain energy with a precision competing with *ab initio* calculations. To illustrate this point, I present in Fig. 9.3(b) the total strain energy ΔE in seventeen isomers of C₃₈ obtained using various approaches. The strain energy ΔE_{tot}^{DFT} based on DFT, which is expected to represent closely the experimental results, is not only significantly lower than the predicted values, $\Delta E_{tot}^{Tersoff}$, based on the Tersoff potential [54] but also differs from this popular bond-order potential in the prediction of relative stabilities.

Next I demonstrate that accurate energy estimates may be obtained even for geometries optimized using simple potentials with only bond stretching and bond bending terms such as the Keating potential [219,220]

$$\Delta E_K = \frac{1}{2} \alpha_K \sum_{\substack{\langle i,j \rangle \\ i < j}} \frac{(r_{ij}^2 - R^2)^2}{R^2} + \frac{1}{2} \beta_K \sum_{\substack{\langle i,j,k \rangle \\ j < k}} \frac{(\mathbf{r_{ij}} \cdot \mathbf{r_{ik}} + \frac{1}{2}R^2)^2}{R^2} \,. \tag{9.10}$$

The first term sums over nearest neighbor pairs and the second term over nearest neighbor triplets, where j and k share the same neighbor i. DFT calculations for graphene yield R = 1.42 Å as bond length, 120° as bond angle, $\alpha_K = 11.28 \text{ eV}/\text{Å}^2$ and $\beta_K = 4.14 \text{ eV}/\text{Å}^2$. Strain energies for Keating optimized fullerenes are shown in Fig. 9.3(b). Whereas the Keating optimized geometry is close to the DFT optimized geometry, the Keating strain energy $\Delta E_{tot}^{Keating}$ clearly underestimates the DFT values and does not correctly represent the relative stabilities of the different isomers. As an alternative, I used the Keating optimized geometry to obtain the curvature strain energy $\Delta E_C^{Keating}$ using the continuum approach. I found that this approach represents the relative stabilities of isomers adequately and compares well to ΔE_{tot}^{DFT} . The curvature strain energy values are somewhat lower than the DFT values, since energy penalties associated with bond stretching and bending do not appear in the continuum approach. The small value of such corrections reflects the fact that in equilibrated structures, bond lengths and angles are near their optimum. The largest errors are expected in frustrated structures, where not all bond lengths and angles can be optimized simultaneously.

One of the key findings of this study is that continuum elasticity theory provides not only a fast, but also a relatively robust way to determine relative stabilities that are, to some degree, insensitive to the precise geometry. I illustrate this point in Fig. 9.3(c), where I compare different ways to determine the total strain energy ΔE in all C₃₈ isomers discussed in Fig. 9.3(b). ΔE_{tot}^{DFT} , shown by the solid line, is the difference between the total energy in DFT of DFT-optimized C₃₈ isomers and 38 carbon atoms in the graphene structure. ΔE_C^{DFT} , given by the dashed line, is the curvature energy based on the DFT-optimized geometry. $\Delta E_C^{Keating}$, given by the dash-dotted line, is the curvature energy based on the Keating-optimized geometry. I note that all expressions provide an accurate representation of relative stabilities. As mentioned above, the fact that ΔE_C is about 10% lower than ΔE_{tot} is caused by my neglecting the stretching and bending of discrete atomic bonds in the continuum approach.



Figure 9.4: (Color online) Strain energy ΔE in carbon nanostructures with respect to the graphene reference system. (a) Comparison between DFT-based total energies ΔE_{tot}^{DFT} and the curvature energy $\Delta E_C^{Keating}$ based on Keating-optimized geometries for all fullerene isomers considered in Fig. 9.3(a). (b) Comparison between DFT-based strain energies $\Delta E_{tot}^{DFT}/n$ and curvature energies per atom $\Delta E_C^{Keating}/n$ for Keating-optimized geometries of fullerenes, nanotubes and schwarzites. Dashed lines represent agreement between DFT and continuum elasticity results.

Encouraged by the level of agreement for C₃₈, I present in Fig. 9.4(a) the correlation between the curvature energy $\Delta E_C^{Keating}$ and ΔE_{tot}^{DFT} based on DFT for all fullerenes discussed in Fig. 9.3(a). The narrow spread of the data points close to the $\Delta E_C^{Keating} = \Delta E_{tot}^{DFT}$ line confirms that the continuum elasticity approach is competitive in accuracy with computationally much more involved *ab initio* calculations.

To demonstrate the generality of my approach, I extend it from near-spherical fullerenes to nanotubes with cylindrical symmetry and schwarzites with local negative Gaussian curvature. Since nanotubes and schwarzites are infinitely large, I compare stabilities on a per-atom basis in these structures. Besides results for the fullerenes discussed in Figs. 9.3 and 9.4(a), Fig. 9.4(b) displays results for nanotubes with radii ranging between 2.5 - 9.0 Å and for schwarzite structures with 152, 192 and 200 carbon atoms per unit cell. These results again indicate excellent agreement between curvature energies in Keating-optimized structures and



Figure 9.5: (a)Atomic structure of a polygonal nanotorus containing non-hexagonal rings. (b) Energy differences per atom ΔE_{tot}^{DFT} based on DFT and $\Delta E_{tot}^{Keating}$ based on the Keating potential are presented next to curvature energies $\Delta E_c^{Keating}$ for Keating-optimized geometries.

DFT-based strain energies. This agreement is particularly impressive, since the spread of atomic binding energies extends over more than 1 eV.

My continuum elastic method was also applied to polygonal carbon nanotori. Unlike the polyhex nanotori rolled up from carbon nanutubes, the polygonal nanotori also contain non-hexagonal rings to release the large in-plane strain, as an example shown in Fig. 9.5(a). The results of my methodology to a subset of 22 polygonal nanotori are shown in Fig. 9.5(b). Here the strain energy calculated through Eq. (9.5) with geometry optimized by Keating potential is represented by the green squares, energy calculated with the accurate DFT method by black dots, and the Keating potential energy for the Keating-optimized optimized geometry by red rhombi. My results show clearly that for Keating-optimized geometries, strain energies based on Eq. (9.5) reproduce my *ab initio* results rather well. On the other side, strain energies estimated using Keating potential alone not only significantly underestimates the strain, but also do not follow the correct general trend. This firmly establishes the applicability of the continuum methodology to polygonal nanotori under investigation.



Figure 9.6: Local Gaussian curvature G (left panels) and local curvature energy $\Delta E_c/A$ (right panels) across the surface of selected nanotori. Representative examples shown are (a) the flattened C₃₂₀ nanotorus with 320 atoms and (b) the elongated C₂₈₀ nanotorus with 280 atoms. G and $\Delta E_c/A$ are interpolated from their values at the atomic sites.

The distribution of the local Gaussian curvature G_i and the local curvature energy per area, $\Delta E_c^{(i)}/A_0 = D[2k_i^2 - (1 - \alpha)G_i]$, across the surface of two representative nanotori is shown in Fig. 9.6. In both cases the positively curved segments, shown in red and yellow in the left panels, are concentrated near the loci of pentagons along the outer perimeter. The negatively curved segments, shown in blue, are concentrated near the loci of heptagons along the inner perimeter. Specifically, the heptagons along the inner perimeter of the C₃₂₀ nanotorus in Fig. 9.6(a) are well separated from the pentagons along the outer perimeter. This is different from the axially elongated C₂₈₀ torus of Fig. 9.6(b), where pentagon-heptagon pairs in the upper and lower planes form an azulene-like pattern. As a consequence, the Gaussian curvature is more evenly distributed in the latter. I emphasize again that for closed nanotori, the summation of the local Gaussian curvatures is strictly zero as dictated by the Gauss-Bonnet theorem.

The distribution of the local curvature energy is even more intriguing. I observed some degree of correlation between the absolute value of the local Gaussian curvature and the curvature energy. This should imply, at least for the nanotori investigated, that the two local curvatures k_i and G_i are not entirely independent. Yet the value of this correlation has its limitations, as shown in Fig. 9.6. Whereas in the flattened C₃₂₀ nanotorus in Fig. 9.6(a) the curvature energy is rather evenly distributed across the structure, the strain is clearly largest near the upper and lower ends of the C₂₈₀ nanotorus in Fig. 9.6(b). This curvature energy distribution in the right panels differs obviously from the Gaussian curvature distribution in the left panels. The reason for this finding is that in these extreme structures, I can not truly decouple k_i and G_i . In C₂₈₀, $G_i\approx 0$ and k_i is constant in the central 'tubular segments'. Only at the upper and lower ends, a large mean curvature k_i is required to connect the inner and the outer tube. The flatter C₃₂₀ nanotorus lacks 'tubular segments' with $G_i\approx 0$. Therefore, the Gaussian curvature energy are better correlated and more evenly distributed in this isomer.

As suggested at the outset, my approach to estimate relative stabilities is particularly valuable for unexplored systems such as monolayers of blue phosphorus, [33] where model potentials have not yet been proposed. My DFT-PBE results for a blue phosphorene monolayer indicate A = 4.78 Å² as the projected area per atom, D = 0.84 eV and $\alpha = 0.10$. The monolayer structure, shown in the top panel of Fig. 9.7(a), has an effective thickness of 1.27 Å. This structure can be rolled up into phosphorene nanotubes with different radii R using the approach used in the construction of carbon nanotubes. [50] As seen in Fig. 9.7(b), the strain energy for this geometry, obtained using continuum elasticity theory, agrees very well down to very small radii with results obtained using much more involved DFT calculations [173].



Figure 9.7: (a) Perspective view of the planar structure of a blue phosphorene monolayer (top), which has been rolled up to a nanotube with radius R (bottom). (b) Comparison between the strain energy per atom $\Delta E_C/n$ based on continuum elasticity theory and $\Delta E_{tot}^{DFT}/n$ based on DFT in blue phosphorene nanotubes. The dashed line represents agreement between DFT and continuum elasticity results.

9.4 Discussion

Given a set of points in space, such as atomic positions, it is possible to construct a smooth surface that contains all these points in order to characterize its shape everywhere, and to eventually determine the deformation energy using the continuum elasticity approach.

I illustrate this point by tessellating the smooth surface of a graphitic nanocapsule, consisting of a cylinder capped by hemispheres at both ends and representing C_{120} , in different ways. My results in Fig. 9.8 show that the average curvature energy $\langle \Delta E_C \rangle$ is rather insensitive to the tessellation density. The horizontal dashed line at $\langle \Delta E_C \rangle = 0.099 \text{ eV}/\text{Å}^2$, representing an extrapolation to a dense tessellation, is $\approx 5\%$ higher than the exact continuum elasticity value of 0.093 eV/Å², obtained for an ideal capsule with cylinder and hemisphere radius R = 3.55 Å. The small difference arises from my approximate way to estimate the mean curvature k on the cylinder surface and at the interface between the cylinder and the hemisphere. The extrapolated value is also close to the value of $\langle \Delta E_{tot}^{DFT} \rangle = 0.100 \text{ eV}/\text{Å}^2$



Figure 9.8: Average curvature energy $\langle \Delta E_C \rangle$ per area of a nanocapsule tessellated by a honeycomb lattice with different numbers of vertices. The vertical dash-dotted red line indicates that the capsule represents the C₁₂₀ structure. The inset shows, how the capsule surface can be tessellated by a honeycomb lattice with 120 vertices or atoms, shown by the white lines, and also with 480 vertices, shown by the red lines. The horizontal dashed black line represents an extrapolation to an infinitely dense tessellation.

based on the DFT-optimized C_{120} capsule.

The reverse process to determine atomic positions from the shape alone is not unique. An informative example is the structure of a carbon nanotube. Whereas the precise atomic structure within each nanotube is defined by the chiral index, many nanotubes with different chiral indices share essentially the same diameter and the same local curvature. Thus, given only the diameter of a (wide) hollow cylinder representing a nanotube, it is impossible to uniquely identify the chiral index and thus the atomic position. As a matter of fact, identifying the precise atomic positions is not necessary, since according to continuum elasticity theory, supported by experimental evidence, the stability of nanotubes depends only on the tube diameter. [50]

From its construction, the continuum elasticity description of local and global stability is best suited for very large structures with small local curvatures. Therefore, the high level of agreement between its predictions and *ab initio* results in structures with large local curvatures is rather impressive. Among the different allotropes, I find the continuum elasticity description to be most accurate for carbon nanotubes, where all bond lengths are at their equilibrium value. In fullerenes and schwarzites, the presence of non-hexagonal rings, including pentagons and heptagons, prevents a global optimization of bond lengths and bond angles, reducing the agreement with DFT results.

My stability results are consistent with the pentagon adjacency rule that provides an energy penalty of 0.7 - 0.9 eV for each pair of adjacent pentagons, [221–223] which causes an increase of the local curvature. While this rule is surely useful, it can not compare the stability of isomers with isolated pentagons or structures of different size.

What I consider the most significant benefit of my approach to determine local strain is to identify the least stable sites in a structure. Local curvature and in-plane strain play the key role in both local stability and local electronic structure, [52] which also controls the chemical reactivity. [51,53] Thus, my approach can identify the most reactive and the least stable sites, which control the stability of the entire system.

9.5 Summary

In conclusion, I have introduced a fast method to determine the local curvature in 2D systems with arbitrary shape. The curvature information, combined with elastic constants obtained for a planar system, provides an accurate estimate of the local stability in the framework of continuum elasticity theory. Relative stabilities of graphitic structures including fullerenes, nanotori, nanotubes and schwarzites, as well as phosphorene nanotubes calculated using this approach, agree closely with *ab initio* density functional calculations. The continuum elasticity approach can be applied to all 2D structures and is particularly attractive in complex systems with known structure, where the quality of parameterized force fields has not been established.

Chapter 10

Conclusions

2D materials have attracted a lot of attention since the successful exfoliation of graphene. Lack of a fundamental band gap in graphene turned out into an unsurmountable obstacle for electronics applications. TMDs, which have nonzero band gap and are chemical stable, have become the most promising 2D candidates for the semiconducting channel materials. However, the performance of TMD-based devices is still not satisfactory, mainly due to their low carrier mobility. Additional challenges come from the small size of synthesized samples, defects, contacts, and the limitations in the tuning of band gaps in electronic devices.

Few-layer black phosphorus has emerged as a new, promising material in 2014. This field grows fast due to the nonzero band gap and high carrier mobility in black phosphorus. Anisotropic transport, tunable band gap, and various stable phases make phosphorene, the monolayer of black phosphorus a unique 2D material. The biggest challenge for the application of phosphorene is its insufficient chemical stability in air. In all phosphorene structures, each phosphorus atom is sp³ hybridized, has three covalent bonds and one lone electron pair. The lone pair with energy near the Fermi level easily reacts with oxygen atoms in the air. This will finally form phosphorus oxides or phosphoric acids, resulting in the degradation of the phosphorene structure. The most efficient way to avoid this is to protect the posphorene channels by capping them on both sides. The capping layers can be the chemically stable and insulating hexagonal boron nitride (h-BN), aluminum oxide, or polymer overcoating. Since phosphorus has several phases with nearly equivalent stability, it may be difficult to synthesize high-quality pure-phase phosphorene on a large scale. Multi-layer phosphorene has a much better stability than a mono-layer and is also easier to obtain in the experiment. Thus current phosphorene-based devices are mostly using multi-layer phosphorene, and their performance can be optimized by controlling the thickness of phophorene samples.

As stated before, all materials in the current 2D-semiconductor market have their particular advantages and disadvantages. It is thus still an important issue to search and design novel 2D semiconductors to address particular disadvantages and display advanced mechanical and electrical properties. Besides traditional layered black phosphorus and the recently discovered blue phosphorus, more structural phases for layered phosphorus have been found, including semiconductors a with tunable band gap and an anisotropic carrier mobility. Similar to phosphorus, all the group V elements, such as arsenic and antimony, have layered allotropes due to their similar chemical properties. Even 2D nitrogen has been predicted to be stable at low temperatures. In addition to the elemental semiconductors, also compounds of group V elements, such as As_xP_{1-x} and Sb_xAs_{1-x} , are promising candidates for 2D semiconductors, with properties tunable by changing the stoichiometry.

On the other hand, similar to h-BN which is isoelectronic to graphene and shares its honeycomb structure, group IV and group VI compounds, such as SiS, SnSe, are isoelectronic to phosphporus and may share some of its properties. These compounds have stable layered structures similar to group V elements, but can have very different properties. It is very possible to solve the problem that most of the 2D group V structures are chemically unstable by exploring the behavior of other isoelectronic structures. Even though not isoelectronic to group V systems, combination of sp^2 carbon and sp^3 phosphorus in a single 2D structure further widens the scope of the 2D structural family. Identifying the optimum method for synthesis of all these 2D structures will remain the main challenge for the upcoming generation of experimental scientists.

APPENDIX

APPENDIX

As mentioned in Chapter 3, there is more than one isomer for La@C₆₀(CF₃)_n with $n \ge 2$. To find the most stable isomers of La@C₆₀(CF₃)_n, I calculated different geometries with n trifluomethyls attached on C₆₀ in different arrangements. The results for n = 2, 3, 4 and 5 are shown in Fig. A.1, A.2, A.3 and A.4, respectively. In general, coupled with more than one CF₃ prefer to be separated in a para arrangement, which can be best seen in the case of n = 2 as shown in Fig. A.1. The most stable isomer has the two CF₃s attached at the para-position in one hexagon shown in Fig. A.1(a). The two CF₃s are too crowded and less stable when they are closer as shown in Fig. A.1 (d), (e), (j). It is also less stable when they are two far away as shown in Fig. A.1 (b), (c), (f), (g), (h), (i). For the case of n = 3, the most stable isomer is the one with all three CF₃s in para arrangement, which has a C_{2v} symmetry as shown in Fig. A.2 (a). The second most stable one shown in Fig. A.2 (f) has a C₃ symmetry, which is only 0.108 eV less stable. For n = 4 and n = 5they do not like all the CF₃s para arranged any more. As shown in Fig. A.3 (a), when there are four CF_{3s} , they prefer to be separated to two para-arranged pairs of CF_{3s} . The one with all four CF_{3s} in para arrangement is slightly less stable with 0.051 eV in energy, as shown in Fig. A.3 (e). Both these most stable two isomers for n = 4 have a C_{2v} symmetry. When n = 5, four of the five CF_{3s} like to be in para arrangement and with the left one a little far away, as shown in Fig. A.4 (a). The one with all five CF₃s is para arrangement in 0.857 eV less stable, as shown in Fig. A.4 (b).



Figure A.1: Ten different isomers of La@C₆₀(CF₃)_n with n = 2. In each subfigure ball-andstick model of the optimized structure is shown at the top, the relative DFT-PBE energy with respect to the most stable isomer is listed in the middle and the corresponding Schlegel diagram of C₆₀ with trifluoromethyl sites indicated by red dots is shown at the bottom.



Figure A.2: Six different isomers of La@C₆₀(CF₃)_n with n = 3. In each subfigure ball-andstick model of the optimized structure is shown at the top, the relative DFT-PBE energy with respect to the most stable isomer is listed in the middle and the corresponding Schlegel diagram of C₆₀ with trifluoromethyl sites indicated by red dots is shown at the bottom.



Figure A.3: Ten different isomers of La@C₆₀(CF₃)_n with n = 4. In each subfigure ball-andstick model of the optimized structure is shown at the top, the relative DFT-PBE energy with respect to the most stable isomer is listed in the middle and the corresponding Schlegel diagram of C₆₀ with trifluoromethyl sites indicated by red dots is shown at the bottom.



Figure A.4: Ten different isomers of La@C₆₀(CF₃)_n with n = 5. In each subfigure ball-andstick model of the optimized structure is shown at the top, the relative DFT-PBE energy with respect to the most stable isomer is listed in the middle and the corresponding Schlegel diagram of C₆₀ with trifluoromethyl sites indicated by red dots is shown at the bottom.

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