LOW ENERGY RESONANT ELECTRON SCATTERING FROM HOMONUCLEAR DIATOMIC MOLECULES WITH PARTIAL BORN-OPPENHEIMER BREAKDOWN

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This is to certify that the

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Homonuclear Diatomic Molecules with
Partial Born-Oppenheimer Breakdown

presented by

Kenneth Penfield Winters

has been accepted towards fulfillment
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George V. Nazaroff
Major professor

Date 9/12/72

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ABSTRACT

LOW ENERGY RESONANT ELECTRON SCATTERING FROM HOMONUCLEAR DIATOMIC MOLECULES WITH PARTIAL BORN-OPPENHEIMER BREAKDOWN

By

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In some homonuclear diatomic molecules, such as H_2 and N_2, there appears to be a single-particle resonance in the low energy (1-10 ev) elastic and inelastic electron scattering, although there is no stable negative ion capable of being formed. I have developed a method of treating these resonances with a one-determinant Hartree-Fock wave function, with the molecular part frozen in the undistorted ground state.

First, I use potential scaling to find a bound state function for the negative ion. Then, considering the combination of the bound orbital for the scattering electron and a plane wave to be a zeroth-order wave-function, I obtain the asymptotic form of the first-order wave-function. This is a first-order estimate of the asymptotic form of the scattering function, from which I obtain estimates of the scattering amplitudes and phase shifts for elastic scattering and for vibrational excitation.

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Very simple trial calculations were done for H_2, but the results were inconclusive. The elastic scattering shows a definite resonance, but the calculated scattering amplitudes, for both the elastic and inelastic scattering, do not reflect experimental results.

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Kenneth Penfield Winters

A THESIS

Submitted to
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I owe a different kind of debt to my parents, who have given various sorts of assistance, not the least of which is the IBM Selectric which I am using at this moment.

Many other people should be thanked, but I can name only a few: Dr. Harrison, who consented to be second reader; Yndvrei Hibaru and Caellyn y'Vearn, who helped with the typing; the MSU Chemistry Department and Computer Center; and all those who, for their own reasons, preferred to use the CDC 6500 while I was using the CDC 3600.

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INTRODUCTION

In the scattering of low energy (1-10ev.) electrons from small diatomic molecules, the inelastic scattering involving vibrational excitation would be expected to be quite small unless there is a resonance in this energy region. In several such molecules, H_2 and N_2 for instance, there is an apparent resonance structure at low energies.[1] Neither the ground state nor any reasonable excited state of these molecules form a bound negative-ion state.

In the case of O_2, the attraction between the molecule and the electron is strong enough to form a stable O_2^- ion. For the similar but less electronegative N_2, the interaction potential of the molecule and electron should be strongly attractive, but not strong enough to form a bound N_2^- ion. If this ion were fairly long-lived, the inelastic scattering would be closely related to the vibrational states of the ion. The process would be divided into three parts: First, the electron is captured. Then, the negative ion exists for a period of time in a particular vibrational state. Finally, the electron escapes and the molecule is left in some vibrational state. For this description to be good, the ion must exist long enough that the Born-Oppenheimer coördinate separation for the nuclear and electronic

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coördinates can be applied, leading to well defined vibrational states.

In N_2 the resonant state does not appear to exist long enough for this to be the case. The negative ion exists for about the period of one vibration of the molecule.[2] Thus, the capture and escape of the electron are not separate events, and there is no period during which the Born-Oppenheimer separation is a safe assumption. The breadth of the resonant structure in H_2 scattering suggests that this is also a very short-lived state.

To describe the inelastic scattering from H_2, N_2, and other similar molecules, I will develope a formalism in which I do not make the Born-Oppenheimer coördinate separation between the coördinates of the nuclei and the coördinates of the scattered electron. I will work within the structure of a one-determinant Hartree-Fock wave function. This is possible because the molecule, though distorted by the presence of the scattered electron, remains electronically in the ground state. To describe the resonant part of the scattering function, I will use potential scaling to obtain a bound negative ion function. I will then obtain the scattering by considering it to be a perturbation of a zeroth-order state consisting of the bound resonant function and a plane wave.

To test the formalism, I have made highly simplified

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calculations for H_2. The results of these are presented at the end of Chapter VI.

[1] G.J.Schulz, Physical Review 135, A988 (1964).

[2] A.Herzenberg and F.Mandl, Proc.Roy.Soc.(London) A270, 48 (1962).

Chapter

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Chapter I. A One Determinant Wave Function for the System.

I define $\Psi^M_J(1,2...N,N+1,\vec{R})$ as the wave function of the total system with total angular momentum J and z-component M_J=M. Ψ^M_J is a sum over j and ℓ of functions which are also eigenfunctions of molecular rotation angular momentum, j, and orbital angular momentum of the scattered electron, ℓ.

$$\Psi^M_J = \sum_{j,\ell} \Psi^M_{J j \ell}(1,2...N+1,\vec{R}) \qquad (1.1)$$

Each $\Psi^M_{Jj\ell}$ is a function of the spatial and spin coördinates of the N+1 electrons and of the relative spatial coördinates of the nuclei, anti-symmetrized with respect to the electronic coördinates. They are constructed by writing, first, a product of the target molecule electronic functions and a spin-orbital which is a function of the coördinates of the scattering electron and of the nuclear coördinates:

$$\Psi^{JMj\ell}_{Product} = \chi_1(1)\chi_2(2)...\chi_N(N)\chi^{JMj\ell}_{N+1}(N+1,\vec{R}) \qquad (1.2)$$

I now operate on the product function with the anti-symmetrizer, $\mathcal{A}$, to give the desired function:

$$\Psi^M_{Jj\ell}(1,2...N+1,\vec{R}) = \mathcal{A}\,\Psi^{JMj\ell}_{Product} \qquad (1.3)$$

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Note that $\chi_{N+1}^{JMj\ell}(N+1,\vec{R})$ is an eigenfunction of the $\hat{J}^2$, $\hat{J}_z$, $\hat{j}^2$, and $\hat{\ell}^2$ operators. Define also

$$\chi_{N+1}^{JM}(N+1,\vec{R}) = \sum_{j,\ell} \chi_{N+1}^{JMj\ell}(N+1,\vec{R}) \tag{1.4}$$

and observe that

$$\begin{aligned}\Psi_J^M &= \sum_{j,\ell} \mathcal{A}\, \chi_1(1)\ldots\chi_N(N)\chi_{N+1}^{JMj\ell}(N+1,\vec{R}) \\ &= \mathcal{A}\, \chi_1(1)\ldots\chi_N(N) \sum_{j,\ell} \chi_{N+1}^{JMj\ell}(N+1,\vec{R}) \\ &= \mathcal{A}\, \chi_1(1)\ldots\chi_N(N)\chi_{N+1}^{JM}(N+1,\vec{R}) \quad . \end{aligned} \tag{1.5}$$

In some cases I will find a uniform notation for orbitals to be useful, therefor I will define the following alternate notation:

$$\chi_i^{JMj\ell}(k,\vec{R}) \equiv \chi_i^{JM}(k,\vec{R}) \equiv \chi_i(k) \ , i \leq N, \text{ all } J,M,j,\ell. \tag{1.6}$$

I can now write:

$$\Psi_J^M = \sum_{j,\ell} \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) \tag{1.7}$$

$$= \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JM}(i,\vec{R}) \quad . \tag{1.8}$$

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Writing the wave-function as I have, I am assuming that Born-Oppenheimer separation is a good approximation for the relative motions of the target electrons and the nuclei. It is for this reason that I do not write $\chi_{N+1}^{JMj\ell}(1,\vec{R})$ as the product of an electronic and a nuclear function. I expand it as a sum of such products utilizing Clebsch-Gordon coëfficients:[1]

$$\chi_{N+1}^{JMj\ell} = \sum_{\nu m_\ell m_j} C(j\ell J, m_j m_\ell M)\ \phi_{k\ell m_\ell}^{elec}(\vec{r}_{N+1})\alpha(N+1)$$

$$\phi_{\nu j m_j}^{nuc}(\vec{R}) \quad . \qquad (1.9)$$

where ν is the vibrational quantum number.

I am using two systems of coördinates in this problem. One is the molecular coördinate system with the origin at the center of mass of the molecule and the z-axis fixed to the molecular axis. This is not an inertial frame of reference, and a rigorous treatment of a problem in such a coördinate system would require the inclusion of centrifugal and coriolus "forces". The other coördinate system is the external system with the same origin as the molecular system, but with the z-axis fixed in some arbitrary direction. The $\hat{J}^2$, $\hat{J}_z$, $\hat{\ell}^2$, $\hat{\ell}_z$, $\hat{j}^2$, and $\hat{j}_z$ operators are defined in the external coördinate system. The expansion in (1.9) requires that $\vec{r}_{N+1}$ and $\vec{R}$ be expressed in the external coordinate system. Electronic angle coördinates in this non-rotating frame of reference will

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Note also that all Clebsch-Gordon coëfficients for which $m_\ell + m_j \neq M$ vanish. In some cases I will write $C(j_1 j_2 j, m_1 m_2)$ for $C(j_1 j_2 j, m_1 m_2\ m_1+m_2)$.

The k subscript on ϕ^{elec} is an energy variable and depends on ν and j. The electronic function is an eigenfunction of the $\hat{\ell}^2$ and $\hat{\ell}_z$ operators with eigenvalues $\ell(\ell+1)$ and m_ℓ respectively. The nuclear function is an eigenfunction of the $\hat{j}^2$ and $\hat{j}_z$ operators with eigenvalues $j(j+1)$ and m_j respectively. I define them by

$$\phi^{elec}_{k\ell m_\ell}(\vec{r}) = f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j,\ell m_\ell}(\vec{r})\ Y_{\ell m_\ell}(\Omega') \equiv f^{\beta}(\vec{r}) Y_{\ell m_\ell}(\Omega') \tag{1.10}$$

and $$\phi^{nuc}_{\nu j m_j}(\vec{R}) = \chi_\nu(R)\ Y_{j m_j}(\Omega_R) \quad , \tag{1.11}$$

where the $\chi_\nu(R)$ are the vibrational functions of the undisturbed diatomic molecule and the f^β are unknown. Note that a different set of solutions, $f^\beta(r)$, will be obtained for each initial state, specified by ν_0, j_0, m_{j_0}, J, and M. I am not assuming a given initial ℓ_0 but will take the initial state to be an incoming plane wave.

I can now write the total wave function as

$$\Psi_J^M = \mathcal{A}\, \chi_1(1)\ldots\chi_N(N+1) \sum_{j\ell\nu m_\ell m_j} C(j\ell J, m_j m_\ell M)$$

$$f^\beta(r_{N+1})\chi_\nu(R)\alpha(N+1)Y_{\ell m_\ell}(\Omega'_{N+1})Y_{jm_j}(\Omega_R) \quad . \tag{1.12}$$

I can also write

$$\Psi_J^M = \mathcal{A}\, \chi_1(1)\ldots\chi_N(N) \sum_{j\ell\nu} f^\beta(r_{N+1})\chi_\nu(R)\alpha(N+1)$$

$$\mathcal{Y}_{JMj\ell}(\Omega'_{N+1},\Omega_R) \quad . \tag{1.13}$$

where $\mathcal{Y}_{JMj\ell}(\Omega'_{N+1},\Omega_R) = \sum_{m_\ell m_j} C(j\ell J, m_j m_\ell M) Y_{\ell m_\ell}(\Omega'_{N+1})$

$$Y_{jm_j}(\Omega_R) \quad . \tag{1.14}$$

This angle function is an eigenfunction of $\hat{J}^2, \hat{J}_z, \hat{j}^2$, and $\hat{\ell}^2$ with eigenvalues of $J(J+1), M, j(j+1)$, and $\ell(\ell+1)$, respectively, but is not an eigenfunction of $\hat{j}_z$ or $\hat{\ell}_z$.

Whether I use (1.12) or (1.13) I can express Ψ_J^M in terms of functions all of which are known except for the f^β . To determine the f^β , I will derive an expression for the integral

$$I_J^M = \langle \Psi_J^M | \hat{\mathcal{H}} - E | \Psi_J^M \rangle \tag{1.15}$$

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and then for the variation in I_J^M corresponding to an arbitrary variation in the f^β. If the molecule is originally in the ν_0 and j_0 vibrational and rotational states then

$$E = E_{Mol} + E_{\nu_0} + E_{j_0} + 1/2k_0^2 , \qquad (1.16)$$

where E_{Mol} is the electronic energy at equilibrium internuclear distance, R_0, as given by the molecular electronic wave function actually used in the above equations, and E_{ν_0} and E_{j_0} are the vibrational and rotational energies of the ν_0 and j_0 states, respectively.

[1] M.E.Rose, Elementary Theory of Angular Momentum, ChapterIII, John Wiley&Sons, New York, 1957.

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Chapter II. The Variational Integral, I_J^M.

To find I_J^M I must know $\hat{\mathcal{H}}$. In this case it is

$$\hat{\mathcal{H}} = -1/2 \sum_{u=1}^{N+1} \nabla_u^2 - \sum_{u=1}^{N+1} \left(\frac{Z}{r_{u\alpha}} + \frac{Z}{r_{u\beta}} \right) + \sum_{u>v}^{N+1} \frac{1}{r_{uv}}$$

$$+V(R) - \frac{1}{2\mu_N}\nabla_R^2 \ , \qquad (2.1)$$

where α and β designate the two nuclei, μ_N is the reduced mass of the nuclei, and Z is the nuclear charge. The electronic function and the nuclear-electronic attraction (except for the scattered electron) are evaluated at $R=R_0$. The actual variation in molecular electronic energy with R is combined with coulombic repulsion in V(R).

The kinetic energy operator, $-\frac{1}{2\mu}\nabla^2$, can be written as

$$-\frac{1}{2\mu}\nabla^2 = \frac{-1}{2\mu r^2}\left(\frac{d}{dr} r^2 \frac{d}{dr} \right) + \frac{\hat{\ell}^2}{2\mu r^2} \ . \qquad (2.2)$$

Using atomic units, for an electron, $\mu=1$. This formulation of ∇^2 is not entirely correct for the molecular electrons, since their angular coördinates are not expressed in an inertial frame of reference. The neglected coriolus and centrifugal forces, however, are very small near the center of the coördinate system, becoming significant only for the scattered electron when it is far from the molecule (I have already tacitly assumed this by writing the vibrational functions as $\chi_v(R)$ rather than $\chi_{vj}(R)$.) ; and the angular

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coördinates of the scattered electron are expressed in an inertial frame of reference.

Define the operators

$$\hat{f}(u;\vec{R}) = -1/2\ \nabla_u^2 - \frac{Z}{r_{u\alpha}} - \frac{Z}{r_{u\beta}} \tag{2.3}$$

$$\hat{f}(R) = \frac{-1}{2\mu_N R^2}\frac{d}{dR}\left(R^2 \frac{d}{dR} \right) + V(R) \tag{2.4}$$

I can now express $\hat{\mathcal{H}} - E$ in the form

$$\hat{\mathcal{H}} - E = \sum_{u=1}^{N+1} \hat{f}(u;\vec{R}) + \sum_{u>v}^{N+1} \frac{1}{r_{uv}} + \hat{f}(R) + \frac{\hat{j}^2}{2\mu_N R^2} - E \quad . \tag{2.5}$$

Note that the ∇^2 parts of the $\hat{f}(u;\vec{R})$ and the $1/r_{uv}$ (unless $u = N+1$) depend only on electronic coördinates, and that $\hat{f}(R)$ and $\hat{j}^2$ depend only on nuclear coördinates. In addition, when $\hat{f}(u;\vec{R})$ acts on a molecular spin-orbital, it is taken to be $\hat{f}(u) = \hat{f}(u;\vec{R}_0)$, which is independent of $\vec{R}$. Thus, the $Z/r_{N+1,\alpha}$, $Z/r_{N+1,\beta}$, and $1/r_{N+1,v}$ terms are the only ones depending on both.

Using (2.5) I obtain the following expression for I_J^M:

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$$I_J^M = \sum_{jj'\ell\ell'} \left\{ \sum_{u=1}^{N+1} \langle \Psi^M_{Jj\ell} | \hat{f}(u;\vec{R}) | \Psi^M_{Jj'\ell'} \rangle + \sum_{u>v}^{N+1} \right.$$

$$\langle \Psi^M_{Jj\ell} | \frac{1}{r_{uv}} | \Psi^M_{Jj'\ell'} \rangle + \langle \Psi^M_{Jj\ell} | \hat{f}(R) | \Psi^M_{Jj'\ell'} \rangle$$

$$\left. + \langle \Psi^M_{Jj\ell} | \frac{\hat{j}^2}{2\mu_N R^2} | \Psi^M_{Jj'\ell'} \rangle + \langle \Psi^M_{Jj\ell} | -E | \Psi^M_{Jj'\ell'} \rangle \right\} . \tag{2.6}$$

Any of the above integrals may be represented by the expression

$$I^M_{Jjj'\ell\ell'\alpha} \equiv \langle \langle \Psi^M_{Jj\ell} | \hat{O}_\alpha(u,v;\vec{R}) | \Psi^M_{Jj'\ell'} \rangle_{\substack{\text{electronic} \\ \text{coördinates}}} \rangle_{\vec{R}} \tag{2.7}$$

where $\hat{O}_\alpha(u,v;\vec{R})$ is the appropriate operator. I will now investigate the properties of the electronic integral above. Here the notation in (1.6) and (1.7) will prove useful:

$$\Psi^M_{Jj\ell} = \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) \tag{2.8}$$

so that

$$I(R)^M_{Jjj'\ell\ell'} \equiv \langle \Psi^M_{Jj\ell} | \hat{O} | \Psi^M_{Jj'\ell'} \rangle_{\text{elec.}}$$

where

$x^{JMj'z'}$

I also

and the

$$= \langle \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) |\hat{O}| \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

$$= \langle \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) |\hat{O}| \mathcal{A}^{\dagger} \mathcal{A} \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

$$= \langle \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) |\hat{O}| \; \| \chi^{JMj'\ell'} \| (\vec{R}) \rangle_{elec}$$

(2.10)

where $\| \chi^{JMj'\ell'} \| (\vec{R})$ is the determinant function:

$$\| \chi^{JMj'\ell'} \| (\vec{R}) \equiv \begin{vmatrix} \chi_1^{JMj'\ell'}(1,\vec{R}) & \chi_2^{JMj'\ell'}(1,\vec{R}) & \cdots & \chi_{N+1}^{JMj'\ell'}(1,\vec{R}) \\ \chi_1^{JMj'\ell'}(2,\vec{R}) & \chi_2^{JMj'\ell'}(2,\vec{R}) & \cdots & \chi_{N+1}^{JMj'\ell'}(2,\vec{R}) \\ \vdots & \vdots & & \vdots \\ \chi_1^{JMj'\ell'}(N+1,\vec{R}) & \chi_2^{JMj'\ell'}(N+1,\vec{R}) & \cdots & \chi_{N+1}^{JMj'\ell'}(N+1,\vec{R}) \end{vmatrix}$$

(2.11)

I also define the electronic overlap integrals:

$$D_{u,v}^{JMjj'\ell\ell'}(\vec{R}) \equiv \langle \chi_u^{JMj\ell}(1,\vec{R}) | \chi_v^{JMj'\ell'}(1,\hat{\vec{R}}) \rangle_{elec}$$

(2.12)

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$$\underline{D}^{JMjj'\ell\ell'}(\vec{R}) \equiv \begin{bmatrix} D_{1,1}^{JMjj'\ell\ell'}(\vec{R}) & D_{1,2}^{JMjj'\ell\ell'}(\vec{R}) & \cdots & D_{1,N+1}^{JMjj'\ell\ell'}(\vec{R}) \\ D_{2,1}^{JMjj'\ell\ell'}(\vec{R}) & D_{2,2}^{JMjj'\ell\ell'}(\vec{R}) & \cdots & D_{2,N+1}^{JMjj'\ell\ell'}(\vec{R}) \\ \vdots & \vdots & & \vdots \\ D_{N+1,1}^{JMjj'\ell\ell'}(\vec{R}) & D_{N+1,2}^{JMjj'\ell\ell'}(\vec{R}) & \cdots & D_{N+1,N+1}^{JMjj'\ell\ell'}(\vec{R}) \end{bmatrix} \tag{2.13}$$

This expression is not as complex as it appears since only the overlap integrals involving the scattering orbital actually depend on the various superscripts and $\vec{R}$. Thus,

$$D_{u,v}^{JMjj'\ell\ell'}(\vec{R}) = \delta_{uv} \ , \ u,v \leq N. \tag{2.14}$$

In addition, $D_{u,N+1}^{JMjj'\ell\ell'}(\vec{R})$ and $D_{N+1,u}^{JMjj'\ell\ell'}(\vec{R})$ are zero if u is even due to the α-spin of the scattering orbital. Thus:

$$D^{JMjj'\ell\ell'}(\vec{R}) = \begin{pmatrix} 1 & 0 & \cdots & 0 & D^{JMjj'\ell\ell'}_{1,N+1}(\vec{R}) \\ 0 & 1 & \cdots & 0 & 0 \\ 0 & 0 & \cdots & 0 & D^{JMjj'\ell\ell'}_{3,N+1}(\vec{R}) \\ \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 \\ D^{JMjj'\ell\ell'}_{N+1,1}(\vec{R}) & 0 & \cdots & 0 & D^{JMjj'\ell\ell'}_{N+1,N+1}(\vec{R})\delta_{\ell\ell',\delta_{jj'}} \end{pmatrix}$$

(2.15)

I can express the first and second order minors in terms of the unsigned minors:

$$|| D^{JMjj'\ell\ell'}(\vec{R}) ||^{up} \equiv (-1)^{u+p} || D^{JMjj'\ell\ell'}(\vec{R}) ||^{up}_{M}$$

(2.16)

and

$$|| D^{JMjj'\ell\ell'}(\vec{R}) ||^{uv,pq} \equiv$$

$$(-1)^{u+v+p+q} P(u>v) P(p>q) || D^{JMjj'\ell\ell'}(\vec{R}) ||^{uv,pq}_{MM}$$

(2.17)

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The unsigned minors are the determinants of the matrices obtained by deleting the indicated row and column (or rows and columns) from the overlap matrix $D^{JMjj'\ell\ell'}(\vec{R})$. P(statement) is a parity operator which equals +1 if "statement" is true and -1 if "statement" is false. Explicit expressions for the first and second order minors will be developed in an appendix. Minors of the determinant wave function $\| \chi^{JMj'\ell'} \| (\vec{R})$ are defined analogously to those of the overlap matrix.

Returning to equation (2.10), consider the case when $\hat{O} = \hat{1}$. Then

$$I(\vec{R})_{JMjj'\ell\ell'} = < \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \ \| \chi^{JMj'\ell'} \| (\vec{R}) >_{elec} \tag{2.18}$$

Expanding $\| \chi^{JMj'\ell'} \| (\vec{R})$ along row 1 gives

$$I(R)_{JMjj'\ell\ell'} = < \prod_{i=2}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \chi_1^{JMj\ell}(1,\vec{R}) | \sum_{p=1}^{N+1} \chi_p^{JMj'\ell'}(1,\vec{R}) \| \chi^{JMj'\ell'} \| 1p(\vec{R}) > \tag{2.19}$$

$$= < \prod_{i=2}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \sum_{p=1}^{N+1} D_{1,p}^{JMjj'\ell\ell'}(\vec{R})$$

$$\| \chi^{JMj'\ell'} \|^{lp}(\vec{R}) > \tag{2.20}$$

$$= < \prod_{i=2}^{N+1} \chi_i^{JMj\ell}(\vec{R}) | \begin{vmatrix} D_{1,1}^{JMjj'\ell\ell'}(\vec{R}) & \cdots & D_{1,N+1}^{JMjj'\ell\ell'}(\vec{R}) \\ \chi_1^{JMj'\ell'}(2,\vec{R}) & \cdots & \chi_{N+1}^{JMj'\ell'}(2,\vec{R}) \\ \vdots & & \vdots \\ \chi_1^{JMj'\ell'}(N+1,\vec{R}) & \cdots & \chi_{N+1}^{JMj'\ell'}(N+1,\vec{R}) \end{vmatrix} > \tag{2.21}$$

Expanding this determinant successively along the 2^{nd} through $N+1^{st}$ rows gives

$$I(\vec{R})_{JMjj'\ell\ell'} = <\Psi^M_{Jj\ell}|\Psi^M_{Jj'\ell'}>_{elec}$$

$$= \| D^{JMjj'\ell\ell'}(\vec{R}) \| . \tag{2.22}$$

I will next consider the case where $\hat{O} = 1/r_{uv}$. Then

$$I(\vec{R})_{JMjj'\ell\ell'} = < \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \frac{1}{r_{uv}} |$$

$$\| \chi^{JMj'\ell'} \| (\vec{R}) >_{elec} \tag{2.23}$$

Expand the determinant wave-function along the u^{th} and

v^{th} rows

where

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v^{th} rows:

$$I(\vec{R})_{JMjj'\ell\ell'} = < \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) |\frac{1}{r_{uv}}|$$

$$\sum_{p,q}^{N+1} \chi_p^{JMj'\ell'}(u,\vec{R})\chi_q^{JMj'\ell'}(v,\vec{R})$$

$$|| \chi^{JMj'\ell'} ||^{uv,pq}(\vec{R})>_{elec} \qquad (2.24)$$

$$= < \prod_{i\neq u,v}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \sum_{p,q}^{N+1} g_{uv,pq}^{JMjj'\ell\ell'}(\vec{R})$$

$$|| \chi^{JMj'\ell'} ||^{uv,pq}(\vec{R})>_{elec} \qquad (2.25)$$

where

$$g_{uv,pq}^{JMjj'\ell\ell'}(\vec{R}) \equiv <\chi_u^{JMj\ell}(1,\vec{R})\chi_v^{JMj\ell}(2,\vec{R})$$

$$|\frac{1}{r_{12}}|\chi_p^{JMj'\ell'}(1,\vec{R})\chi_q^{JMj'\ell'}(2,\vec{R})>_{elec} \qquad (2.26)$$

I can change the sum over p and q to a sum over p>q by substituting

$$g_{uv,pq}^{JMjj'\ell\ell'}(\vec{R}) \equiv <\chi_u^{JMj\ell}(1,\vec{R})\chi_v^{JMj\ell}(2,\vec{R})|\frac{1}{r_{12}}(1-P_{12})$$

$$|\chi_p^{JMj'\ell'}(1,\vec{R})\chi_q^{JMj'\ell'}(2,\vec{R})>_{elec} \qquad (2.27)$$

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where P_{12} exchanges the coördinates of electrons 1 and 2. Thus

$$I(\vec{R})_{JMjj'\ell\ell'} = \left\langle \prod_{i\neq u,v}^{N+1} \chi_i^{JMj\ell}(1,\vec{R}) \right| \sum_{p>q} g_{uv,pq}^{JMjj'\ell\ell'}(\vec{R}) \left\| \chi^{JMj'\ell'} \right\|^{uv,pq}(\vec{R}) \Big\rangle_{elec} \tag{2.28}$$

Expanding the second order determinant successively along each row and integrating over the appropriate electronic coördinates I find that

$$\left\langle \prod_{i\neq u,v}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) \right| \left\| \chi^{JMj'\ell'} \right\|^{uv,pq}(\vec{R}) \Big\rangle_{elec} = \left\| D^{JMjj'\ell\ell'}(\vec{R}) \right\|^{uv,pq} . \tag{2.29}$$

So that,

$$I(\vec{R})_{JMjj'\ell\ell'} = \langle \Psi_{Jj\ell}^{M} | \frac{1}{r_{uv}} | \Psi_{Jj'\ell'}^{M} \rangle_{elec} = \sum_{p>q} g_{uv,pq}^{JMjj'\ell\ell'}(\vec{R}) \left\| D^{JMjj'\ell\ell'}(\vec{R}) \right\|^{uv,pq} . \tag{2.30}$$

Next consider the integral for which $\hat{O} = \hat{f}(u;\vec{R})$:

Expand

Defining

and not

$$I(\vec{R})_{JMjj'\ell\ell'} = \Big\langle \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) \,|\hat{f}(u;\vec{R})|$$

$$|| \chi^{JMj'\ell'} ||\,(\vec{R})\Big\rangle_{elec} \qquad (2.31)$$

Expand the determinant function along the u^{th} row:

$$I(\vec{R})_{JMjj'\ell\ell'} = \Big\langle \prod_{i\neq u}^{N+1} \chi_i^{JMj\ell}(i,\vec{R})$$

$$\Big|\Big\langle \chi_u^{JMj\ell}(u,\vec{R})\,|\hat{f}(u;\vec{R})|\sum_{p=1}^{N+1} \chi_p^{JMj'\ell'}(u,\vec{R})\Big\rangle_u$$

$$|| \chi^{JMj'\ell'} ||^{up}(\vec{R})\Big\rangle_{other\ electrons} \qquad (2.32)$$

Defining

$$f_{up}^{JMjj'\ell\ell'}(\vec{R}) \equiv \Big\langle \chi_u^{JMj\ell}(1,\vec{R})\,|\hat{f}(1;\vec{R})|\,\chi_p^{JMj'\ell'}(1,\vec{R})\Big\rangle_{elec}$$

(2.33)

and noting that

$$\Big\langle \prod_{i\neq u}^{N+1} \chi_i^{JMj\ell}(i,\vec{R})\Big|\ || \chi^{JMj'\ell'} ||^{up}(\vec{R})\Big\rangle_{elec} =$$

$$|| D^{JMjj'\ell\ell'}(\vec{R}) ||^{up}\ ,$$

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$$I(\vec{R})_{JMjj'\ell\ell'} = \langle \Psi^{M}_{Jj\ell} | \hat{f}(u;\vec{R}) | \Psi^{M}_{Jj'\ell'} \rangle$$

$$= \sum_{p=1}^{N+1} f^{JMjj'\ell\ell'}_{up}(\vec{R}) \| D^{JMjj'\ell\ell'}(\vec{R}) \|^{up} . \qquad (2.34)$$

Next, evaluate the integral when $\hat{O}=1/R^2$:

$$I(\vec{R})_{JMjj'\ell\ell'} =$$

$$< \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \frac{1}{R^2} | \| \chi^{JMj'\ell'} \| (\vec{R}) >_{elec} .$$

(2.35)

Expanding the determinant function successively along rows 1 through N+1, I find that

$$I(\vec{R})_{JMjj'\ell\ell'} = \frac{1}{R^2} \| D^{JMjj'\ell\ell'}(\vec{R}) \| . \qquad (2.36)$$

The remaining integral from equation (2.7) is

$$I(\vec{R})_{JMjj'\ell\ell'} = < \prod_{i=1}^{N+1} \chi_i^{JMj\ell}(i,\vec{R}) | \hat{f}(R) | \| \chi^{JMj'\ell'} \| (\vec{R}) >_{elec}$$

(2.37)

By the procedure used in (2.10) I can show that

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$$I(\vec{R})_{JMjj'\ell\ell'} = \langle \Psi^{M}_{Jj\ell} | \hat{f}(R) | \Psi^{M}_{Jj'\ell'} \rangle_{elec}$$

$$= \langle \| \chi^{JMj\ell} \| (\vec{R}) | \hat{f}(R) | \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

(2.38)

I separate (2.38) into two separate integrals

$$I(\vec{R})_{JMjj'\ell\ell'} =$$

$$\langle \| \chi^{JMj\ell} \| (\vec{R}) | \frac{-1}{2\mu_N R^2} \frac{d}{dR}\left(R^2 \frac{d}{dR}\right) | \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

$$+ \langle \| \chi^{JMj\ell} \| (\vec{R}) | V(R) | \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

(2.39)

The second integral can be evaluated immediately:

$$\langle \| \chi^{JMj\ell} \| (\vec{R}) | V(R) | \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) \rangle_{elec}$$

$$= V(R) \| D^{JMjj'\ell\ell'}(\vec{R}) \| . \qquad (2.40)$$

To evaluate the first integral I note that

$$\frac{d}{dR} \prod_{i=1}^{N+1} \chi_i^{JMj'\ell'}(i,\vec{R}) = \prod_{i=1}^{N} \chi_i(i) \frac{d}{dR} \chi_{N+1}^{JMj'\ell'}(N+1,\vec{R}) .$$

(2.41)

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This is a consequence of the fact that the molecular electronic wave functions are derived with the assumption of Born-Oppenheimer separation. Thus the first integral (which I will call I_1) can be written

$$I_1 = \Big\langle \sum_{p=1}^{N+1} \| \chi^{JMj\ell} \|^{N+1,p}(\vec{R}) \chi_p^{JMj\ell}(N+1,\vec{R}) \Big| \frac{-1}{2\mu_N R^2} \Big|$$

$$\prod_{i=1}^{N} \chi_i^{JMj'\ell'}(i,\vec{R}) \frac{d}{dR}\left[R^2 \frac{d}{d\vec{R}} \chi^{JMj'\ell'}(N+1,\vec{R})\right] \Big\rangle \tag{2.42}$$

I define

$$D^{(2)JMjj'\ell\ell'}_{p,N+1}(\vec{R}) \equiv \Big\langle \chi_p^{JMj\ell}(i,\vec{R}) \Big| \frac{-1}{2\mu_N R^2} \frac{d}{dR}\left[R^2 \frac{d}{dR}\right] \Big|$$

$$\chi_{N+1}^{JMj'\ell'}(i,\vec{R}) \Big\rangle_{elec} \tag{2.43}$$

Integrating over the coördinates of electrons 1 through N in (2.42) and substituting from (2.43), I obtain

$$I_1 = \sum_{p=1}^{N+1} \| D^{JMjj'\ell\ell'}(\vec{R}) \|^{p,N+1} D^{(2)JMjj'\ell\ell'}_{p,N+1}(\vec{R}) \ . \tag{2.44}$$

Thus,

$$I(\vec{R})_{JMjj'\ell\ell'} = \langle \Psi^M_{Jj\ell} | \hat{f}(\vec{R}) | \Psi^M_{Jj'\ell'} \rangle_{elec}$$

$$= V(R) \|D^{JMjj'\ell\ell'}(\vec{R})\| + \sum_{p=1}^{N+1} \|D^{JMjj'\ell\ell'}(\vec{R})\|^{p,N+1}$$

$$D^{(2)JMjj'\ell\ell'}_{p,N+1}(\vec{R}) \quad . \tag{2.45}$$

Substituting expressions from (2.34), (2.30), (2.45), (2.36), and (2.22) for the integrals in equation (2.6), I obtain an expression for I^M_J:

$$\begin{aligned} I^M_J = \sum_{jj'\ell\ell'} \Bigg\{ & \sum_{u=1}^{N+1} \sum_{p=1}^{N+1} \int d\vec{R}\ f^{JMjj'\ell\ell'}(\vec{R}) \|D^{JMjj'\ell\ell'}(\vec{R})\|^{up} \\ & + \sum_{u>v}^{N+1} \sum_{p>q}^{N+1} \int d\vec{R}\ g^{JMjj'\ell\ell'}_{uv,pq}(\vec{R}) \|D^{JMjj'\ell\ell'}(\vec{R})\|^{uv,pq} \\ & + \sum_{p}^{N+1} \int d\vec{R}\ D^{(2)JMjj'\ell\ell'}_{p,N+1}(\vec{R}) \|D^{JMjj'\ell\ell'}(\vec{R})\|^{p,N+1} \\ & + \int d\vec{R}\ V(R) \|D^{JMjj'\ell\ell'}(\vec{R})\| \\ & + \int d\vec{R} \left[\frac{j(j+1)}{2\mu_N}\right] \frac{1}{R^2} \|D^{JMjj'\ell\ell'}(\vec{R})\| \\ & + \int d\vec{R}\ (-E) \|D^{JMjj'\ell\ell'}(\vec{R})\| \Bigg\} \quad . \end{aligned} \tag{2.46}$$

I can combine the last three terms to give

$$\begin{aligned} I^M_J = \sum_{jj'\ell\ell'} \Bigg\{ & \sum_{p,u}^{N+1} \int d\vec{R}\ \|D^{JMjj'\ell\ell'}(\vec{R})\|^{up} f^{JMjj'\ell\ell'}_{up}(\vec{R}) \\ & + \sum_{u>v}^{N+1} \sum_{p>q}^{N+1} \int d\vec{R}\ \|D^{JMjj'\ell\ell'}(\vec{R})\|^{uv,pq} g^{JMjj'\ell\ell'}_{uv,pq}(\vec{R}) \end{aligned}$$

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$$+ \sum_{p}^{N+1} \int d\vec{R} \; \|D^{JMjj'\ell\ell'}(\vec{R})\|^{p,N+1} \; D^{(2)JMjj'\ell\ell'}_{p,N+1}(\vec{R})$$

$$+ \int d\vec{R} \; \|D^{JMjj'\ell\ell'}(\vec{R})\| \left[V(R) + \frac{j(j+1)}{2\mu_N R^2} - E\right] \Big] \; . \tag{2.47}$$

The determinant of the matrix of overlap integrals and its minors can be expressed explicitly in terms of individual overlap integrals as in tables (1) and (2) below, which are derived in an appendix. I can delete superscripts which apply only to the $N+1^{st}$ orbital from terms not involving the $N+1^{st}$ orbital, with $\vec{R}$ where the expression depends only on R, and R where the expression is R independent. Equation (2.47) then becomes:

$$I^M_J = \sum_{jj'\ell\ell'} \Bigg[\sum_{u=1}^{N} \int d\vec{R} \; \{D^{JMj\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'}$$

$$- \sum_{i\neq u}^{N} D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R})\} \; f_{uu}$$

$$+ \sum_{u\neq p}^{N} \int d\vec{R} \; D^{JMj\ell}_{N+1,u}(\vec{R}) D^{JMj'\ell'}_{p,N+1}(\vec{R}) f_{up}$$

$$- \sum_{u=1}^{N} \int d\vec{R} \; D^{JMj\ell}_{N+1,u}(\vec{R}) f^{JMj'\ell'}_{u,N+1}(\vec{R})$$

$$- \sum_{u=1}^{N} \int d\vec{R} \; D^{JMj'\ell'}_{u,N+1}(\vec{R}) f^{JMj\ell}_{N+1,u}(\vec{R})$$

n	
$1+\sqrt{2}$	
$1+\sqrt{3}$	
$1+\sqrt{4}$	
$1+\sqrt{5}$	
$1+\sqrt{6}$	

TABLE 1: FIRST ORDER MINORS

u	p	$\|\| D^{JMjj'\ell\ell'}(\vec{R}) \|\|^{up}$
$<N+1$	$=u$	$D^{JMj\ell}_{N+1,N+1}(\vec{R})\,\delta_{jj'}\,\delta_{\ell\ell'}$ $- \sum_{i\neq u}^{N} D^{JMjj'\ell\ell'}_{N+1,i}(\vec{R})\, D^{JMjj'\ell\ell'}_{i,N+1}(\vec{R})$
$<N+1$	$\neq u, <N+1$	$D^{JMjj'\ell\ell'}_{N+1,u}(\vec{R})\, D^{JMjj'\ell\ell'}_{p,N+1}(\vec{R})$
$<N+1$	$=N+1$	$-D^{JMjj'\ell\ell'}_{N+1,u}(\vec{R})$
$=N+1$	$<N+1$	$-D^{JMjj'\ell\ell'}_{p,N+1}(\vec{R})$
$=N+1$	$=N+1$	1

TABLE 2: SECOND ORDER MINORS

u	p	q	$\|D^{JMjj'\ell\ell'}(\vec{R})\|^{uv,pq}$ $u>v, p>q$
$<N+1$	$=u$	$=v$	$D^{JMj\ell}_{N+1,N+1}(\vec{R})\,\delta_{\ell\ell'}\delta_{jj'}$
			$-\sum_{i\neq u,v}^{N} D^{JMij'\ell\ell'}_{N+1,i}(\vec{R})\,D^{JMjj'\ell\ell'}_{i,N+1}(\vec{R})$
	$=u$	$\neq v$	$D^{JMjj'\ell\ell'}_{N+1,v}(\vec{R})\,D^{JMjj'\ell\ell'}_{q,N+1}(\vec{R})$
	$=v$		$-D^{JMjj'\ell\ell'}_{N+1,u}(\vec{R})\,D^{JMjj'\ell\ell'}_{q,N+1}(\vec{R})$
	$<N+1$	$=u$	$-D^{JMjj'\ell\ell'}_{N+1,v}(\vec{R})\,D^{JMjj'\ell\ell'}_{p,N+1}(\vec{R})$
	$<N+1, \neq u$	$=v$	$D^{JMjj'\ell\ell'}_{N+1,u}(\vec{R})\,D^{JMjj'\ell\ell'}_{p,N+1}(\vec{R})$
	$=N+1$	$=v$	$-D^{JMjj'\ell\ell'}_{N+1,u}(\vec{R})$
		$=u$	$D^{JMjj'\ell\ell'}_{N+1,v}(\vec{R})$
$=N+1$	$=v$		$D^{JMjj'\ell\ell'}_{q,N+1}(\vec{R})$
	$<N+1$	$=v$	$-D^{JMjj'\ell\ell'}_{p,N+1}(\vec{R})$
	$=N+1$	$=v$	1

$$+ \int d\vec{R}\ \Gamma^{JMjj'\ell\ell'}_{N+1,N+1}(\vec{R})$$

$$+ \sum_{u>v}^{N} \int d\vec{R}\ \{D^{JMj\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'}$$

$$- \sum_{i\neq u,v}^{N} D^{JMj\ell}_{N+1,i}(\vec{R})D^{JMj'\ell'}_{i,N+1}(\vec{R})\}\ g_{uv,uv}$$

$$* \quad + \sum_{u>v,q}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,v}(\vec{R})D^{JMj'\ell'}_{q,N+1}(\vec{R})\ g_{uv,uq}$$

$$* \quad - \sum_{u>v>q}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,u}(\vec{R})D^{JMj'\ell'}_{q,N+1}(\vec{R})\ g_{uv,vq}$$

$$* \quad - \sum_{p>u>v}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,v}(\vec{R})D^{JMj'\ell'}_{p,N+1}(\vec{R})\ g_{uv,pu}$$

$$* \quad + \sum_{u,p>v}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,u}(\vec{R})D^{JMj'\ell'}_{p,N+1}(\vec{R})\ g_{uv,pv}$$

$$\dagger \quad - \sum_{u>v}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,u}(\vec{R})\ g^{JMj'\ell'}_{uv,N+1\ v}(\vec{R})$$

$$\dagger \quad + \sum_{u>v}^{N} \int d\vec{R}\ D^{JMj\ell}_{N+1,v}(\vec{R})\ g^{JMj'\ell'}_{uv,N+1\ u}(\vec{R})$$

$$\dagger \quad + \sum_{v>q}^{N} \int d\vec{R}\ D^{JMj'\ell'}_{q,N+1}(\vec{R})\ g^{JMj\ell}_{N+1\ v,vq}(\vec{R})$$

$$\dagger \quad - \sum_{p>v}^{N} \int d\vec{R}\ D^{JMj'\ell'}_{p,N+1}(\vec{R})\ g^{JMj\ell}_{N+1\ v,pv}(\vec{R})$$

$$+ \sum_{v=1}^{N} \int d\vec{R}\ g^{JMjj'\ell\ell'}_{N+1\ v,N+1\ v}(\vec{R})$$

$$+ \int d\vec{R}\ D^{(2)JMjj\ell\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'}$$

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$$- \sum_{p=1}^{N} \int d\vec{R}\; D^{JMj\ell}_{N+1,p}(\vec{R}) D^{(2)JMj'\ell'}_{p,N+1}(\vec{R})$$

$$+ \int d\vec{R}\; \{D^{JMj\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'} - \sum_{i}^{N} D^{JMj\ell}_{N+1,i}(\vec{R})$$

$$D^{JMj'\ell'}_{i,N+1}(\vec{R})\} \left[V(R) + \frac{j'(j'+1)}{2\mu_N R^2} - E\right] \Bigg) \,. \qquad (2.48)$$

In the above equation the four terms labeled with an asterisk can be combined after rearranging indices of summation, as can those labeled with a dagger. Thus:

$$I^M_J = \sum_{jj'\ell\ell'} \Bigg(\sum_{u=1}^{N} \int d\vec{R}\; \{D^{JMj\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'}$$

$$- \sum_{i\neq u}^{N} D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R})\} f_{uu}$$

$$+ \sum_{u\neq p}^{N} \int d\vec{R}\; D^{JMj\ell}_{N+1,u}(\vec{R}) D^{JMj'\ell'}_{p,N+1}(\vec{R})\; f_{up}$$

$$- \sum_{u=1}^{N} \int d\vec{R}\; \{D^{JMj\ell}_{N+1,u}(\vec{R}) f^{JMj'\ell'}_{u,N+1}(\vec{R})$$

$$+ f^{JMj\ell}_{N+1,u}(\vec{R}) D^{JMj'\ell'}_{u,N+1}(\vec{R})\} + \int d\vec{R}\; f^{JMjj'\ell\ell'}_{N+1,N+1}(\vec{R})$$

$$+ \sum_{u>v}^{N} \int d\vec{R}\; \{D^{JMj\ell}_{N+1,N+1}(\vec{R})\delta_{jj'}\delta_{\ell\ell'}$$

$$- \sum_{i\neq u,v}^{N} D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R})\} g_{uv,uv}$$

$$+ \sum_{\substack{uvq \\ (all \neq)}}^{N} \int d\vec{R}\; D^{JMj\ell}_{N+1,v}(\vec{R}) D^{JMj'\ell'}_{q,N+1}(\vec{R})\; g_{uv,uq}$$

$$+ \sum_{u \neq v}^{N} \int d\vec{R}\; \{ D^{JMj\ell}_{N+1,v}(\vec{R}) g^{JMj'\ell'}_{uv,N+1\;u}(\vec{R}) + D^{JMj'\ell'}_{v,N+1}(\vec{R})$$

$$g^{JMj\ell}_{N+1\;u,uv}(\vec{R}) \}$$

$$+ \sum_{v=1}^{N} \int d\vec{R}\; g^{JMjj'\ell\ell'}_{N+1\;v,N+1\;v}(\vec{R})$$

$$+ \int d\vec{R}\; D^{(2)JMjj\ell\ell}_{N+1,N+1}(\vec{R}) \delta_{jj'} \delta_{\ell\ell'}$$

$$- \sum_{p=1}^{N} \int d\vec{R}\; D^{JMj\ell}_{N+1,p}(\vec{R}) D^{(2)JMj'\ell'}_{p,N+1}(\vec{R})$$

$$+ \int d\vec{R}\; \{ D^{JMj\ell}_{N+1,N+1}(\vec{R}) \delta_{jj'} \delta_{\ell\ell'} - \sum_{j=1}^{N} D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R}) \}$$

$$\left(V(R) + \frac{j'(j'+1)}{2\mu_N R^2} - E \right) \Bigg) \quad . \tag{2.49}$$

I now expand the scattering spin-orbital so as to explicitly express its dependence on nuclear angles, where convenient. The integral $D^{JMj\ell}_{N+1,N+1}(\vec{R})$ can be written as follows:

$$D^{JMj\ell}_{N+1,N+1}(\vec{R}) = \sum_{\nu\nu' m_j m_j' m_\ell m_\ell'} C^*(j\ell J, m_j m_\ell M)$$

$$C(j\ell J,m_j'm_\ell'M)\langle f^\beta(r_1)Y_{\ell m_\ell}(\Omega_1')\alpha(1)$$

$$|f^\beta_{\nu'm_j'm_\ell'}(r_1)Y_{\ell m_\ell'}(\Omega_1')\alpha(1)\rangle_1 \chi^*_\nu(R)Y^*_{jm_j}(\Omega_R)$$

$$\chi_{\nu'}(R)Y_{jm_j'}(\Omega_R)$$

$$= \sum_{\nu\nu'm_jm_j'm_\ell m_\ell'} |C(j\ell J,m_jm_\ell M)|^2\delta_{m_\ell m_\ell'}\langle f^\beta(r)|$$

$$r^2|f^\beta_{\nu'm_j'm_\ell'}(r)\rangle_r \chi^*_\nu(R)\chi_{\nu'}(R)Y^*_{jm_j}(\Omega_R)Y_{jm_j}(\Omega_R)$$

(2.50)

where $f^\beta_{\nu'm_j'm_\ell'} \equiv f^{JM,\nu_0 j_0 m_{j_0}}_{\nu' jm_j',\ell m_\ell'}$. Note that if $m_\ell = m_\ell'$ then $m_j = m_j'$. The subscripts $_1$ and $_r$ on the integrals indicate integration over all coördinates of electron 1 and over only the radical coördinate of electron 1, respectively.

Integrating over Ω_R, the nuclear angle coördinate:

$$\int d\Omega_R\ D^{JMj\ell}_{N+1,N+1}(\vec{R}) = \sum_{\nu\nu'm} |C(j\ell J,m\ M-m\ M)|^2$$

$$\langle f^\beta(r)|r^2|f^\beta_{\nu'}(r)\rangle\ R^2\chi^*_\nu(R)\chi_{\nu'}(R) \qquad (2.51)$$

The characteristics of the Clebsch-Gordon coëfficients allow me to simplify this equation, producing

$$\int d\Omega_R \, D^{JMj\ell}_{N+1,N+1}(\vec{R}) = \sum_{\nu\nu'} \langle f^{\beta}(r) | r^2 | f^{\beta}_{\nu'}(r) \rangle$$

$$R^2 \underline{\chi}^*_{\nu}(R) \underline{\chi}_{\nu'}(R) \, . \qquad (2.52)$$

Now consider the product $D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R})$. It can be expanded as

$$D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R}) = \sum_{\nu\nu' m_j m_\ell m_j' m_\ell'} C^*(j\ell J, m_j m_\ell M)$$

$$C(j'\ell' J, m_j' m_\ell' M) \langle f^{\beta}(r) Y_{\ell m_\ell}(\Omega') \alpha(1) | \chi_i(1) \rangle$$

$$\underline{\chi}^*(R) Y^*_{jm_j}(\Omega_R) \langle \chi_i(1) | f^{\beta}_{\nu' j' \ell' m_\ell'}(r) Y_{\ell' m_\ell'}(\Omega') \alpha(1) \rangle$$

$$\underline{\chi}_{\nu'}(R) Y_{j' m_j'}(\Omega_R) \, . \qquad (2.53)$$

But $Y_{\ell m_\ell}(\Omega')$ must be expressed in terms of the molecule-centered angle Ω_1 and the molecular orientation Ω_R . It then becomes

$$Y_{\ell m_\ell}(\Omega_1') = \sum_m D^{\ell}_{m m_\ell}(-\phi_R, -\theta_R, \phi_R) Y_{\ell m}(\Omega_1) \qquad (2.54)$$

Thus the electronic integrals in (2.53) which are functions of Ω_R can be written in more convenient form as

$$\langle \chi_i(1) | f^{\beta}_{\nu' j' \ell' m_\ell'}(r) Y_{\ell' m_\ell'}(\Omega') \alpha(1) \rangle =$$

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$$\sum_{m'} D^{\ell'}_{m',m_\ell}(-\phi_R,-\theta_R,\phi_R)\langle\chi_i(1)|f^{\beta}_{\nu',j,\ell',m_\ell}(r)$$

$$Y_{\ell',m'}(\Omega)\alpha(1)\rangle \qquad (2.55)$$

Substituting this expression into (2.53) gives

$$D^{JMj\ell}_{N+1,i}(\vec{R})D^{JMj'\ell'}_{i,N+1}(\vec{R}) = \sum_{\nu\nu' m_j m_\ell m m_j' m_\ell' m'} C^*(j\ell J,m_j m_\ell M)$$

$$C(j'\ell' J,m_j' m_\ell' M)\; D^{\ell}_{mm_\ell}{}^*(-\phi_R,-\theta_R,\phi_R)\; D^{\ell'}_{m',m_\ell}(-\phi_R,-\theta_R,\phi_R)$$

$$\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_i(1)\rangle\langle\chi_i(1)|f^{\beta}_{\nu',j',\ell',m_\ell}(r)Y_{\ell',m'}(\Omega)$$

$$\alpha(1)\rangle Y^*_{jm_j}(\Omega_R)Y_{j',m_j'}(\Omega_R)\chi^*_\nu(R)\chi_{\nu'}(R)\ . \qquad (2.56)$$

If I now integrate both sides of this equation over Ω_R, most of the terms on the right can be written outside the integral. I obtain

$$\int d\Omega_R\; D^{JMj\ell}_{N+1,i}(\vec{R})D^{JMj'\ell'}_{i,N+1}(\vec{R}) = \sum_{\nu\nu' m_j m_\ell m m_j' m_\ell' m'}$$

$$C^*(j\ell J,m_j m_\ell M)\; C(j'\ell' J,m_j' m_\ell' M)\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_i(1)\rangle$$

$$\langle\chi_i(1)|f^{\beta}_{\nu',j',\ell',m_\ell}(r)Y_{\ell',m'}(\Omega)\alpha(1)\rangle\chi^*_\nu(R)\chi_{\nu'}(R)$$

$$\int d\Omega_R\; D^{\ell}_{mm'}{}^*(-\phi_R,-\theta_R,\phi_R)\; D^{\ell'}_{m',m_\ell}(-\phi_R,-\theta_R,\phi_R)$$

$$Y^*_{jm_j}(\Omega_R)Y_{j',m_j'}(\Omega_R)\ . \qquad (2.57)$$

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In order to evaluate the nuclear angle integral in the above expression, I must rearrange it considerably. I can make use of the following relationships:[3]

$$Y^{*}_{jm_j}(\theta_R,\phi_R) = \left(\frac{2j+1}{4\pi}\right)^{1/2} D^{j}_{m_j 0}(\phi_R,\theta_R,-\phi_R) \qquad (2.58)$$

and

$$D^{j}_{m',m}(\alpha\beta\gamma) = e^{-im'\alpha}\, d^{j}_{m',m}(\beta)\, e^{-im\gamma}$$

$$= e^{-im\gamma}\, d^{j}_{mm'}(-\beta)\, e^{-im'\alpha}$$

$$= D^{j}_{mm'}(\gamma-\beta\alpha) \qquad (2.59)$$

Now I can rewrite the spherical harmonics in (2.57) as

$$Y^{*}_{jm_j}(\theta_R,\phi_R) = \left(\frac{2j+1}{4\pi}\right)^{1/2} D^{j}_{0m_j}(-\phi_R,-\theta_R,\phi_R) \qquad \text{and}$$

$$Y_{j'm_j'}(\theta_R,\phi_R) = \left(\frac{2j'+1}{4\pi}\right)^{1/2} D^{j'}_{0m_j'}(-\phi_R,-\theta_R,\phi_R) \qquad (2.60)$$

The angle integral can now be written as

$$I_\Omega \equiv \int d\Omega_R\, D_{mm'}{}^{*}(-\phi_R,-\theta_R,\phi_R) D^{\ell'}_{m',m_\ell}(-\phi_R,-\theta_R,\phi_R) Y^{*}_{jm_j}(\Omega_R)$$

$$Y_{j'm_j'}(\Omega_R)$$

$$= \int d\Omega_R \left(\frac{2j+1}{4\pi}\right)^{1/2} \left(\frac{2j'+1}{4\pi}\right)^{1/2}$$

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$$D^{\ell'}_{m'm_\ell'}(-\phi_R,-\theta_R,\phi_R)D^{j}_{0m_j}(-\phi_R,-\theta_R,\phi_R)$$

$$D^{\ell\ *}_{mm}(-\phi_R,-\theta_R,\phi_R)D^{j'\ *}_{0m_j'}(-\phi_R,-\theta_R,\phi_R) \qquad (2.61)$$

I can now use the identity:[4]

$$D^{j_1}_{\mu_1 m_1}\ D^{j_2}_{\mu_2 m_2} = \sum_j C(j_1 j_2 j;\mu_1\ \mu_2\ \mu_1+\mu_2)$$

$$C(j_1 j_2 j;m_1\ m_2\ m_1+m_2)D^{j}_{\mu_1+\mu_2,m_1+m_2}\ , \qquad (2.62)$$

allowing me to write (2.61) as:

$$\int d\Omega_R\ D^{\ell\ *}_{mm_\ell}(-\phi_R,-\theta_R,\phi_R)\ D^{\ell'}_{m'm_\ell'}(-\phi_R,-\theta_R,\phi_R)$$

$$Y^{*}_{jm_j}(\Omega_R)Y_{j'm_j'}(\Omega_R)$$

$$= \left[\frac{2j+1}{4\pi}\right]^{1/2}\left[\frac{2j'+1}{4\pi}\right]^{1/2}\sum_{j_1 j_2} C(\ell' j j_1,m'0m')$$

$$C(\ell' j j_1,m_\ell' m_j m_\ell'+m_j)C(\ell j' j_2,m0m)$$

$$C(\ell j' j_2,m_\ell m_j' m_\ell+m_j')\int d\Omega_R\ D^{j_1}_{m'\ m_\ell'\ m_\ell'+m_j}(-\phi_R,-\theta_R,$$

$$\phi_R)D^{j_2\ *}_{m\ m_\ell+m_j'}(-\phi_R,-\theta_R,\phi_R) \qquad (2.63)$$

This angle integral can be written as two integrals over ϕ_R and θ_R respectively. The first can be evaluated immediately

R^2

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d^{j}_{m+n}

$$R^2 \int_0^{2\pi} d\phi e^{im'\phi}\, e^{-i(m_\ell'+m_j)\phi}\, e^{-im\phi}\, e^{i(m_\ell+m_j')\phi} \int_0^{\pi} \sin\theta d\theta$$

$$d^{j_1}_{m',\, m_\ell'+m_j}(-\theta) d^{j_2}_{m,\, m_\ell+m_j'}(-\theta)$$

$$= R^2 \delta_{m',\, m+m_j-m_j'-m_\ell+m_\ell'} \int_0^{\pi} \sin\theta d\theta\, d^{j_1}_{m',\, m_\ell'+m_j}(-\theta)$$

$$d^{j_2}_{m,\, m_\ell+m_j'}(-\theta) \qquad (2.64)$$

To evaluate the remaining integral, I expand the $d^j_{mm'}(\theta)$.

$$d^{j_1}_{m+m_j-m_j'-m_\ell+m_\ell',\, m_\ell'+m_j}(-\theta)\; d^{j_2}_{m,\, m_\ell+m_j'}(-\theta)$$

$$= \{(j_1+m+m_j-m_j'-m_\ell+m_\ell')!\; (j_1-m-m_j+m_j'+m_\ell-m_\ell')!$$

$$(j_1+m_\ell'+m_j)!\; (j_1-m_\ell'-m_j)!\; (j_2+m)!\; (j_2-m)!$$

$$(j_2+m_\ell+m_j')!\; (j_2-m_\ell-m_j')!\}^{1/2}$$

$$\sum_{k_1 k_2} (-1)^{k_1+k_2} / \{(j_1-m-m_j+m_j'+m_\ell-m_\ell'-k_1)!$$

$$(j_1+m_\ell'+m_j-k_1)!\; (k_1+m-m_j'-m_\ell)\; k_1!\; (j_2-m-k_2)!$$

$$(j_2+m_\ell+m_j'-k_2)!\; (k_2+m-m_\ell-m_j')!\; k_2!\}$$

$$\left(\cos\frac{\theta}{2}\right)^{2(j_1+j_2-k_1-k_2-m+m_j'+m_\ell)}$$

$$\left(\sin\frac{\theta}{2}\right)^{2(k_1+k_2+m-m_j'-m_\ell)} \qquad (2.65)$$

This integral can be evaluated by making the substitution $\alpha = \theta/2$ and integrating by parts.

$$\int_{\Omega}^{\pi} \left(\cos\frac{\theta}{2}\right)^{2(j_1+j_2-k_1-k_2-m+m_j'+m_\ell)} \left(\sin\frac{\theta}{2}\right)^{2(k_1+k_2+m-m_j'+m_\ell)} \sin\theta\, d\theta$$

$$= 4 \int_0^{\pi/2} (\cos\alpha)^{2(j_1+j_2-k_1-k_2-m+m_j'+m_\ell)+1} (\sin\alpha)^{2(k_1+k_2+m-m_j'-m_\ell)+1}\, d\alpha$$

$$= 2\, \frac{(j_1+j_2-k_1-k_2-m+m_j'+m_\ell)!\ (k_1+k_2+m-m_j'-m_\ell)!}{(j_1+j_2+1)!} \tag{2.66}$$

I now define

$$I_\Omega \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \equiv 2\delta_{m',m+m_j-m_j'-m_\ell+m_\ell'} \left(\frac{2j+1}{4\pi}\right)^{1/2} \sum_{j_1 j_2} C(\ell' j j_1, m'0)\, C(\ell' j j_1, m_\ell'\, m_j)$$

$$C(\ell j' j_2, m0)\, C(\ell j' j_2, m_\ell\, m_j')$$

$$\{(j_1+m+m_j-m_j'-m_\ell+m_\ell')!\ (j_1-m-m_j+m_j'+m_\ell-m_\ell')!$$

$$(j_1+m_\ell'+m_j)!\ (j_1-m_\ell'-m_j)!\ (j_2+m)!\ (j_2-m)!$$

$$(j_2+m_\ell+m_j')!\ (j_2-m_\ell-m_j)!\ ^{1/2}$$

$$\sum_{k_1k_2} (-1)^{k_1+k_2} \ /\ \{(j_1-m-m_j+m_j'+m_\ell-m_\ell'-k_1)!$$

$$(j_1+m_\ell'+m_j-k_1)!\ (k_1+m-m_j'-m_\ell)!\ k_1!\ (j_2-m-k_2)!$$

$$(j_2+m_\ell+m_j'-k_2)!\ (k_2+m-m_\ell-m_j')!\ k_2!\ \}$$

$$\frac{(j_1+j_2-k_1-k_2-m+m_j'+m_\ell)!}{(j_1+j_2+1)!}\ (k_1+k_2+m-m_j'+m_\ell)! \qquad (2.67)$$

The angle integral in the right side of (2.57) can now be written as

$$\int d\Omega_R\ D^{\ell\ *}_{mm_\ell}(-\phi_R,-\theta_R,\phi_R)D^{\ell'}_{m'm_\ell'}(-\phi_R,-\theta_R,\phi_R)Y^*_{jm_j}(\Omega_R)$$

$$Y_{j'm_j'}(\Omega_R) = R^2\ I_\Omega\begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \qquad (2.68)$$

I now define

$$I^{JM}_\Omega\begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \equiv C^*(j\ell J, m_j\ m_\ell\ M)$$

$$C(j'\ell'J, m_j'\ m_\ell'\ M)\ I_\Omega\begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m \end{pmatrix} \qquad (2.69)$$

so that I can now write equation (2.57) as

$$\int d\Omega_R \; D^{JMj\ell}_{N+1,i}(\vec{R}) D^{JMj'\ell'}_{i,N+1}(\vec{R}) = \sum_{\nu\nu' m_j m_\ell m m_j' m_\ell' m'} \langle f^\beta(r) Y_{\ell m}(\Omega)$$

$$\alpha(1)|\chi_i(1)\rangle\langle\chi_i(1)|f^\beta_{\nu',j'\ell' m_\ell'}(r) Y_{\ell' m'}(\Omega)\alpha(1)\rangle \chi^*_\nu(R)$$

$$\chi_{\nu'}(R)\; R^2\; I^{JM}_\Omega \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \qquad (2.70)$$

The nuclear angle dependence of the other terms in equation (2.49) is similar to that of the second term evaluated above, and can be integrated similarly. I can therefore write equation (2.49) in the form:

$$I^M_J = \sum_{j\ell\nu\nu' m_j m_\ell} \Bigg\{ |C(j\ell J, m_j m_\ell M)|^2 \int R^2 dR \langle f^\beta(r)|r^2|f^\beta_{\nu'}(r)\rangle$$

$$\chi^*_\nu(R)\chi_{\nu'}(R) \left[\sum_u^N f_{uu} + \sum_{u>v}^N g_{uv,uv} + V(R) + \frac{j(j+1)}{2\mu_N R^2} - E \right]$$

$$- \frac{1}{2\mu_N} \int dR \langle f^\beta(r)|r^2|f^\beta_{\nu'}(r)\rangle \chi^*_\nu(R) \frac{d}{dR} R^2 \frac{d}{dR} \chi_{\nu'}(R) \Bigg]$$

$$+ \sum_{jj'\ell\ell'\nu\nu' m_j m_j' m_\ell m_\ell' m m'} I^{JM}_\Omega \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix}$$

$$\Bigg[- \sum_{i\neq u}^N \int dR \; \chi^*_\nu(R)\chi_{\nu'}(R) \langle f^\beta(r) Y_{\ell m}(\Omega)\alpha(1)|\chi_i(1)\rangle$$

$$\langle\chi_i(1)|f^\beta_{\nu',j'\ell' m_\ell'} Y_{\ell' m'}(\Omega)\alpha(1)\rangle f_{uu}\; R^2$$

$$+ \sum_{u\neq p}^N \int dR \; \chi^*_\nu(R)\chi_{\nu'}(R) \langle f^\beta(r) Y_{\ell m}(\Omega)\alpha(1)|\chi_u(1)\rangle$$

$$\langle\chi_p(1)|f^\beta_{\nu',j'\ell' m_\ell'} Y_{\ell' m'}(\Omega)\alpha(1)\rangle f_{up}\; R^2$$

$$- \sum_{u=1}^{N} \int dR \underline{\chi}_{\nu}^{*}(R) \underline{\chi}_{\nu'}(R) [\langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \chi_u(1)\rangle\langle\chi_u(1)|$$

$$|\hat{f}(1;R)| f^{\beta}_{\nu',j',\ell',m_{\ell}} Y_{\ell',m'}(\Omega)\alpha(1)\rangle + \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1)|$$

$$|\hat{f}(1;R)|\chi_u(1)\rangle\langle\chi_u(1)| f^{\beta}_{\nu',j',\ell',m_{\ell}} Y_{\ell',m'}(\Omega)\alpha(1)\rangle] R^2$$

$$+ \int dR \underline{\chi}_{\nu}^{*}(R) \underline{\chi}_{\nu'}(R) \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} |$$

$$| f^{\beta}_{\nu',j',\ell',m_{\ell}}(r) Y_{\ell',m'}(\Omega)\alpha(1)\rangle R^2$$

$$- \sum_{u>v}^{N} \int dR \underline{\chi}_{\nu}^{*}(R) \underline{\chi}_{\nu'}(R) \sum_{i\neq u,v}^{N} \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1)|\chi_i(1)\rangle$$

$$\langle\chi_i(1)| f^{\beta}_{\nu',j',\ell',m_{\ell}}(r) Y_{\ell',m'}(\Omega)\alpha(1)\rangle \, g_{uv,uv} \, R^2$$

$$+ \sum_{\substack{uvq \\ (all\neq)}}^{N} \int dR \underline{\chi}_{\nu}^{*}(R) \underline{\chi}_{\nu'}(R) \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1)|\chi_v(1)\rangle\langle\chi_q(1)|$$

$$| f^{\beta}_{\nu',j',\ell',m_{\ell}}(r) Y_{\ell',m'}(\Omega)\alpha(1)\rangle \, g_{uv,uq} \, R^2$$

$$+ \sum_{u\neq v}^{N} \int dR \, [\langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1)|\chi_v(1)\rangle\langle\chi_u(1)\chi_v(1)|$$

$$\frac{1}{r_{12}}(1-P_{12}) | f^{\beta}_{\nu',j',\ell',m_{\ell}}(r_1) Y_{\ell',m'}(\Omega_1)\alpha(1)\chi_u(2)\rangle$$

$$+ \langle f^{\beta}(r_1) Y_{\ell',m'}(\Omega_1)\alpha(1)\chi_u(2)|\frac{1}{r_{12}}(1-P_{12})|$$

$$\chi_u(1)\chi_v(1)\rangle\langle\chi_v(1)| f^{\beta}_{\nu',j',\ell',m_{\ell}}(r) Y_{\ell',m'}(\Omega)\alpha(1)\rangle]$$

$$\underline{\chi}_{\nu}^{*}(R) \underline{\chi}_{\nu'}(R) \, R^2$$

$$+ \sum_{v=1}^{N} \int dR\ \chi_v^*(R)\chi_{v'}(R) \langle f^{\beta}(r_1)Y_{\ell m}(\Omega_1)\alpha(1)\chi_v(2)$$

$$\left|\frac{1}{r_{12}}(1-P_{12})\right| f^{\beta}_{v',j',\ell',m_\ell}(r_1)Y_{\ell',m'}(\Omega_1)\alpha(1)\chi_v(1)\rangle R^2$$

$$+ \frac{1}{2\mu_N} \sum_{p=1}^{N} \int dR\ \chi_v^*(R) \langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_p(1)\rangle$$

$$\langle\chi_p(1)|f^{\beta}_{v',j',\ell'}(r)Y_{\ell',m'}(\Omega)\alpha(1)\rangle \left(\frac{d}{dR}R^2\frac{d}{dR}\chi_{v'}(R)\right)$$

$$- \sum_{i=1}^{N} \int dR\ \chi_v^*(R)\chi_{v'}(R) \langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_i(1)\rangle\langle\chi_i(1)|$$

$$|f^{\beta}_{v',j',\ell',m_\ell},Y_{\ell',m'}(\Omega)\alpha(1)\rangle \left(V(R) + \frac{j'(j'+1)}{2\mu_N R^2} - E \right)R^2 \Big)$$

$$+ \sum_{j\ell vv'} \int dR \langle f^{\beta}(1)| \left(-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{2}\right)|f^{\beta}_{v'}(1)\rangle$$

$$\chi_v^*(R)\chi_{v'}(R)\ R^2 \qquad (2.71)$$

The last term of the above equation and the term containing $\frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)}$ are a decomposition of the $f^{JMjj'\ell\ell'}_{N+1,N+1}(R)$ term.

The vibrational functions are defined as an orthonormal set of solutions of the equation

$$\left(-\frac{1}{2\mu_N}\frac{d}{dR}R^2\frac{d}{dR} + V(R) - E_v \right)\chi_v(R) = 0. \qquad (2.72)$$

I can use this identity to eliminate the derivatives with respect to R from equation (2.71). I will assume that the j(j+1) terms can be neglected, since the rotational

energy is very small compared to the vibrational energy. I can now perform the integration over R in most of the integrals in equation (2.71).

Also observe that

$$E_{Mol} = \langle \mathcal{A}\, \chi_1(1)\chi_2(2)\ldots\chi_N(N) \mid \hat{\mathcal{H}}_{Mol} \mid \mathcal{A}\chi_1(1)$$

$$\chi_2(2)\ldots\chi_N(N)\rangle = \sum_{u=1}^{N} f_{uu} + \sum_{u>v}^{N} g_{uv,uv} \qquad (2.73)$$

so that

$$F_\nu - E + \sum_{u}^{N} f_{uu} + \sum_{u>v}^{N} g_{uv,uv} = E_\nu - E + E_{Mol}$$

$$= E_\nu - E_{\nu_0} - 1/2\ k_{\nu_0}^2 \qquad (2.74)$$

Equation (2.71) can now be rearranged an simplified to the following:

$$I_J^M = \sum_{j\ell\nu m_j m_\ell} |C(j\ell J, m_j m_\ell M)|^2 \langle f^\beta(r)| \left\{ -\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{2} + r^2\{E_\nu - E_{\nu_0} - 1/2\ k_{\nu_0}^2\} \right\} |f^\beta(r)\rangle$$

$$+ \sum_{jj'\nu\nu' m_j m_j' m_\ell m_\ell' mm'} I_\Omega^{JM} \begin{bmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{bmatrix}$$

$$\left\{ \sum_{\nu'} \int R\ \chi_\nu^*(R)\chi_{\nu'}(R) \left\{ \langle f^\beta(r)Y_{\ell m}(\Omega)\alpha(1)|\right.\right.$$

$$\frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} | f^{\beta}_{\nu',j',\ell',m_{\ell}'}(r) Y_{\ell',m'}(\Omega)\alpha(1) \rangle$$

$$- \sum_{u=1}^{N} \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \chi_u(1) \rangle \langle \chi_u(1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} |$$

$$| f^{\beta}_{\nu',j',\ell',m_{\ell}'}(r) Y_{\ell',m'}(\Omega)\alpha(1) \rangle \Big] \, dR$$

$$+ \sum_{u=1}^{N} \Big[\langle f^{\beta}(r_1) Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2) | \frac{1}{r_{12}}(1-P_{12}) | f^{\beta}_{j',\ell',m_{\ell}'}(r_1)$$

$$Y_{\ell',m'}(\Omega_1)\alpha(1)\chi_u(2) \rangle$$

$$- \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \chi_u(1) \rangle \langle \chi_u(1) | f^{\beta}_{j',\ell',m_{\ell}'}(r) Y_{\ell',m'}(\Omega)$$

$$\alpha(1) \rangle (E_{\nu} - E)$$

$$- \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \hat{f}(1) | \chi_u(1) \rangle \langle \chi_u(1) | f^{\beta}_{j',\ell',m_{\ell}'}(r)$$

$$Y_{\ell',m'}(\Omega)\alpha(1) \rangle$$

$$- \langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \chi_u(1) \rangle \langle \chi_u(1) | - \frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr}$$

$$+ \frac{\ell'(\ell'+1)}{2r^2} | f^{\beta}_{j',\ell',m_{\ell}'}(r) Y_{\ell',m'}(\Omega)\alpha(1) \rangle$$

$$+ \sum_{v \neq u}^{N} \Big[\langle f^{\beta}(r) Y_{\ell m}(\Omega)\alpha(1) | \chi_u(1) \rangle \langle \chi_v(1) | f^{\beta}_{j',\ell',m_{\ell}'}(r)$$

$$Y_{\ell',m'}(\Omega)\alpha(1) \rangle \, f_{uv}$$

$$-\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_u(1)\rangle\langle\chi_u(1)|f^{\beta}_{j',\ell',m_\ell}(r)Y_{\ell',m'}(\Omega)$$

$$\alpha(1)\rangle\, \mathcal{E}_{vv}$$

$$+\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_v(1)\rangle\langle\chi_u(1)\chi_v(2)|\frac{1}{r_{12}}(1-P_{12})|$$

$$|f^{\beta}_{j',\ell',m_\ell}(r_1)Y_{\ell',m'}(\Omega_1)\alpha(1)\chi_u(2)\rangle$$

$$+\langle f^{\beta}(r_1)Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2)|\frac{1}{r_{12}}(1-P_{12})|\chi_u(1)\chi_v(2)\rangle$$

$$\langle\chi_v(1)|f^{\beta}_{j',\ell',m_\ell}(r)Y_{\ell',m'}(\Omega)\alpha(1)\rangle$$

$$+\sum_{\substack{p\neq v,u}}^{N}\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_v(1)\rangle\langle\chi_p(1)|f^{\beta}_{j',\ell',m_\ell}(r)$$

$$Y_{\ell',m'}(\Omega)\alpha(1)\rangle\, \mathcal{E}_{uv,up}$$

$$-\sum_{\substack{p>u\\ \neq v}}^{N}\langle f^{\beta}(r)Y_{\ell m}(\Omega)\alpha(1)|\chi_v(1)\rangle\langle\chi_v(1)|f^{\beta}_{j',\ell',m_\ell}(r)$$

$$Y_{\ell',m'}(\Omega)\alpha(1)\rangle\, \mathcal{E}_{up,up}\Big]\Big]\Big] \quad . \tag{2.75}$$

Equation (2.75) will serve as an expression for the integral $\langle\Psi^{M}_{Jj\ell}|\hat{\mathcal{H}}-E|\Psi^{M}_{Jj',\ell'}\rangle$. This will be used in chapter (III) to develop a variational equation for the scattering functions f^{β}, which are assumed to be the only unknown factors in the equation.

[1] Rose.op.cit. p.60.

[2] Rose,op.cit. p.58.

Chapter III. The Variational Equation for the Scattering Function.

I will now determine the equation which the scattering functions f^{β} must satisfy in order that the variation of the integral $I_J^M = \langle \Psi | \hat{\mathcal{H}} - E | \Psi \rangle$, minus the surface term, will be zero with respect to an arbitrary small variation in the f^{β}. The functions which satisfy this equation will be taken to be the solutions which I am seeking. Ignoring second order terms, the variation is given by the sum of the variation from the left and the variation from the right. The variation from the left is as follows:

$$\delta_{left} I_J^M = \sum_{j\ell\nu j'\ell'\nu' m_j m_\ell m_j' m_\ell'} \langle \delta f^{\beta}(r_1) | \Bigg[$$

$$\left(-\frac{1}{2}\frac{d}{dr_1} r_1 \frac{d}{dr_1} + \frac{\ell(\ell+1)}{2} + [\mathcal{E}_\nu - \mathcal{E}_{\nu_0} - 1/2\, k_{\nu_0}^2] r_1^2 \right)$$

$$\delta_{jj'}\delta_{\ell\ell'}\delta_{\nu\nu'}\delta_{m_j m_j'}\delta_{m_\ell m_\ell'}$$ free space part

$$+$$ interaction

$$+ I_\Omega^{JM} \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \Bigg[$$

$$\int R^2 \chi_\nu^*(R) \chi_{\nu'}(R) \Bigg\{ \langle Y_{\ell m}(\Omega_1) | \frac{Z}{r_1 \alpha(R)} + \frac{Z}{r_2 \beta(R)}$$

$$| Y_{\ell' m'}(\Omega_1) \rangle_{\Omega_1} - \sum_{u=1}^{N} \langle Y_{\ell m}(\Omega_1) \alpha(1)$$ vibrational coupling through nuclear attraction

$$| \chi_u \rangle \langle \chi_u | \frac{Z}{r_1 \alpha(R)} + \frac{Z}{r_2 \beta(R)}$$

$$|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle \Big] \, dR$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \Big[\langle Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2)|\frac{1}{r_{12}}(1-P_{12})|Y_{\ell',m'}(\Omega_1)$$

$$\alpha(1)\chi_u(2)\rangle$$

coulomb and exchange integral

$$- \langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_u\rangle\langle\chi_u|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle(\varepsilon_\nu - E)$$

exchange

$$-\langle Y_{\ell m}(\Omega_1)\alpha(1)|\hat{f}(1)|\chi_u\rangle\langle\chi_u|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle$$

$$- \langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_u\rangle\langle\chi_u| - \frac{1}{2r_1}\frac{d}{dr_1}r_1^2\frac{d}{dr_1} + \frac{\ell'(\ell'+1)}{2r_1^2}$$

$$|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle$$

one-electron operator with exchange

$$+ \sum_{v\neq u}^{N} \Big[\langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_u\rangle\langle\chi_v|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle f_{uv}$$

$$-\langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_u\rangle\langle\chi_u|Y_{\ell',m'}(\Omega_1)\alpha(1)\rangle f_{vv}$$

$$+ \langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_v\rangle\langle\chi_u(1)\chi_v(2)|\frac{1}{r_{12}}(1-P_{12})$$

$$|Y_{\ell',m'}(\Omega_1)\alpha(1)\ \chi_u(2)\rangle$$

coulomb and exchange integral with second exchange

$$+ \langle Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2)\left|\frac{1}{r_{12}}(1-P_{12})\right|\chi_u(1)\chi_v(2)\rangle$$

$$\langle \chi_v | Y_{\ell' m'}(\Omega_1)\alpha(1)\rangle$$

$$+ \sum_{p\neq v,u}^{N} \langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_v\rangle\langle\chi_p|Y_{\ell' m'}(\Omega_1)\alpha(1)\rangle\, g_{uv,up}$$

$$- \sum_{\substack{p<u \\ \neq v}}^{N} \langle Y_{\ell m}(\Omega_1)\alpha(1)|\chi_v\rangle\langle\chi_v|Y_{\ell' m'}(\Omega_1)\alpha(1)\rangle\, g_{up,up} \Bigg) \Bigg) \Bigg) \left|f^{\beta}_{\nu' j' \ell' m_\ell'}(r_1)\right\rangle_{r_1} \qquad (3.1)$$

I will make a convenient abbreviation by taking the entire quantity within the outermost parentheses in equation (3.1) and deleting it, writing only the parentheses enclosing the parameters on which it depends. Equation (3.1) can then be written

$$\delta_{\text{left}}\, I_J^M = \sum_{j\ell\nu j'\ell'\nu' m_j m_\ell m_j' m_\ell'} \langle \delta f^{\beta}(r_1)| \begin{pmatrix} j & \ell & \nu & m_j & m_\ell \\ j' & \ell' & \nu' & m_j' & m_\ell' \end{pmatrix} \left|f^{\beta}_{\nu' j' \ell' m_\ell'}(r_1)\right\rangle_{r_1} \qquad (3.2)$$

The variation from the right will be

$$\delta_{right}\, I_J^M = \delta_{left}\, I_J^{M\,*} - \Big\{ \sum_{j\ell\nu} \langle \delta f^\beta(r) | - \frac{1}{2}\frac{d}{dr} r^2 \frac{d}{dr}$$

$$|f^\beta(r)\rangle_r \Big\}^* + \Big\{ \sum_{j\ell\nu} \langle f^\beta(r) | - \frac{1}{2}\frac{d}{dr} r^2 \frac{d}{dr} |$$

$$|\delta f^\beta(r)\rangle_r \Big\} \quad . \tag{3.3}$$

I can now write the total variation as

$$\delta' I_J^M = \delta_{left}\, I_J^M + \delta_{right}\, I_J^M$$

$$= \delta_{left}\, I_J^M + \delta_{left}\, I_J^{M\,*} + \sum_{j\ell\nu} \Big\{ \langle \delta f^\beta(r) | \frac{1}{2}\frac{d}{dr} r^2 \frac{d}{dr} |$$

$$|f^\beta(r)\rangle_r^* - \langle f^\beta(r) | \frac{1}{2}\frac{d}{dr} r^2 \frac{d}{dr} |\delta f^\beta(r)\rangle_r \Big\} \tag{3.4}$$

I do not want, however, to set the complete variation equal to zero, but rather the variation minus the surface term. In place of $\delta' I_J^M$ I define:

$$\delta I_J^M = \delta_{left}\, I_J^M + \delta_{left}\, I_J^{M*} \quad . \tag{3.5}$$

When I set δI_J^M equal to zero, I obtain the equation which the radial scattering functions $f^\beta(r)$ must satisfy.

$$\delta I_J^M = 0$$

$$= \sum_{jj'\ell\ell'\nu\nu'm_j m_j' m_\ell m_\ell'} \langle \delta f^\beta(r_1) | \begin{pmatrix} j & \ell & \nu & m_j & m_\ell \\ j' & \ell' & \nu' & m_j' & m_\ell' \end{pmatrix} | f^\beta_{\nu' j' \ell'}(r_1) \rangle_{r_1} + \sum_{jj'\ell\ell'\nu\nu'm_j m_j' m_\ell m_\ell'} \langle \delta f^\beta(r_1) | \begin{pmatrix} j & \ell & \nu & m_j & m_\ell \\ j' & \ell' & \nu' & m_j' & m_\ell' \end{pmatrix} | f^\beta_{\nu' j' \ell'}(r_1) \rangle^*_{r_1}$$

(3.6)

But this equation is equivalent to

$$I^M_J = 2 \, \mathrm{Re} \left[\sum_{jj'\ell\ell'\nu\nu'm_j m_j' m_\ell m_\ell'} \langle \delta f^\beta(r) | \begin{pmatrix} j & \ell & \nu & m_j & m_\ell \\ j' & \ell' & \nu' & m_j' & m_\ell' \end{pmatrix} | f^\beta_{\nu' j' \ell'}(r) \rangle \right]$$

(3.7)

where $\mathrm{Re}(x+iy) = x$.

Since the $f^\beta(r)$ are arbitrary complex functions, the above equation implies that

$$\sum_{j'\ell'\nu' m_j' m_\ell'} \begin{pmatrix} j & \ell & \nu & m_j & m_\ell \\ j' & \ell' & \nu' & m_j' & m_\ell' \end{pmatrix} | f^\beta_{\nu' j' \ell'}(r) \rangle = 0$$

(3.8)

for all ν, j, ℓ, m_j, and m_ℓ.

To use this equation, I need some explicit form for the $f^{\beta}(r)$ containing variational parameters. These can then be evaluated by requiring them to satisfy (3.8). A very important factor which is pertinent to the form of these scattering functions is that I am using a one determinant wave function for a system in which resonant scattering is dominant. Such systems must normally be described by a two or more determinant system, but since this is a single-particle resonance where the molecule is not electronically excited, I can use a one-determinant function. I must then compromise between the goals of having the correct asymptotic form for the wave function and having the polarization of the target well described. This difficulty will be further discussed in Chapter IV and Appendix B.

Chapter IV. The form of the Scattering Function.

In scattering of an electron by a molecule, the complete electronic wave function can be written in the form

$$\Psi(N+1) = \sum_{i=1} c_i \mathcal{A}\, \Psi_i^{\text{Molecule}}(N)\psi_i^{\text{Scattering}}(1) \qquad (4.1)$$

where the $\Psi_i^{\text{Molecule}}(N)$ are the wave-functions of the various states of the molecule and $\mathcal{A}$ is the anti-symmetrizing operator. If correlation within the molecule is neglected, the $\Psi_i^{\text{Molecule}}(N)$ are the one determinant Hartree-Fock wave functions. The $\psi_i^{\text{Scattering}}(1)$ are scattering spin orbitals which I will assume to have α-spin.

This method is generally impractical because of the need for a large number of molecular excited state functions which are not in general known. If there are no molecular excited states near or below the energy of the scattered electron, a reasonable approximation of the above function can be made by

$$\Psi(N+1) = \mathcal{A}\, \Psi_1^P(N)\psi(1) \qquad (4.2)$$

where $\Psi_1^P(N)$ is a distorted ground state function. To obtain the correct assymptotic form I will split this function into two parts

$$\Psi(N+1) = \mathcal{A}(\Psi^M(N)\psi^S(1) + c\Psi^P(N)\psi^B(1)) \qquad (4.3)$$

where $\Psi^M(N)$ is the undistorted ground state function, $\Psi^P(N)$ is a distorted ground state function, $\psi^S(1)$ is a scattering function, and $\psi^B(1)$ is a bound state function. The asymptotic form is now correct:

$$\Psi(N+1) \rightarrow \mathcal{A}\Psi^M(N)\psi^S(1) \quad \text{as} \quad r_{scat} \rightarrow \infty \; . \tag{4.4}$$

I choose the incoming electron beam to be travelling along the z-axis of a non-rotating spherical coördinate system centered at the center of mass of the molecule, so that I can write ψ^S as

$$\psi^S = (e^{ikz} + e^{ikr} f(r,\theta,\phi)) = \Big(\sum_{\ell=0}^{\infty} i^{\ell}(2\ell+1)j_{\ell}(kr) P_{\ell}(\cos\theta) + e^{ikr} f(r,\theta,\phi) \Big) \tag{4.5}$$

where $f(r,\theta,\phi) \rightarrow \frac{1}{r}f(\theta,\phi)$ as $r\rightarrow\infty$. I can write the Legendre polynomials in terms of spherical harmonics.

$$(2\ell+1)P_{\ell}(\cos\theta) = (4\pi(2\ell+1))^{1/2} Y_{\ell 0}(\theta,\phi) \tag{4.6}$$

I can also expand $f(r,\theta,\phi)$ in terms of radial functions and spherical harmonics as

$$f(r,\theta,\phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} f_{\ell m}(r) Y_{\ell m}(\theta,\phi) \tag{4.7}$$

where $f_{\ell m}(r) \rightarrow \frac{1}{r}f_{\ell m}$ as $r\rightarrow\infty$. Equation (4.5) now can be

expressed as

$$\psi^S = \sum_{\ell=0}^{\infty} \left(i^\ell \sqrt{4\pi(2\ell+1)}\, j_\ell(kr) Y_{\ell 0}(\theta,\phi) + e^{ikr} \sum_{m=-\ell}^{+\ell} f_{\ell m}(r) Y_{\ell m}(\theta,\phi)\right) \tag{4.8}$$

For a spherically symmetrical interaction $f_{\ell m} = 0$ for $m \neq 0$, but for scattering from molecules this is not generally the case. The complete electronic wave function is now of the form:

$$\Psi(N+1) = \mathcal{A}(\psi^M(N)\psi^S(1) + c\psi^P(N)\psi^B(1)) \tag{4.9}$$

$$+ \mathcal{A}\psi^M(N) \sum_{\ell=0}^{\infty} \left(i^\ell \sqrt{4\pi(2\ell+1)}\, j_\ell(kr) Y_{\ell 0}(\theta,\phi) + \frac{e^{ikr}}{r} \sum_{m=-\ell}^{+\ell} f_{\ell m}(\theta,\phi)\right) \text{ as } r \to \infty. \tag{4.10}$$

I also wish to consider vibrational and rotational excitation. If the diatomic molecule is initially in the state specified by ν_0, j_0, m_{j_0}, then the asymptotic form of the function will be

$$\Psi(N+1,R) \underset{r\to\infty}{\to} \mathcal{A}\psi^M(N) \sum_{\ell=0}^{\infty} \left(i^\ell \sqrt{4\pi(2\ell+1)}\, j_\ell(k_{\nu_0 j_0} r)\right.$$

$$\left. Y_{\ell 0}(\theta,\phi)\chi_{\nu_0}(R) Y_{j_0 m_{j_0}}(\theta_R,\phi_R)\right)$$

$$+ \sum_{\nu} \sum_{j=0}^{\infty} \frac{e^{ik_{\nu j}r}}{r} \sum_{m=-\ell}^{+\ell} \sum_{m_j=-j}^{+j} f_{\ell m,\nu_0 j_0 m_{j_0},\nu j m_j}$$

$$Y_{\ell m}(\theta,\phi)\chi_{\nu}(R)Y_{jm_j}(\theta_R,\phi_R)) \qquad (4.11)$$

where $\chi_{\nu}(R)$ and $Y_{jm_j}(\theta_R,\phi_R)$ are the nuclear vibrational and rotational functions, respectively. Let $k_0 \equiv k_{\nu_0 j_0}$. So that the complete function is compatible with this asymptotic form, I replace $\psi^S(1)$ with

$$\psi^S(1,\vec{R}) = \sum_{\ell=0}^{\infty} (i^{\ell}\sqrt{4\pi(2\ell+1)}\, j_{\ell}(k_{\nu_0 j_0}r)Y_{\ell 0}(\theta,\phi)$$

$$\chi_{\nu_0}(R)Y_{j_0 m_{j_0}}(\theta_R,\phi_R) + \sum_{\nu} \sum_{j=0}^{\infty} e^{ik_{\nu j}r} \sum_{m=-\ell}^{+\ell} \sum_{m_j=-j}^{+j}$$

$$f_{m\ell,\nu_0 j_0 m_{j_0}\nu j m_j}(r)Y_{\ell m}(\theta,\phi)\chi_{\nu}(R)Y_{jm_j}(\theta_R,\phi_R)) \qquad (4.12)$$

I now have a scattering function consisting of a plane wave with the molecule in the initial state and outgoing waves with the molecule in all the accessible vibrational and rotational states. This can be written in the form

$$\psi^S(1,\vec{R}) = \sum_{\nu j m_j} \chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1)\chi_{\nu}(R)Y_{jm_j}(\theta_R,\phi_R)$$

$$(4.13)$$

where the electronic functions are

$$\chi^{S}_{\nu_0 j_0 m_{j_0}, \nu j m_j}(1) = \sum_{\ell=0}^{\infty} \Big[i^{\ell}\sqrt{4\pi(2\ell+1)}\; j_{\ell}(k_{\nu_0 j_0} r) Y_{\ell 0}(\theta,\phi)$$

$$\delta_{\nu\nu_0}\, \delta_{j j_0}\, \delta_{m_j m_{j_0}} + e^{ik_{\nu j} r} \sum_{m=-\ell}^{+\ell} f_{m\ell, \nu_0 j_0 m_{j_0}, \nu j m_j}(r)$$

$$Y_{\ell m}(\theta,\phi)\Big]\alpha(1) \; . \qquad (4.14)$$

Since I expect Born-Oppenheimer breakdown to be important in the resonant scattering process, I will also include molecular vibrational and rotational functions in the bound state orbital:

$$C\psi^{B}(1) = \sum_{\nu j m_j} C_{\nu j m_j} \chi^{B}_{\nu j m_j}(1) \underline{\chi}_{\nu}(R) Y_{j m_j}(\theta_R, \phi_R),$$

where

$$r\chi^{B}_{\nu j m_j}(1) \to 0 \quad \text{as} \quad r \to \infty \; . \qquad (4.15)$$

The $C_{\nu j m_j}$ are unknown constants giving the weighting factors for the different molecular states. It would be possible to obtain vibrational functions for the bound state function $\Psi^{P}(N)\psi^{B}(1)$ and use them for the $\underline{\chi}_{\nu}(R)$ in this expression. The regular molecular vibrational functions are a complete set and may also be used. The vibrational functions and their coëfficients will be discussec more fully in the following chapter.

The total wave function can now be written

$$\Psi(N+1,\vec{R}) = \sum_{\nu j m_j} \left(\mathcal{A}\,\Psi^M(N)\chi^S_{\nu_0 j_0 m_{j_0}\nu j m_j}(1) + C_{\nu j m_j}\right.$$

$$\left.\mathcal{A}\,\Psi^P(N)\chi^B_{\nu j m_j}(1)\right)\chi_\nu(R)Y_{j m_j}(\theta_R,\phi_R). \quad (4.16)$$

I now wish to determine a reasonable one-determinant approximation to the above two-determinant electronic function which will be easier to work with. I have shown in Appendix B that the best function which can be obtained without doing most of the work required for the two-determinant function is obtained by neglecting the polarization and replacing $\Psi^P(N)$ by $\Psi^M(N)$.

The effects of the polarization are approximated by potential scaling when the bound state spin-orbital is calculated in Chapter V. The wave function I am now using is

$$\Psi(N+1,\vec{R}) = \mathcal{A}\,\Psi^M(N) \sum_{\nu j m_j} \left(\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1)\right.$$

$$\left. + C_{\nu j m_j}\chi^B_{\nu j m_j}(1)\right)\chi_\nu(R)Y_{j m_j}(\theta_R,\phi_R) \quad (4.17)$$

By writing a set of different bound state functions $\chi^B_{\nu j m_j}$, I am assuming some breakdown of the Born-Oppenheimer separation between the nuclear motion and the motion of the scattered electron. This is reasonable for molecules such as N_2 where the N_2^- resonance is believed

to exist about the same length of time as the vibrational period of the N_2 molecule.[1] The rotational motion, however, is much slower and I cannot justify Born-Oppenheimer breakdown with respect to rotational motion.[2] Equation (4.17) now becomes

$$\Psi(N+1,\vec{R}) = \mathcal{A}\,\Psi^M(N) \sum_{\nu j m_j} (\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu}\chi^B_{\nu}(1))\underline{\chi}_{\nu}(R)Y_{jm_j}(\theta_R,\phi_R) \qquad (4.18)$$

Using equation (4.14) this is equivalent to

$$\Psi(N+1,\vec{R}) = \mathcal{A}\,\Psi^M(N) \sum_{\nu j m_j} \Big(\sum_{\ell=0}^{\infty} (i^{\ell}\sqrt{4\pi(2\ell+1)}\, j_{\ell}(k_0 r)Y_{\ell 0}(\theta,\phi)\delta_{\nu\nu_0}\delta_{jj_0}\delta_{m_j m_{j_0}} + e^{ik_{\nu j}r} \sum_{m=-\ell}^{+\ell} f_{m\ell,\nu_0 j_0 m_{j_0},\nu j m_j}(r)Y_{\ell m}(\theta,\phi))\alpha(1) + C_{\nu}\chi^B_{\nu}(1))\underline{\chi}_{\nu}(R)Y_{jm_j}(\theta_R,\phi_R) \qquad (4.19)$$

This function still represents scattering of a plane wave. To conveniently handle the rotational functions I need to express Ψ as a combination of states which are eigenfunctions of total angular momentum, J, z-component, M, electronic angular momentum, ℓ, and rotational angular momentum, j.

That is, electrons in a particular spherical wave scattering from a molecule in a particular rotational state, with the system in a particular total angular momentum s ate. These can be obtained as

$$\Psi^{JMj\ell}(N+1,\vec{R}) = P^{JMj\ell}|\Psi(N+1,\vec{R})> \tag{4.20}$$

where $P^{JMj\ell}$ is a projection operator for the $JMj\ell$ state. Then

$$\Psi^{JMj\ell}(N+1,\vec{R}) = P^{JMj\ell}\mathcal{A}\Psi^{M}(N)\sum_{\nu j'm_j}\{\chi^{S}_{\nu_0 j_0 m_{j_0},\nu j'm_j}(1) + C_{\nu}\chi^{B}_{\nu}(1)\}\chi_{\nu}(R)Y_{j'm_j}(\theta_R,\phi_R)$$

$$= \mathcal{A}P^{JMj\ell}\Psi^{M}(N)\sum_{\nu j'm_j}\{\chi^{S}_{\nu_0 j_0 m_{j_0},\nu j'm_j}(1) + C_{\nu}\chi^{B}_{\nu}(1)\}$$

$$\chi_{\nu}(R)Y_{j'm_j}(\theta_R,\phi_R) \tag{4.21}$$

The angle function for state $JMj\ell$ can be written

$$\mathcal{Y}^{JMj\ell}(\theta,\phi,\theta_R,\phi_R) = \sum_{m m_j} C(j\ell J, m_j m M)Y_{\ell m}(\theta,\phi)Y_{jm_j}(\theta_R,\phi_R) \tag{4.22}$$

So $P^{JMj\ell}$ can be written

$$P^{JMj\ell} = \sum_{mm_j} |C(j\ell J, m_j m M)|^2 \; |Y_{\ell m}(\theta,\phi) Y_{jm_j}(\theta_R,\phi_R)\rangle$$

$$\langle Y_{\ell m}(\theta,\phi) Y_{jm_j}(\theta_R,\phi_R)| \qquad (4.23)$$

In Appendix C the resulting function is shown to be:

$$\Psi^{JMj\ell}(N+1,\vec{R}) = \Psi^{M}(N) \sum_{\nu m_\ell m_j} C(j\ell J, m_j m_\ell M)^2$$

$$i^{\ell}\sqrt{4\pi(2\ell+1)}\; j_\ell(k_0 r)\delta_{m_j m_{j_0}}\delta_{m_\ell 0}\delta_{\nu\nu_0}\delta_{jj_0}$$

$$+ e^{ik_{\nu j}r} f_{\ell m_\ell,\nu_0 j_0 m_{j_0},\nu j m_j}(r) + \sum_i \delta_{i,(\ell-\ell_0)/2}$$

$$C_{\nu i} f_{\nu i}(r)\; I(jm_j \ell m_\ell m_0) \Big] Y_{\ell m_\ell}(\theta,\phi) Y_{jm_j}(\theta_R,\phi_R)$$

$$\alpha(1)\chi_\nu(R) \quad . \qquad (4.24)$$

$I(jm_j\ell m_\ell m_0)$ is an angular integral which can be written entirely in terms of the five given quantum numbers. The expression is given in Appendix C. The numbers ℓ_0 and m_0 are the angular quantum numbers for which $Y_{\ell_0 m_0}$ has the same symmetry as the bound part of the scattering function.

Before the scattering function can be evaluated, the bound state part of the function must be known. This will be evaluated in Chapter V.

[1] Herzenberg and Mandl, op.cit.

[2] A.S.Davydov,Quantum Mechanics,p.503,1968.

Chapter V. The Bound State Wave-Function.

The bound state function will describe the negative ion which is formed temporarily. This is the $N+1^{st}$ orbital of a one-determinant function:

$$\Psi^B(N+1,\vec{R}) = \mathcal{A}\chi_1(1)\chi_2(2)\ldots\chi_N(N)\chi^B_{N+1}(N+1,\vec{R}) \qquad (5.1)$$

Orbitals 1 through N are the orbitals from the unperturbed ground state Hartree-Fock function for the neutral molecule. Using the standard Hartree-Fock approach we would write the integral $\langle\Psi^B|\hat{H}|\Psi^B\rangle = E$ and then vary the function χ_{N+1} to obtain the minimum energy, with the constraint that χ_{N+1} remains normalized and orthogonal to the other orbitals.

In many cases this is not a good method. First, I am using an unpolarizable molecular function, frozen in its unperturbed form. Thus, the $N+1^{st}$ electron "sees" a much weaker potential than the actual one. Second, the actual potential is not strong enough to have a bound state in many molecules. H_2 and N_2, two of the molecules I am most interested in, do not have bound negative ion states. Thus, if χ^B_{N+1} is varied without restriction, it will approach the wave function of a free electron at zero energy.

One solution to this problem is to restrict the variation. The orbital is not allowed to approximate a free electron wave-function, and a bound state function results. The form of the function depends on the exact restriction on the variation. A similar method, also commonly used, is to vary the function only until the energy becomes relatively stable with respect to further variation, not to a rigorous minimum. This method is open to the same criticisms as the first.

Another method is to alter the interaction between the scattered electron and the molecule so that there is an actual bound state solution. The function may then be varied without restriction to get the function for this bound state. Increasing the apparent nuclear charge or decreasing the electronic repulsion will make the potential of the molecule more attractive, but either of these destroys the electrical neutrality of the molecule. Thus any finite change in either will add a 1/r coulombic tail to the molecular potential and create an infinite number of bound states. I can avoid this by increasing the nuclear and electronic parts of the interaction by the same amount. I have assumed that the scattered electron "sees" an attractive potential of the same order of magnitude as that necessary for the existence of a bound state. If this assumption is justified, multiplying the potential by a reasonably

sized number should produce an equation with a bound state solution. This is the function which I will use for χ^B_{N+1} . Part of this potential scaling amounts to a replacement for the polarization potential which I lost by freezing the core. The rest converts the resonant state, which has an energy above zero, to a bound state which can be obtained more easily.

First, I need the original Hartree-Fock equation for χ^B_{N+1} , with the unscaled potential. I must evaluate

$$E = \langle \Psi^B(N+1) | \hat{\mathcal{H}} | \Psi^B(N+1) \rangle \qquad (5.2)$$

This integral is the same as I^M_J , expressed in equation (2.46), with two changes. First, this integral involves $\hat{\mathcal{H}}$ instead of $\hat{\mathcal{H}}$-E so the last term in (2.46) is absent. Second, I need not consider the various angular momentum states designated by the J,M,j',j,ℓ',and ℓ superscripts.

Here the minors of the overlap matrix are much simpler since the bound state function is normalized and orthogonal to the other orbitals. The $N+1^{st}$ orbital is

$$\chi^B_{N+1}(1;\vec{R}) = \sum_\nu C_\nu \chi^B_{N+1,\nu}(1) \underline{\chi}_\nu(R) Y_{jm_j}(\Omega_R) \qquad (5.3)$$

where the C_ν are unknown constants, the $\chi^B_{N+1,\nu}$ are unknown electronic functions, and the $\underline{\chi}_\nu$ and Y_{jm_j} are known nuclear vibrational and rotational functions.

The normalization condition is

$$\sum_{\nu\nu'} C^*_\nu C_{\nu'} < \langle \chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu'}(1) \rangle_{elec} \chi_\nu(R)$$

$$Y^*_{jm_j}(\Omega_R)\chi_{\nu'}(R)Y_{jm_j}(\Omega_R)\rangle_{nuclear} \equiv 1 \qquad (5.4)$$

but the vibrational and rotational functions are orthonormal so this is equivalent to

$$\sum_{\nu} |C_\nu|^2 \langle \chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu}(1) \rangle_{elec} \equiv 1 \qquad (5.5)$$

I also require that

$$\langle \chi^D_{N+1,\nu}(1) | \chi^D_{N+1,\nu}(1) \rangle \equiv 1 \ , \qquad (5.6)$$

so that

$$\sum_{\nu} |C_\nu|^2 = 1 \qquad (5.7)$$

Define the pure electronic overlap integral, between the various electronic functions:

$$D^{\nu\nu'}_{N+1,N+1} \equiv \langle \chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu'}(1) \rangle \ . \qquad (5.8)$$

The overlap integral for the resonance function with itself is thus:

$$D_{N+1,N+1}(\vec{R}) = \sum_{\nu\nu'} C^*_{\nu} C_{\nu'} D^{\nu\nu'}_{N+1,N+1} \chi_{\nu}(R) Y^*_{jm_j}(\Omega_R)$$

$$\chi_{\nu'}(R) Y_{jm_j}(\Omega_R) \quad . \tag{5.9}$$

The other overlap integrals are

$$D_{uv}(\vec{R}) \equiv \delta_{uv} \quad \text{unless } u=v=N+1 \quad . \tag{5.10}$$

The determinant of overlap integrals is

$$\| D(\vec{R}) \| = D_{N+1,N+1}(\vec{R}) \quad . \tag{5.11}$$

Its minors are

$$\| D(\vec{R}) \|^{uv} = \delta_{uv} \times \begin{cases} 1 & u \neq N+1 \\ D_{N+1,N+1}(\vec{R}) & u=N+1 \end{cases} \tag{5.12}$$

and

$$\| D(\vec{R}) \|^{uv,pq} = \delta_{up}\delta_{vq} \times \begin{cases} 1 & u \neq N+1 \quad u>v, p>q \\ D_{N+1,N+1}(\vec{R}) & u=N+1 \quad u>v, p>q \end{cases} \tag{5.13}$$

I define the nuclear kinetic energy term,

$$D^{(2)}_{N+1,N+1}(\vec{R}) \equiv \sum_{\nu\nu'} C^*_\nu C_{\nu'} D^{\nu\nu'}_{N+1,N+1} \chi_\nu(R) Y^*_{jm_j}(\Omega_R)$$

$$\frac{-1}{2\mu_N R^2} \frac{d}{dR} R^2 \frac{d}{dR} \chi_{\nu'}(R) Y_{jm_j}(\Omega_R) \qquad (5.14)$$

the electronic kinetic energy and nuclear attraction term,

$$f_{N+1,N+1}(\vec{R}) \equiv \sum_{\nu\nu'} C^*_\nu C_{\nu'} f^{\nu\nu'}_{N+1,N+1}(R) \chi_\nu(R) Y^*_{jm_j}(\Omega_R)$$

$$\chi_{\nu'}(R) Y_{jm_j}(\Omega_R) \qquad (5.15)$$

and the coulombic and exchange term,

$$g_{N+1\ u,N+1\ u}(\vec{R}) \equiv \sum_{\nu\nu'} C^*_\nu C_{\nu'} g^{\nu\nu'}_{N+1\ u,N+1\ u}$$

$$\chi_\nu(R) Y^*_{jm_j}(\Omega_R) \chi_{\nu'}(R) Y_{jm_j}(\Omega_R) \qquad (5.16)$$

In these expressions, the one-electron integral is

$$f^{\nu\nu'}_{N+1,N+1}(R) \equiv \langle \chi^B_{N+1,\nu}(1) | \hat{f}(1,\vec{R}) | \chi^B_{N+1,\nu'}(1) \rangle$$

$$(5.17)$$

$$= \langle \chi^B_{N+1,\nu}(1) | -1/2\nabla^2 | \chi^B_{N+1,\nu'}(1) \rangle - \langle \chi^B_{N+1,\nu}(1) |$$

$$\frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} | \chi^{B}_{N+1,\nu'}(1) > \qquad (5.18)$$

$$= T_{\nu\nu'} - V_{\nu\nu'}(R) \qquad (5.19)$$

where $T_{\nu\nu'}$ is the kinetic energy and $V_{\nu\nu'}(R)$ is the nuclear attraction as a function of internuclear distance; and the coulombic and exchange integral is

$$g^{\nu\nu'}_{N+1\ u,N+1\ u} \equiv \langle \chi^{B}_{N+1,\nu}(1)\chi_u(2) | \frac{1}{r_{12}}(1-P_{12}) |$$

$$\chi^{B}_{N+1,\nu'}(1)\chi_u(2) \rangle \quad . \qquad (5.20)$$

The energy is now given by

$$E = \sum_{u=1}^{N} \int d\vec{R}\ f_{uu}\ D_{N+1,N+1}(\vec{R})$$

$$+ \sum_{u>v}^{N} \int d\vec{R}\ g_{uv,uv}\ D_{N+1,N+1}(\vec{R})$$

$$+ \int d\vec{R}\ D^{(2)}_{N+1,N+1}(\vec{R})$$

$$+ \int d\vec{R} \left[\frac{j(j+1)}{2\mu_N R^2} + V(R) \right] D_{N+1,N+1}(\vec{R})$$

$$+ \int d\vec{R}\ f_{N+1,N+1}(\vec{R})$$

$$+ \sum_{u=1}^{N} \int d\vec{R}\ g_{N+1\ u,N+1\ u}(\vec{R}) \qquad (5.21)$$

From the normalization condition, equation (5.5), and the definition of $D_{N+1,N+1}(\vec{R})$, equation (5.9):

$$\int d\vec{R}\, D_{N+1,N+1}(\vec{R}) = 1 \tag{5.22}$$

I can combine the third and fourth integrals as

$$I = \sum_{\nu\nu'} C_\nu^* C_{\nu'} D^{\nu\nu'}_{N+1,N+1} \int d\vec{R}\, \chi_\nu(R) Y^*_{jm_j}(\Omega_R) \left\{ \frac{j(j+1)}{2\mu_N R^2} + V(R) - \frac{1}{2\mu_N R^2} \frac{d}{dR} R^2 \frac{d}{dR} \right\} \chi_{\nu'}(R) Y_{jm_j}(\Omega_R) \tag{5.23}$$

Deleting the rotational energy term, as in Chapter II,

$$I = \sum_{\nu\nu'} C_\nu^* C_{\nu'} D^{\nu\nu'}_{N+1,N+1} \delta_{\nu\nu'} E_\nu$$

$$= \sum_\nu |C_\nu|^2 E_\nu \tag{5.24}$$

where E_ν is the energy of the ν^{th} vibrational state. Recall that the $\chi^B_{N+1,\nu}(1)$ are normalized, although not orthogonal: equation (5.6). The fifth term is

$$\int d\vec{R}\, f_{N+1,N+1}(\vec{R}) = \sum_{\nu\nu'} C_\nu^* C_{\nu'} \int d\vec{R}\, f^{\nu\nu'}_{N+1,N+1}(R)$$

$$\chi_\nu(R)Y^*_{jm_j}(\Omega_R)\chi_{\nu'}(R)Y_{jm_j}(\Omega_R)$$

$$= \sum_{\nu\nu'} C^*_\nu C_{\nu'} \int R^2 dR \chi_\nu(R) \left(T_{\nu\nu'} - V_{\nu\nu'}(R)\right) \chi_{\nu'}(R)$$

$$= \sum_\nu |C_\nu|^2 \; T_{\nu\nu} - \sum_{\nu\nu'} C^*_\nu C_{\nu'} \int R^2 dR \chi_\nu(R) V_{\nu\nu'}(R) \chi_{\nu'}(R) \tag{5.25}$$

The last integral is

$$\int d\vec{R}\; g_{N+1\;u,N+1\;u}(\vec{R}) = \sum_{\nu\nu'} C^*_\nu C_{\nu'}\, g^{\nu\nu'}_{N+1\;u,N+1\;u}$$

$$\int d\vec{R}\; \chi_\nu(R)Y^*_{jm_j}(\Omega_R)\chi_{\nu'}(R)Y_{jm_j}(\Omega_R)$$

$$= \sum_\nu |C_\nu|^2 g^{\nu\nu}_{N+1\;u,N+1\;u} \quad . \tag{5.26}$$

Equation (5.21) now becomes

$$E = \sum_{u=1}^{N} f_{uu} + \sum_{u>v}^{N} g_{uv,uv} + \sum_\nu |C_\nu|^2 E_\nu + \sum_\nu |C_\nu|^2$$

$$T_{\nu\nu} - \sum_{\nu\nu'} C^*_\nu C_{\nu'} \int R^2 dR \chi_\nu(R) V_{\nu\nu'}(R) \chi_{\nu'}(R)$$

$$+ \sum_{u=1}^{N} \sum_\nu |C_\nu|^2 g^{\nu\nu}_{N+1\;u,N+1\;u} \tag{5.27}$$

I can now make an arbitrary variation of χ^B_{N+1} . The resulting variation in energy will be

$$\delta E = \sum_{\nu} E_{\nu}\delta|C_{\nu}|^2 + \sum_{\nu} T_{\nu\nu}\ \delta|C_{\nu}|^2$$

$$+ \sum_{\nu} |C_{\nu}|^2 \delta\langle\chi^{B}_{N+1,\nu}(1)|\ -\tfrac{1}{2}\nabla^2|\chi^{B}_{N+1,\nu}(1)\rangle$$

$$- \sum_{\nu\nu'} \Big\{(\delta C^{*}_{\nu})C_{\nu'} \int R^2 dR\chi_{\nu}(R)V_{\nu\nu'}(R)\chi_{\nu'}(R)$$

$$+ C^{*}_{\nu}(\delta C_{\nu'}) \int R^2 dR\chi_{\nu}(R)V_{\nu\nu'}(R)\chi_{\nu'}(R)$$

$$+ C^{*}_{\nu}C_{\nu'} \int R^2 dR\chi_{\nu}(R)\ \delta\langle\chi^{B}_{N+1,\nu}(1)|\frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)}$$

$$|\chi^{B}_{N+1,\nu'}(1)\rangle\chi_{\nu'}(R)\Big\}$$

$$+ \sum_{u=1}^{N} \sum_{\nu} \delta|C_{\nu}|^2 g^{\nu\nu}_{N+1\ u,N+1\ u}$$

$$+ \sum_{u=1}^{N} \sum_{\nu} |C_{\nu}|^2\ \delta\langle\chi^{B}_{N+1,\nu}(1)\chi_{u}(2)|\frac{1}{r_{12}}(1-P_{12})$$

$$|\chi^{B}_{N+1,\nu}(1)\chi_{u}(2)\rangle \qquad (5.28)$$

This can be written as

$$\delta E = \sum_{\nu} (\delta C^{*}_{\nu})C_{\nu} \Big(E_{\nu} + T_{\nu\nu} + \sum_{u=1}^{N} g^{\nu\nu}_{N+1\ u,N+1\ u}\Big)$$

$$+ \sum_{\nu} |C_{\nu}|^2 \Big\{\langle\delta\chi^{B}_{N+1,\nu}(1)|-\tfrac{1}{2}\nabla^2|\chi^{B}_{N+1,\nu}(1)\rangle$$

$$+ \sum_{u=1}^{N} \langle\delta\chi^{B}_{N+1,\nu}(1)\chi_{u}(2)|\frac{1}{r_{12}}(1-P_{12})|\chi^{B}_{N+1,\nu}(1)$$

$$\chi_u(2)>\Big]$$

$$- \sum_{\nu\nu'} \Big[(\delta C_\nu^*) C_{\nu'} \int R^2 dR \chi_\nu(R) V_{\nu\nu'}(R) \chi_{\nu'}(R)$$

$$+ C_\nu^* C_{\nu'} \int R^2 dR \chi_\nu(R) < \delta\chi^B_{N+1,\nu}(1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)}$$

$$| \chi^B_{N+1,\nu}(1) > \chi_{\nu'}(R) \Big]$$

$$+ \text{Complex conjugate} \qquad (5.29)$$

The variation must be constrained so that χ^B_{N+1} remains normalized. This can be done by using Lagrange multipliers. The variation of the normalization condition is

$$\sum_\nu' \Big[(\delta C_\nu^*) C_\nu < \chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu}(1) >$$

$$+ |C_\nu|^2 < \delta\chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu}(1) > \Big]$$

$$+ \text{Complex conjugate} = 0 \qquad (5.30)$$

There is an additional normalization restriction:

$$< \chi^B_{N+1,\nu}(1) | \chi^B_{N+1,\nu}(1) > = 1 \qquad (5.6)$$

This gives the conditions

$$\langle \delta\chi^{B}_{N+1,\nu}(1) | \chi^{B}_{N+1,\nu}(1) \rangle + \text{Complex conjugate} = 0$$

for all ν. (5.31)

Substituting (5.6) and (5.31) into (5.30), I find

$$\sum_{\nu} (\delta C^{*}_{\nu} C_{\nu} + C^{*}_{\nu} \delta C_{\nu}) = 0 \qquad (5.32)$$

I can combine (5.29),(5.32), and (5.31) using Lagrange multipliers:

$$\sum_{\nu} \delta C^{*}_{\nu} C_{\nu} \Big(E_{\nu} + T_{\nu\nu} + \sum_{u=1}^{N} g^{\nu\nu}_{N+1\ u,N+1\ u} \Big)$$

$$+ \sum_{\nu} |C_{\nu}|^{2} \Big[\langle \delta\chi^{B}_{N+1,\nu}(1) | -\tfrac{1}{2}\nabla^{2} | \chi^{B}_{N+1,\nu}(1) \rangle + \sum_{u=1}^{N} \langle \delta\chi^{B}_{N+1,\nu}(1)\chi_{u}(2) | \frac{1}{r_{12}}(1-P_{12}) | \chi^{B}_{N+1,\nu}(1)\chi_{u}(2) \rangle \Big]$$

$$- \sum_{\nu\nu'} \Big[\delta C^{*}_{\nu} C_{\nu'} \int R^{2} dR \underline{\chi}_{\nu}(R) V_{\nu\nu'}(R) \underline{\chi}_{\nu'}(R)$$

$$+ C^{*}_{\nu} C_{\nu'} \int R^{2} dR \underline{\chi}_{\nu}(R) \langle \delta\chi^{B}_{N+1,\nu}(1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} | \chi^{B}_{N+1,\nu}(1) \rangle \underline{\chi}_{\nu'}(R) \Big]$$

$$+ \lambda_{C} \sum_{\nu} \delta C^{*}_{\nu} C_{\nu}$$

$$+ \sum_{\nu} \lambda_{\nu} \langle \delta\chi^{B}_{N+1,\nu}(1) | \chi^{B}_{N+1,\nu}(1) \rangle$$

$$+ \text{Complex conjugate} = 0 \qquad (5.33)$$

For my present purposes I will seek only a rough approximation to the solution for the above equation. I can expand χ^{B} as

$$\chi^{B}_{N+1,\nu}(1) = \sum_{i=0}^{\infty} f_{\nu i}(r) Y_{\ell_0+2i,m_0}(\Omega)\alpha(1) \qquad (5.34)$$

An arbitrary function, $f(r,\theta,\phi)$, with the same angular symmetry as the spherical harmonic $Y_{\ell_0 m_0}(\theta,\phi)$, can be expanded as

$$f(r,\theta,\phi) = \sum_{i=0}^{\infty} f_i(r) Y_{\ell_0+2i,m_0}(\theta,\phi) \; . \qquad (5.35)$$

Since I am concerned with the effect of the bound state function on low energy scattering, I will use only the first two terms of this sequence:

$$\chi^{B}_{N+1,\nu}(1) = (f_{\nu 0}(r) Y_{\ell_0 m_0}(\Omega) + f_{\nu 1}(r) Y_{\ell_0+2,m_0}(\Omega))\alpha(1) \qquad (5.36)$$

I shall also assume that the correlation between the electronic and nuclear motion is primarily angular

and not radial. Qualitatively, the effect of the Y_{ℓ_0+2,m_0} term is to shift the electron density toward the molecular axis and away from the plane perpendicular to the axis, or vice versa. The assumption I am making is that the difference in the electronic functions for different vibrational states can be fairly well approximated by this shift along the axis. Thus, the radial functions are the same for all ν, only the relative importance of the two terms changes. This has the consequence that

$$\chi^B_{N+1,\nu} = (f_0(r)C_{\nu 0}Y_{\ell_0 m_0}(\Omega) + f_1(r)C_{\nu 1}Y_{\ell_0+2,m_0}(\Omega))\alpha(1) \tag{5.37}$$

where $f_0(r)$ and $f_1(r)$ are normalized functions. Then,

$$\chi^B_{N+1}(1;\vec{R}) = \sum_\nu C_\nu(C_{\nu 0}f_0(r)Y_{\ell_0 m_0}(\Omega) + C_{\nu 1}f_1(r) Y_{\ell_0+2,m_0}(\Omega))\alpha(1)\ \chi_\nu(R)Y_{jm_j}(\Omega_R) \tag{5.38}$$

The overall trend for the C_ν should be a decrease as ν increases. I will choose a set of C_ν to approximate this trend rather than attempt a direct solution of equation (5.33). For a given diatomic molecule, with a given observed resonant energy, there is a limit to

the vibrational states energetically accessible. I will designate the first state not energetically available by ν_m. I choose the C_ν to be

$$C_\nu = C(\nu-\nu_m) \ . \tag{5.39}$$

Since $$\sum_\nu C_\nu^2 = 1 \ , \tag{5.7}$$

$$C = \left[\sum_{\nu=0}^{\nu_m} (\nu-\nu_m)^2 \right]^{-1/2} \tag{5.40}$$

I have chosen the proportionality in (5.39) to be an approximate fit to the trend observed by Schulz for vibrational excitation of N_2.[1] The angular correlation described by $C_{\nu 0}$ and $C_{\nu 1}$ is probably a small effect relative to the approximation made for the C_ν. Therefore I will let

$$C_{\nu 0} = C_0 \quad \text{and} \quad C_{\nu 1} = C_1 \quad \text{for all } \nu. \tag{5.41}$$

Let $$\chi^B_{N+1}(1) = \left(C_0 f_0(r) Y_{\ell_0 m_0}(\Omega) + C_1 f_1(r) Y_{\ell_0+2, m_0}(\Omega)\right) \alpha(1) \tag{5.42}$$

The constants C_0 and C_1 and the functions f_0 and f_1 will be calculated at equilibrium internuclear distance. The effect of Born-Oppenheimer breakdown is now included

entirely in the coëfficients C_ν. The $N+1^{st}$ orbital is now

$$\chi^B_{N+1}(1;\vec{R}) = \left[C_0 f_0(r) Y_{\ell_0 m_0}(\Omega) + C_1 f_1(r) Y_{\ell_0+2, m_0}(\Omega)\right]$$

$$\alpha(1) \sum_\nu C(\nu-\nu_m)\chi_\nu(R) Y_{jm_j}(\Omega_R) \qquad (5.43)$$

Equation (5.33) can now be greatly simplified: The terms involving variation of the C_ν are zero since the C_ν are now fixed. Since the nuclear attraction is evaluated at $R=R_0$ it no longer couples vibrational states and the $C_\nu C^*_\nu$, factor in this term is replaced by $|C_\nu|^2$. Since the $\chi^B_{N+1,\nu}$ are all replaced by χ^B_{N+1}, we can factor out and delete the term $\sum_\nu |C_\nu|^2$. Equation (5.33) is now reduced to

$$\langle \delta\chi^B_{N+1}(1)| \left[-\tfrac{1}{2}\nabla^2 + \lambda + \left[-\frac{Z}{r_{1\alpha}(R_0)} - \frac{Z}{r_{1\beta}(R_0)} + \sum_{u=1}^{N} \langle \chi_u(2)|\frac{1}{r_{12}}(1-P_{12})|\chi_u(2)\rangle_2 \right] \right] |\chi^B_{N+1}(1)\rangle$$

$$+ \text{Complex conjugate} = 0 \qquad (5.44)$$

Let $$\hat{V}(1) = -\frac{Z}{r_{1\alpha}} - \frac{Z}{r_{1\beta}} + \sum_{u=1}^{N} \langle \chi_u(2)|\frac{1}{r_{12}}(1-P_{12})$$

$$|\chi_u(2)\rangle_2 \qquad (5.45)$$

Fortunately, $\hat{V}(1)$ is a Hermitian operator and equation (5.44) can be replaced by

$$(-\tfrac{1}{2}\nabla_1^2 + \lambda + \hat{V}(1))\chi^B_{N+1}(1) = 0 \qquad (5.46)$$

As I mentioned at the beginning of the chapter, in many cases equation (5.46) does not have a bound state solution. I will write instead

$$(-\tfrac{1}{2}\nabla_1^2 + \lambda + \gamma\hat{V}(1))\chi^B_{N+1}(1) = 0 \qquad (5.47)$$

For some minimum value of γ, this equation will have a bound state solution at zero energy.

I have calculated an approximate H_2 function and an approximate H_2^- function using single center orbitals with non-integral principle quantum number.[2] The programs used to optimize the functions will be described in Appendix D.

The H_2 function which I used was

$$\Psi(1,2) = \mathcal{A}\phi_1(1)\alpha(1)\phi_1(2)\beta(2) \qquad (5.48)$$

Using one single-center orbital, I obtained the lowest energy for

$$\phi_1(1) = 2.8684\ r^{.23}\ e^{-1.22\ r}\ Y_{00}(\theta,\phi) \qquad (5.49)$$

at R=1.25 (all quantities in atomic units.)
Using the H_2^- function

$$\Psi(1,2,3) = \mathcal{A}\,\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\phi_2(3)\alpha(3) \qquad (5.50)$$

I obtained a bound state function

$$\phi_2(1) = (\ .3803\ r^{.682}\ e^{-.607\ r} + 5.2957\ r^{1.852}$$

$$e^{-2.752\ r}\ )\ Y_{10}(\theta,\phi) \qquad (5.51)$$

When γ is set at 1.824, this function gives the lowest energy, -.0000554 Hartree, or -.00151 ev. The actual energy is .289 Hartree, or 7.85 ev. I can interpret this relationship as follows: The expectation value of the orbital energy is

$$E = \langle\phi_2|\hat{T} + \hat{V}|\phi_2\rangle = 7.85\ \text{e.v.} \qquad (5.52)$$

When I increase γ, I increase the (negative) expectation value of the potential energy. If the virial theorem holds for relative changes in potential and kinetic energy, then increasing $\hat{V}$ by the factor γ will produce an adjustment in the orbital leading to an increase in kinetic energy which will cancel half of the potential energy change. That is the potential energy is

increased by

$$V_\gamma = (\gamma-1) \langle \phi_2 | \hat{V} | \phi_2 \rangle = (\gamma-1)\, V \tag{5.53}$$

and the kinetic energy increases by

$$T_\gamma = -\frac{1}{2} V_\gamma = \frac{1-\gamma}{2} \langle \phi_2 | \hat{V} | \phi_2 \rangle \tag{5.54}$$

so that the change in total energy is

$$T_\gamma + V_\gamma = \left(\frac{1}{2} - \frac{\gamma}{2} - 1 + \gamma \right) V = \frac{\gamma-1}{2} V \tag{5.55}$$

but this change in energy is the energy of the original resonance, since I am changing the energy to zero, and I can now infer that the energy of the resonance is approximately

$$E_r \simeq \frac{1-\gamma}{2} V \tag{5.56}$$

I know that

$$\langle \phi_2 | \hat{T} + \gamma \hat{V} | \phi_2 \rangle = 0. \tag{5.57}$$

Subtracting (5.52) from (5.57)

$$(\gamma-1)\hat{V} = \langle\phi_2|(\gamma-1)\hat{V}|\phi_2\rangle = -7.85 \text{ e.v.} \qquad (5.58)$$

and $E_r \tilde{=} 3.9$ e.v. Within experimental error, this is a perfectly reasonable energy.[3]

[1] Schulz,G.J.,Phys Rev,125,229,(1962).

[2] Joy,H.W. and Parr,Robert G.,J Chem Phys,28,448,(1958).

[3] Schulz,G.J.,Phys Rev,135,A988,(1964).

Chapter VI. The Scattering Amplitudes and Phase Shifts

The radial scattering function corresponding to a given partial wave, final state, and initial state has been designated $f^{\beta}(r)$, where β refers to all the appropriate quantum numbers. Comparing equations (1.9), (1.10), (1.11), and (5.42) with (4.52), I find that the form of this function is

$$f^{\beta}(r) = f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j, \ell m_\ell}(r) = C(j\ell J, M0)\; i^{\ell}\sqrt{4\pi(2\ell+1)}$$

$$j_\ell(k_0 r)\delta_{M m_{j_0}}\delta_{\nu\nu_0}\delta_{jj_0} + C(j\ell J, m_j m_\ell M)$$

$$e^{ik_{\nu j}r}\, f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j m_j}(r) + C(j\ell J, m_j m_\ell M)$$

$$\sum_{i=0}^{1} \delta_{i,(\ell-\ell_0)/2}\; C_i f_i(r) C(\nu-\nu_m) I(j m_j \ell m_\ell m_0)$$

(6.1)

Note that $E_\nu - E_{\nu_0} - 1/2k_0^2 = -1/2k_\nu^2$ (ignoring, as before, the rotational energy term). From Chapter III, these functions must satisfy

$$\sum_{\nu j \ell m_j m_\ell} \left\{ \left[-\frac{1}{2}\frac{d}{dr_1} r_1^2 \frac{d}{dr_1} + \frac{\ell(\ell+1)}{2} - \frac{1}{2}k_\nu^2 r_1^2 \right] \delta_{jj'}\delta_{\nu\nu'} \right.$$

$$\delta_{\ell\ell'}\delta_{m_j m_j'}\delta_{m_\ell m_\ell'}$$

$$+ \sum_{mm'} I_{\Omega}^{JM} \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \Bigg[\int R^2 \chi_{\nu'}^{*}(R) \chi_{\nu}(R)$$

$$\Bigg\{ \langle Y_{\ell' m'}(\Omega_1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} | Y_{\ell m}(\Omega_1) \rangle$$

$$- \sum_{u=1}^{N} \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_u \rangle \langle \chi_u | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} |$$

$$Y_{\ell m}(\Omega_1)\alpha(1) \rangle \Bigg\} dR$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \Bigg\{ \langle Y_{\ell' m'}(\Omega_1)\alpha(1)\chi_u(2) | \frac{1}{r_{12}}(1-P_{12})$$

$$| Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2) \rangle$$

$$- \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_u \rangle \langle \chi_u | Y_{\ell m}(\Omega_1)\alpha(1) \rangle (E_\nu - E)$$

$$- \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \hat{f}(1) | \chi_u \rangle \langle \chi_u | Y_{\ell m}(\Omega_1)\alpha(1) \rangle$$

$$- \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_u \rangle \langle \chi_u | -\frac{1}{2r_1^2} \frac{d}{dr_1} r_1^2 \frac{d}{dr_1}$$

$$+ \frac{\ell(\ell+1)}{2r_1^2} | Y_{\ell m}(\Omega_1)\alpha(1) \rangle$$

$$+ \sum_{v \neq u}^{N} \Bigg\{ \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_u \rangle \langle \chi_v | Y_{\ell m}(\Omega_1)\alpha(1) \rangle f_{uv}$$

$$- \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_u \rangle \langle \chi_u | Y_{\ell m}(\Omega_1)\alpha(1) \rangle f_{vv}$$

$$+ \langle Y_{\ell' m'}(\Omega_1)\alpha(1) | \chi_v \rangle \langle \chi_u(1)\chi_v(2) | \frac{1}{r_{12}}(1-P_{12})$$

$$|Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2)\rangle$$

$$+ \langle Y_{\ell' m'}(\Omega_1)\alpha(1)\chi_u(2)|\frac{1}{r_{12}}(1-P_{12})|\chi_u(1)\chi_v(2)\rangle$$

$$\langle\chi_v|Y_{\ell m}(\Omega_1)\alpha(1)\rangle$$

$$+ \sum_{p\neq v,u}^{N} \langle Y_{\ell' m'}(\Omega_1)\alpha(1)|\chi_v\rangle\langle\chi_p|Y_{\ell m}(\Omega_1)\alpha(1)\rangle g_{uv,up}$$

$$- \sum_{\substack{p<u \\ \neq v}}^{N} \langle Y_{\ell' m'}(\Omega_1)\alpha(1)|\chi_v\rangle\langle\chi_v|Y_{\ell m}(\Omega_1)\alpha(1)\rangle\ g_{up,up} \Big)\Big)\Big)\ |f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j,\ell m_\ell}(r)\rangle = 0$$

for all $j',\ell',\nu',m_j',m_\ell'$. (6.2)

I will assume that the resonant scattering ($\ell=\ell_0$, $\ell_0+2,\ell_0+4,\ldots$ $m=m_0$) is very large compared to the non-resonant and ignore the non-resonant terms as a first approximation. The resonant function is approximately described in the vicinity of the molecule by the bound state orbital, χ^B, which is orthogonal to the molecular orbitals. Therefor I will make the further approximation that the resonant scattering functions are orthogonal to the molecular functions. (In the cases of H_2 and N_2 this is rigorously true due to symmetry.) Equation (6.2) is now approximated by

$$\sum_{j\nu\ell m_j m_\ell} \left\{ \left[-\frac{1}{2}\frac{d}{dr_1} r_1^2 \frac{d}{dr_1} + \frac{\ell(\ell+1)}{2} - 1/2\, k_\nu^2 r_1^2 \right] \right.$$

$$\delta_{jj'}\delta_{\ell\ell'}\delta_{\nu\nu'}\delta_{m_j m_j'}\delta_{m_\ell m_\ell'}$$

$$+ \sum_{mm'} I_\Omega^{JM} \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \left(\int R^2 \chi_{\nu'}^*(R)\chi_\nu(R) \right.$$

$$\langle Y_{\ell' m'}(\Omega_1) | \frac{Z}{r_{1\alpha}(R)} + \frac{Z}{r_{1\beta}(R)} | Y_{\ell m}(\Omega_1) \rangle_{\Omega_1} dR$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \langle Y_{\ell' m'}(\Omega_1)\alpha(1)\chi_u(2) | \frac{1}{r_{12}}(1-P_{12})$$

$$\left. \left. |Y_{\ell m}(\Omega_1)\alpha(1)\chi_u(2)\rangle \right] \right) \left| f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j, \ell m_\ell}(r) \right\rangle = 0$$

for all j', ν', and m_j' and for $\ell' = \ell_0, \ell_0+2, \ldots m_\ell' = m_0$

(6.3)

Note that the mixing of vibrational states occurs entirely in the nuclear attraction term.

I can use the usual expression for $\frac{1}{r_{12}}$ in the last integral:

$$\frac{1}{r_{12}} = \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1) Y_{nm_n}^*(\Omega_2)$$

(6.4)

Similar derivations yield expressions for $1/r_{1\alpha}$ and $1/r_{1\beta}$. These expressions are simpler because the coördinate system is fixed to the molecular axis.

$$1/r_{1\alpha} = \sum_{n=0}^{\infty} \left(\frac{4\pi}{2n+1}\right)^{1/2} \frac{R_<^n}{R_>^{n+1}} Y_{n0}(\Omega_1) \qquad (6.5)$$

and

$$1/r_{1\beta} = \sum_{n=0}^{\infty} \left(\frac{4\pi}{2n+1}\right)^{1/2} (-1)^n \frac{R_<^n}{R_>^{n+1}} Y_{n0}(\Omega_1) \qquad (6.6)$$

where $R_<$ and $R_>$ are the lesser and greater of r_1 and $R/2$, respectively. Multiplying by Z and adding (6.6) to (6.5);

$$\frac{Z}{r_{1\alpha}} + \frac{Z}{r_{1\beta}} = 2Z \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \left(\frac{4\pi}{2n+1}\right)^{1/2} \frac{R_<^n}{R_>^{n+1}} Y_{n0}(\Omega_1) \qquad (6.7)$$

Substituting these expressions into equation (6.3), I obtain

$$\sum_{j\nu\ell m_j m_\ell} \left\{ \left(-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{2} - \frac{1}{2}k_\nu^2 r^2\right) \right.$$

$$\delta_{jj'}\delta_{\nu\nu'}\delta_{\ell\ell'}\delta_{m_j m_j'}\delta_{m_\ell m_\ell'}$$

$$\left. + \sum_{mm'} I_\Omega^{JM} \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \right\} \left\{ 2Z \sum_{\substack{n=0 \\ \text{even}}}^{\infty}

$$\left(\frac{4}{n+1}\right)^{1/2} \int R^2 \chi^*_{\nu'}(R)\chi_\nu(R)\frac{R_<^n}{R_>^{n+1}}\langle Y_{\ell'm'}(\Omega_1)|Y_{n0}(\Omega_1)$$

$$Y_{\ell m}(\Omega_1)\rangle_{\Omega_1} dR$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1}\langle Y_{\ell'm'}(\Omega_1)\alpha(1)\chi_u(2)|$$

$$\frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1)Y^*_{nm_n}(\Omega_2)(1-P_{12})|Y_{\ell m}(\Omega_1)\alpha(1)$$

$$\chi_u(2)\rangle \Big] \Big] \; |f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j,\ell m_\ell}(r)\rangle = 0$$

(6.8)

The angle integral in the nuclear attraction terms can now be evaluated,

$$\langle Y_{\ell'm'}(\Omega_1)|Y_{n0}(\Omega_1)Y_{\ell m}(\Omega_1)\rangle = \left(\frac{(2n+1)(2\ell+1)}{4\pi(2\ell'+1)}\right)^{1/2}$$

$$C(n\ell\ell',0mm')\; C(n\ell\ell',000) \qquad (6.9)$$

Substituting this expression into equation (6.8), and separating the integral into two parts for $2r<R$ and $2r>R$ gives me the following expression

$$\sum_{j\nu\ell m_j m_\ell} \Bigg[\left(-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{2} - \frac{1}{2}k_\nu^2 r^2\right)$$

$$\delta_{jj'}\delta_{\nu\nu'}\delta_{\ell\ell'}\delta_{m_j m_j'}\delta_{m_\ell m_\ell'}$$

$$+ \sum_{mm'} I_\Omega^{JM} \begin{pmatrix} j & \ell & m_j & m_\ell & m \\ j' & \ell' & m_j' & m_\ell' & m' \end{pmatrix} \left\{ 2Z \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \delta_{mm'} \right.$$

$$C(n\ell\ell',0m)C(n\ell\ell',00) \left[\int_0^{2r_1} \frac{R^{n+2}}{2^n r_1^{n+1}} \chi_\nu^*,(R)\chi_\nu(R)dR \right.$$

$$\left. + \int_{2r_1}^{\infty} \frac{2^{n+1} r_1^n}{R^{n-1}} \chi_\nu^*,(R)\chi_\nu(R)dR \right]$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{\ell'm'}(\Omega_1)\alpha(1)\chi_u(2)|$$

$$\frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1)Y_{nm_n}^*(\Omega_2)(1-P_{12})|Y_{\ell m}(\Omega_1)\alpha(1)$$

$$\left. \chi_u(2)\rangle \right\} \Big\} \; |f^{JM,\nu_0 j_0 m_{j_0}}_{\nu j m_j,\ell m_\ell}(r)\rangle = 0$$

(6.10)

Since I am interested in the vibrational excitation only and not the rotational , I shall set $f^\beta(r)=0$ for $j\neq j_0$ and $m_j\neq m_{j_0}$ and replace $k_{\nu j}$ with k_ν.

For convenience, I shall define the following operator

$$\hat{\mathcal{H}}_{\nu\ell m_\ell,\nu'\ell' m_\ell'}(r_1) \equiv \left\{ \left[-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{2} \right.\right.$$

$$\left.\left. - \frac{1}{2}k_\nu^2 r^2 \right] \delta_{\nu\nu'}\delta_{\ell\ell'}\delta_{m_\ell m_\ell'} \right.$$

$$+ \sum_{mm'} I_{\Omega}^{JM} \begin{pmatrix} j_0 & \ell & m_{j_0} & m_\ell & m \\ j' & \ell' & m_{j'} & m_{\ell'} & m' \end{pmatrix} \left\{ 2Z \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \delta_{mm'} \right.$$

$$C(n\ell\ell', 0m) C(n\ell\ell', 00) \left[\int_0^{2r_1} \frac{R^{n+2}}{2^n r_1^{n+1}} \chi_{\nu'}^*(R) \right.$$

$$\left. \left. \chi_\nu(R) dR + \int_{2r_1}^{\infty} \frac{2^{n+1} r_1^n}{R^{n-1}} \chi_{\nu'}^*(R) \chi_\nu(R) dR \right] \right.$$

$$+ \sum_{u=1}^{N} \delta_{\nu\nu'} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{\ell' m'}(\Omega_1) \alpha(1) \chi_u(2) |$$

$$\frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1) Y_{nm_n}^*(\Omega_2) (1 - P_{12}) | Y_{\ell m}(\Omega_1) \alpha(1)$$

$$\left. \chi_u(2) \rangle \right] \left. \right\} \qquad (6.11)$$

I can now write equation (6.10) in the form

$$\sum_{\nu \ell m_\ell} \hat{\mathcal{H}}_{\nu\ell m_\ell, \nu'\ell' m_{\ell'}}(r) | C(j_0 \ell J, m_{j_0} m_\ell M) e^{ik_\nu r}$$

$$f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j_0 m_{j_0}}(r) + C(j_0 \ell J, M0M) i^\ell$$

$$\sqrt{4\pi(2\ell+1)}\, j_\ell(k_\nu r) \delta_{M m_{j_0}} \delta_{\nu\nu_0} + C(j_0 \ell J, m_{j_0} m_\ell M)$$

$$\sum_{i=0}^{l} \delta_{i,(\ell-\ell_0)/2} C_i f_i(r) C(\nu - \nu_m) I(j_0 m_{j_0} \ell m_\ell m_0) \rangle$$

$$= 0 \qquad (6.12)$$

To obtain the scattering amplitude and phase shift,

I will consider the scattering to be a perturbation. First, I will construct a zero order wave function, ψ^0, consisting of the incoming wave and the bound state function, and a zeroth order Hamiltonian, $\hat{\mathcal{H}}^0$, of which ψ^0 is an eigenfunction. Then, I will consider the difference between $\hat{\mathcal{H}}$, defined in equation (6.11), and $\hat{\mathcal{H}}^0$ to be a perturbation, write the resulting equation for the first order wave function, and solve it by means of a Green's function. This proceedure will not, however, produce the correct inelastic scattering since the Green's function will not produce an outgoing wave at the correct energy. To resolve this difficulty, I will include an arbitrarily small, well behaved, term, $\varepsilon C(j_0 \ell J, m_{j_0} m_\ell M)\ e^{ik_\nu r}/(1+k_\nu r)$, $\varepsilon>0$, representing an outgoing wave at the correct energy.

Since the bound state function falls off exponentially at large r, the Green's function at infinity will have the correct form in the limit as $\varepsilon \to 0$, and the first order inelastic scattering will be correct.

The complete zeroth order wave function is

$$\psi^0_{\nu \ell m_\ell}(r) = C(j_0 \ell J, M0M)\ i^\ell \sqrt{4\pi(2\ell+1)}\ j_\ell(k_\nu r)\delta_{Mm_{j_0}}$$

$$\delta_{\nu\nu_0}$$

$$+ C(j_0 \ell J, m_{j_0} m_\ell M) \sum_{i=0}^{l} \delta_{i,(\ell-\ell_0)/2} C_i f_i(r)$$

$$C(\nu-\nu_m) I(j_0 m_{j_0} \ell m_\ell m_0)$$

$$+ \varepsilon C(j_0 \ell J, m_{j_0} m_\ell M) \frac{e^{ik_\nu r}}{k_\nu r + 1} \qquad (6.13)$$

Equation (6.12) now becomes

$$\sum_{\nu \ell m_\ell} \hat{\mathcal{H}}_{\nu \ell m_\ell, \nu' \ell' m_\ell'}(r) \, |C(j_0 \ell J, m_{j_0} m_\ell M) e^{ik_\nu r}$$

$$(f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j_0 m_{j_0}}(r) - \frac{\varepsilon}{k_\nu r + 1}) + \psi^0_{\nu \ell m_\ell}(r)>$$

$$= 0 \qquad (6.14)$$

The zeroth-order Hamiltonian is

$$\hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r) \equiv -\frac{1}{2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{r^2}{2} \frac{\psi^0_{\nu \ell m_\ell}''(r)}{\psi^0_{\nu \ell m_\ell}(r)} + r \frac{\psi^0_{\nu \ell m_\ell}'(r)}{\psi^0_{\nu \ell m_\ell}(r)}$$

(6.15)

so that

$$\hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r) \psi^0_{\nu \ell m_\ell}(r) = 0 \quad . \qquad (6.16)$$

Let

$$\hat{\mathcal{H}}'_{\nu \ell m_\ell, \nu' \ell' m_\ell'}(r) = \hat{\mathcal{H}}_{\nu \ell m_\ell, \nu' \ell' m_\ell'}(r) - \hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r)$$

(6.17)

be assumed to be a perturbation. Then

$$\sum_{\nu \ell m_\ell} \left\{ \hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r) + \lambda \hat{\mathcal{H}}'_{\nu \ell m_\ell, \nu' \ell' m_\ell'}(r) \right\} \left| \psi^0_{\nu \ell m_\ell}(r) \right.$$

$$\left. + \lambda \psi^1_{\nu \ell m_\ell}(r) + \lambda^2 \psi^2_{\nu \ell m_\ell}(r) + \ldots \right\rangle = 0$$

giving (6.18)

$$\sum_{\nu \ell m_\ell} \hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r) \psi^0_{\nu \ell m_\ell}(r) = 0 \quad , \tag{6.19}$$

$$\sum_{\nu \ell m_\ell} \hat{\mathcal{H}}^0_{\nu \ell m_\ell}(r) \psi^1_{\nu \ell m_\ell}(r) = - \sum_{\nu \ell m_\ell} \hat{\mathcal{H}}'_{\nu \ell m_\ell, \nu' \ell' m_\ell'}(r)$$

$$\psi^0_{\nu \ell m_\ell}(r) \quad , \tag{6.20}$$

and so forth.

The outgoing wave in the scattering function can be represented as

$$C(j_0 \ell J, m_{j_0} m_\ell M)\ e^{ik_\nu r}\ f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j_0 m_{j_0}}(r)$$

$$= \lambda \psi^1_{\nu \ell m_\ell}(r) + \lambda^2 \psi^2_{\nu \ell m_\ell}(r) + \ldots \tag{6.21}$$

The term $\varepsilon \frac{e^{ik_\nu r}}{k_\nu r + 1}$ is not included since I am considering ε to be arbitrarily small, although not zero.

To obtain an approximate expression for the first-order scattering, I will separate the set of coupled equations represented by equation (6.20). I am assuming

$$\hat{\mathcal{H}}^0_{\nu\ell m_\ell}(r)\psi^1_{\nu\ell m_\ell}(r) \cong \hat{\mathcal{H}}'_{\nu\ell m_\ell,\nu'\ell' m_\ell'}(r)\psi^0_{\nu\ell m_\ell}(r)$$

$$\text{for all } \nu\ell m_\ell, \nu'\ell' m_\ell' \quad . \tag{6.22}$$

Let the potential energy term in the zeroth order Hamiltonian be represented by

$$V_{\nu\ell m_\ell}(r) = \left\{ \frac{r^2}{2} \frac{\psi^{0\,''}_{\nu\ell m_\ell}(r)}{\psi^0_{\nu\ell m_\ell}(r)} + r\frac{\psi^{0\,'}_{\nu\ell m_\ell}(r)}{\psi^0_{\nu\ell m_\ell}(r)} \right\} \tag{6.23}$$

then

$$\hat{\mathcal{H}}^0_{\nu\ell m_\ell}(r) = -\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + V_{\nu\ell m_\ell}(r) \quad . \tag{6.24}$$

The Green's function for $\hat{\mathcal{H}}^0_{\nu\ell m_\ell}$ will satisfy

$$-\left[-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} + V_{\nu\ell m_\ell}(r)\right]G(r|r') = \delta(r-r') \quad . \tag{6.25}$$

The solution to equation (6.22) can be written in terms of the Green's function:

$$\psi^1_{\nu\ell m_\ell}(r) = -\int_0^\infty G(r|r')\hat{\mathcal{H}}'_{\nu\ell m_\ell,\nu'\ell' m_\ell'}(r')\psi^0_{\nu\ell m_\ell}(r')dr' \tag{6.26}$$

I need an expression for $G(r|r')$ so that I can perform the necessary integration. From (6.25),

$$G(r|r') = \left(\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr} - V_{\nu\ell m_\ell}(r) \right)^{-1} \delta(r-r') \tag{6.27}$$

I can represent the Dirac delta function by the following integral

$$\delta(\vec{r}-\vec{r}') = \frac{1}{(2\pi)^3} \int e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}\, d\vec{k} \quad . \tag{6.28}$$

Integrating both sides of the equation over angles relative to $\vec{r}-\vec{r}'$,

$$4\pi\delta(r-r') = \frac{r^2}{4\pi^2 i|r-r'|} \int \frac{e^{ik|r-r'|}\, d\vec{k}}{k} \quad . \tag{6.29}$$

Integrating over angles relative to $\vec{k}$,

$$\delta(r-r') = \frac{r^2}{8\pi^2 i|r-r'|} \int_{-\infty}^{+\infty} k e^{ik|r-r'|}\, dk \quad . \tag{6.30}$$

I am interested only in the assymptotic behavior of the scattering function. I will find directly the Green's function in the limit as $r\to\infty$ which will give the assymptotic form of the scattering function directly.

$$G^{\infty}(r|r') = \lim_{r\to\infty} G(r|r') \tag{6.31}$$

Consider the limit of $V_{\nu\ell m_\ell}(r)$ as $r\to\infty$:

$$V_{\nu\ell m_\ell}(r) \to \left\{ \frac{r^2}{2}\left[j_\ell(k_0 r)\delta_{\nu\nu_0} + \varepsilon\frac{e^{ik_\nu r}}{k_\nu r}\right]'' + r\left[j_\ell(k_0 r)\delta_{\nu\nu_0} + \varepsilon\frac{e^{ik_\nu r}}{k_\nu r}\right]' \right\} \times \left[j_\ell(k_0 r)\delta_{\nu\nu_0} + \frac{e^{ik_\nu r}}{k_\nu r}\right]^{-1} \tag{6.32}$$

$$\to \left\{ -\frac{rk_0}{2}\cos(k_0 r-(\ell+1)\pi/2)\delta_{\nu\nu_0} - \varepsilon\frac{rk_\nu}{2}e^{ik_\nu r} \right\} \left[\frac{1}{k_0 r}\cos(k_0 r-(\ell+1)\pi/2)\delta_{\nu\nu_0} + \varepsilon\frac{e^{ik_\nu r}}{k_\nu r}\right]^{-1} \tag{6.33}$$

$$\to -\frac{1}{2}r^2k_\nu^2 \tag{6.34}$$

I also need the following expression

$$-\frac{1}{2}\frac{d}{dr}r^2\frac{d}{dr}\frac{r^2}{8\pi^2 i|r-r'|}\int_{-\infty}^{+\infty} ke^{ik|r-r'|}dk = \frac{r^2k^2 - 4rik}{2}\frac{r^2}{8\pi^2 i|r-r'|}\int_{-\infty}^{+\infty} ke^{ik|r-r'|}dk \tag{6.35}$$

So that

$$G^{\infty}(r|r') = \frac{r^2}{8\pi^2 i} \int_{-\infty}^{+\infty} \frac{k\, e^{ik|r-r'|}\, dk}{\left[\frac{r^2k_\nu^2}{2} + \frac{4rik}{2} - \frac{r^2k^2}{2}\right]|r-r'|} \tag{6.36}$$

$$= \frac{1}{4\pi^2 i} \int_{-\infty}^{+\infty} \frac{k\, e^{ik|r-r'|}}{(k_\nu^2 - k^2 + 4ik/r)|r-r'|}\, dk$$

$$= -\frac{e^{ik_\nu|r-r'|}}{4\pi|r-r'|} \to -\frac{e^{ik_\nu r}}{4\pi r}\, e^{-ik_\nu r'} \tag{6.37}$$

Note that, while this becomes the usual Green's function in the limit at large r, there is a difference at small r which in fact automatically selects the outgoing Green's function without requiring or allowing an arbitrary choice from several possible integration contours, leading to either incoming or outgoing waves.

The assymptotic form of the first-order scattering function can now be given in terms of $G^{\infty}(r|r')$:

$$\psi^{1\infty}_{\nu\ell m_\ell}(r) = -\int_0^{\infty} G^{\infty}(r|r')\hat{\mathcal{H}}'_{\nu\ell m_\ell,\nu'\ell' m_{\ell'}}(r')\psi^0_{\nu\ell m_\ell}(r')dr'$$

$$= \frac{e^{ik_\nu r}}{4\pi r} \int_0^{\infty} e^{-ik_\nu r'} \hat{\mathcal{H}}'_{\nu\ell m_\ell,\nu'\ell' m_{\ell'}}(r')\psi^0_{\nu\ell m_\ell}(r')dr' \tag{6.38}$$

Writing out this integral explicitly:

$$\psi^{1\infty}_{\nu\ell m_\ell}(r) = \frac{e^{ik_\nu r}}{4\pi r} \int_0^{\infty} e^{-ik_\nu r'} \left\{ \left[\frac{\ell(\ell+1)}{2} - V_{\nu\ell m_\ell}(r')\right.\right.$$

$$
\begin{aligned}
&- \frac{1}{2}k_\nu^2 r'^2 \Big) \delta_{\nu\nu'} \delta_{\ell\ell'} \delta_{m_\ell m_\ell'} \\
&+ \sum_{mm'} I_\Omega^{JM} \begin{pmatrix} j_0 & \ell & m_{j_0} & m_\ell & m \\ j' & \ell' & m_{j'} & m_{\ell'} & m' \end{pmatrix} \Bigg[2Z \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \delta_{mm'} \\
&C(n\ell\ell', 0m) C(n\ell\ell', 00) \Bigg[\int_0^{2r'} \frac{R^{n+2}}{2^{n_{r'}, n+1}} \chi_\nu^*(R) \\
&\chi_\nu(R) dR + \int_{2r'}^{\infty} \frac{2^{n+1} r_{,}^{n}}{R^{n-1}} \chi_\nu^*(R) \chi_\nu(R)\, dR \Bigg] \\
&+ \sum_{u=1}^{N} \delta_{\nu\nu'} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{\ell' m'}(\Omega_1) \alpha(1) \\
&\chi_u(2) \Big| \frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1) Y_{nm_n}^*(\Omega_2) (1 - P_{12}) \Big| Y_{\ell m}(\Omega_1) \\
&\alpha(1) \chi_u(2) \rangle \Bigg] \Bigg] \Bigg[C(j_0 \ell J, M0M) i^\ell \sqrt{4\pi(2\ell+1)} \\
&j_\ell(k_0 r') \delta_{Mm_{j_0}} \delta_{\nu\nu_0} + C(j_0 \ell J, m_{j_0} m_\ell M) \sum_i \\
&\delta_{i,(\ell-\ell_0)/2}\, C_i f_i(r') C(\nu - \nu_m) I(j_0 m_{j_0} \ell m_\ell m_0) \Bigg] dr'
\end{aligned}
\tag{6.39}
$$

In general, the scattering function would be evaluated by a numerical integration of the right side of equation (6.39). As a specific example, I will use the H_2^- bound state function obtained in Chapter V and find the scattering functions for the p-wave scattering with $\nu_0=0$ and $\nu=0,1,2$. For H_2^-, $\ell_0=1$ and $m_0=0$. I will choose the following more

or less arbitrary values for as yet undetermined quantum numbers:

$$\nu' = \nu_0 = 0$$

$$j' = j_0 = 0$$

$$m_j' = m_{j_0} = 0$$

$$J = \ell' = \ell = 1$$

and $$M = m_\ell' = m_\ell = 0 \quad . \tag{6.40}$$

I find that

$$I_\Omega^{10} \begin{pmatrix} 0 & 1 & 0 & 0 & m \\ 0 & 1 & 0 & 0 & m' \end{pmatrix} = 0 \ , \ m \neq m' \quad . \tag{6.41}$$

Equation (6.39) now becomes

$$\psi_{\nu 10}^{1\infty}(r) = \frac{e^{ik_\nu r}}{4\pi r} \int_0^\infty e^{-ik_\nu r'} \Bigg[(1 - V_{\nu 10}(r') - 1/2\, k_\nu^2 r'^2)\delta_{\nu 0}$$

$$+ \sum_m I_\Omega^{10} \begin{pmatrix} 0 & 1 & 0 & 0 & m \\ 0 & 1 & 0 & 0 & m \end{pmatrix} \Bigg[2 \sum_{n=0,2} C(n11, 0m)$$

$$C(n11, 00) \Bigg(\int_0^{2r'} \frac{R^{n+2}}{2^{n_r', n+1}} \chi_0^*(R)\chi_\nu(R)\, dR$$

$$+ \int_{2r'}^\infty \frac{2^{n+1_r', n}}{R^{n-1}} \chi_0^*(R)\chi_\nu(R)\, dR \Bigg)$$

$$+ \sum_{u=1}^{2} \delta_{\nu 0} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \Big\langle Y_{1m}(\Omega_1)\alpha(1)\chi_u(2)$$

$$\Big| \frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1) Y_{nm_n}^*(\Omega_1)(1 - P_{12}) \Big| Y_{1m}(\Omega_1)\alpha(1)$$

$$\chi_u(2) \Big\rangle \Bigg] \Bigg] C(011, 00) \Big[i\sqrt{12\pi}\, j_1(k_0 r')\delta_{\nu 0}$$

$$+ C(\nu-\nu_m)\, C_0 f_0(r')\, I(00100) \Big] dr' \qquad (6.42)$$

Numerically evaluating the following expressions according to equations (2.67) and (2.69(for I_Ω^{JM} and (4.49) and (4.50) for I(00100):

$$I_\Omega^{10} \begin{pmatrix} 0 & 1 & 0 & 0 & m \\ 0 & 1 & 0 & 0 & m \end{pmatrix} = 1/6\pi \qquad m=0,\pm1 \qquad (6.43)$$

$$I(00100) = .1424 \qquad (6.44)$$

Evaluating the various Clebsch-Gordon coëfficients,[1]

$$\begin{aligned} &C(011,00) = 1 \\ &C(211,00) = -\sqrt{2/5} \\ &C(011,0m)C(011,00) = 1 && m=0,\pm1 \\ &C(211,0m)C(211,00) = -1/5 && m=\pm1 \\ &C(211,0m)C(211,00) = 2/5 && m=0 \end{aligned} \qquad (6.45)$$

I can evaluate the integrals over R by substituting harmonic oscillator functions for $R\chi_\nu(R)$, producing integrals expressible as incomplete gamma functions. The only m dependance in the nuclear attaction terms is in the Clebsch-Gordon coëfficients. Summing them over m gives

$$\sum_{m=-1}^{+1} C(011,0m)C(011,00) = 3$$

$$\sum_{m=-1}^{+1} C(211,0m)C(211,0m) = 0 \qquad (6.46)$$

Thus only the n=0 term is non-zero and the expression becomes

$$1/\pi \left[\frac{1}{r'} \int_0^{2r'} R^2 \chi_0^*(R)\chi_\nu(R)dR + 2\int_{2r'}^{\infty} R\chi_0^*(R)\chi_\nu(R)dR \right]$$

$$\equiv \text{Nuclear Attraction} \qquad (6.47)$$

Making the substitution of harmonic oscillator functions:

$$R^2\chi_\nu^*(R)\chi_{\nu'}(R) = \left[\frac{\sqrt{\beta/\pi}}{2^\nu \nu!}\right]^{1/2} \left[\frac{\sqrt{\beta/\pi}}{2^{\nu'}\nu'!}\right]^{1/2}$$

$$H_\nu(\sqrt{\beta}(R-R_0))H_{\nu'}(\sqrt{\beta}(R-R_0))\, e^{-\beta(R-R_0)^2}\sqrt{\beta}. \qquad (6.48)$$

R_0 is the equilibrium internuclear distance, 1.40 Bohr. The constant $\beta=\sqrt{mk}/\hbar$ where m is the reduced mass for the nuclear motion and k is the force constant for the vibrational motion. In atomic units, $\beta=18.3851^2$. The nuclear attraction term is now

$$\text{Nuclear Attraction} = \left[\frac{\beta}{\pi^{3}2^{\nu}\,\nu!}\right]^{1/2}\left[\frac{1}{r'}\int_{-\sqrt{\beta}R_0}^{\sqrt{\beta}(2r'-R_0)} H_\nu(y)\, e^{-y^2}dy + 2\sqrt{\beta}\int_{\sqrt{\beta}(2r'-R_0)}^{\infty}\frac{1}{\sqrt{\beta}R_0+y}H_\nu(y)\, e^{-y}\,dy\right] \tag{6.49}$$

where $y=\sqrt{\beta}(R-R_0)$.

The first integral can be written in terms of incomplete gamma functions since

$$\int_a^b y^n\, e^{-y^2}dy = \frac{1}{2}\left(\Gamma\left(\frac{n+1}{2},a\right) - \Gamma\left(\frac{n+1}{2},b\right)\right) \tag{6.50}$$

In the second integral, I must first use the binomial expansion on $1/\sqrt{\beta}R_0-y$:

$$\frac{1}{\sqrt{\beta}R_0+y} = \frac{1}{\sqrt{\beta}R_0}\left[1 - \frac{y}{\sqrt{\beta}R_0} + \frac{y^2}{\beta R_0^{\,2}} - \ldots\right] \tag{6.51}$$

At $y=-\sqrt{\beta}R_0$ this sum diverges, representing a singularity in the original expression. This singularity, however, is non-physical, deriving from the use of a symmetric potential. If I keep the first eight terms in the expansion, the error is negligible between $R=R_0/2$ and $R=3R_0/2$, which is the region where the vibrational functions have significant amplitude, and the resulting expression is well behaved at $y=-\sqrt{\beta}R_0$.

The resulting expressions for the nuclear attraction term are different for $2r'<R_0$ and $2r'>R_0$ since the incomplete gamma function $\Gamma(\alpha,x)$ is only defined for $x\geq 0$.

To be able to write the scattering integrals, I need the value of ν_m and the corresponding value of C. I have chosen ν_m to be 3 since no appreciable excitation of the third vibrational level is found at the resonance peak for $\nu=1$ excitation.[3] I now refer to equation (5.40) and find that $C=1/\sqrt{14}$.

The inelastic scattering integrals can now be Written as

$$\psi^{\infty}_{110}(r) = \frac{e^{ik_1 r}}{4\pi r}\int_0^{\infty} e^{-ik_1 r'} \text{ (Nuclear Attraction)}$$

$$\frac{2\times.1424}{\sqrt{14}}\left(.3808\ r'^{.682}\ e^{-.607r'}\right.$$

$$\left. + 5.2957\ r'^{1.852}\ e^{-2.752r'}\right)\ dr' \qquad (6.52)$$

and

$$\psi^{\infty}_{210}(r) = \frac{e^{ik_2 r}}{4\pi r}\int_0^{\infty} e^{-ik_2 r'} \text{ (Nuclear Attraction)}$$

$$\frac{.1424}{\sqrt{14}}\left(.3808\ r'^{.682}\ e^{-.607r'}\right.$$

$$\left. + 5.2957\ r'^{1.852}\ e^{-2.752r'}\right)\ dr' \qquad (6.53)$$

For the elastic scattering expression I must also evaluate the coulombic and exchange integral.

$$I \equiv \sum_m \frac{1}{6\pi} \sum_{u=1}^{2} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{1m}(\Omega_1)\alpha(1)\chi_u(2) |$$

$$\frac{r_<^n}{r_>^{n+1}} Y_{nm_n}(\Omega_1) Y^*_{nm_n}(\Omega_2)(1-P_{12}) | Y_{1m}(\Omega_1)\alpha(1)\chi_u(2)\rangle$$

$$\left(2i\sqrt{3\pi} j_1(kr) + \frac{3\times.1424}{\sqrt{14}} C_0 f_0(r)\right) \tag{6.54}$$

where

$$\chi_1(2) = \phi_1(r_2) Y_{00}(\Omega_2)\alpha(2)$$

$$\chi_2(2) = \phi_1(r_2) Y_{00}(\Omega_2)\beta(2) \tag{6.55}$$

Separating the coulombic and exchange parts and summing over molecular orbitals;

$$I = \sum_m \frac{2}{6\pi} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{1m}(\Omega) | Y_{nm_n}(\Omega) Y_{1m}(\Omega)\rangle$$

$$\langle Y_{00}(\Omega) Y_{nm_n}(\Omega) | Y_{00}(\Omega)\rangle \langle \phi_1(r_2) \frac{r_<^n}{r_>^{n+1}}$$

$$| \phi_1(r_2)\rangle \psi^0(r_1)$$

$$- \sum_m \frac{1}{6\pi} \sum_{n=0}^{\infty} \sum_{m_n=-n}^{+n} \frac{4\pi}{2n+1} \langle Y_{1m}(\Omega) | Y_{nm_n}(\Omega) Y_{00}(\Omega) \rangle$$

$$\langle Y_{00}(\Omega) Y_{nm_n}(\Omega) | Y_{1m}(\Omega) \rangle \langle \phi_1(r_2) | \frac{r_<^n}{r_>^{n+1}}$$

$$| \psi^0(r_2) \rangle \phi_1(r_1) \qquad (6.56)$$

Performing the summations and angle integrals indicated above,

$$I = \frac{1}{\pi} \langle \phi_1(r_2) | \frac{1}{r_>} | \phi_1(r_2) \rangle \psi^0(r_1)$$

$$- \frac{1}{6\pi} \langle \phi_1(r_2) | \frac{r_<}{r_>^2} | \psi^0(r_2) \rangle \phi_1(r_1) \qquad (6.57)$$

The integral for the elastic scattering can now be written:

$$\psi^{\infty}_{010}(r) = \frac{e^{ik_0 r}}{4\pi r} \int_0^{\infty} e^{-ik_0 r'} \Big\{ 1 - \Big(\frac{r'^2}{2} \psi^0(r')'' + r\psi^0(r')' \Big) / \psi^0(r') - \frac{1}{2} k_0^2 r'^2 + \text{Nuclear Attraction} + \frac{1}{\pi} \langle \phi_1(r_2) | \frac{1}{r_>} | \phi_1(r_2) \rangle - \frac{1}{6\pi} \langle \phi_1(r_2) | \frac{r_<}{r_>^2} | \psi^0(r_2) \rangle \frac{\phi_1(r')}{\psi^0(r')} \Big\} \psi^0(r')$$

(6.58)

The coulombic integral and the part of the exchange integral coming from the bound state function can be evaluated using incomplete gamma functions, but the part of the exchange integral involving the Bessel function was integrated numerically.

The numerical integration of the scattering integrals was carried out on the CDC 3600 computer at the Michigan State University Computer Center. The programs and original output are reproduced in Appendix D.

The value of the scattering integral is a complex number which I will call A. The asymptotic form of ψ^1 is therefor:

$$\psi^{\infty} = Ak/4\pi \; e^{ikr}/kr \tag{6.59}$$

The asymptotic form for the complete function is thus

$$\psi^0_{r\to\infty} + \psi^1_{r\to\infty} = \sqrt{\pi}\left[\frac{e^{-i(kr+\pi/2)}}{kr} + \frac{e^{+i(kr-\pi/2)}}{kr}\right]\delta_{\nu 0} + Ak/4\pi \; \frac{e^{ikr}}{kr} \tag{6.60}$$

$$= \sqrt{\pi}\,\frac{e^{-i(kr+\pi/2)}}{kr}\,\delta_{\nu 0} + a\sqrt{\pi}\,\frac{e^{+i(kr-\pi/2+\delta)}}{kr} \tag{6.60}$$

It follows that the scattering amplitude, a^2, and the phase shift, δ, are given by

$$a^2 = \left|\delta_{v0} + \frac{Aki}{4\pi\sqrt{\pi}}\right|^2 \qquad (6.61)$$

and

$$\delta = -i \ln\left(\delta_{v0} + \frac{Aki}{4\pi\sqrt{\pi}}\right) + i \ln(a) \ . \qquad (6.62)$$

The amplitudes and phase shifts have been calculated for fifteen energies from k=.20 to k=.90 (in atomic units), that is,from .57 to 12.0 e.v. The results of these calculations are presented in graph form in Figures 1 and 2, following.

The results show a definite but very broad resonance in the elastic scattering. They also indicate a degree of coupling of vibrational states, in spite of the making of a series of rather drastic approximations. I can state, based on my results, that there is vibrational excitation of hydrogen at low energies due to the breakdown of the Born-Oppenheimer separation between the nuclear and electronic motions.

There is ample opportunity to make higher quality calculations using the formalism which I have developed here. Whether such calculations will produce better results is a question that cannot be answered until such calculations are done. I believe that the method is capable of producing good results.

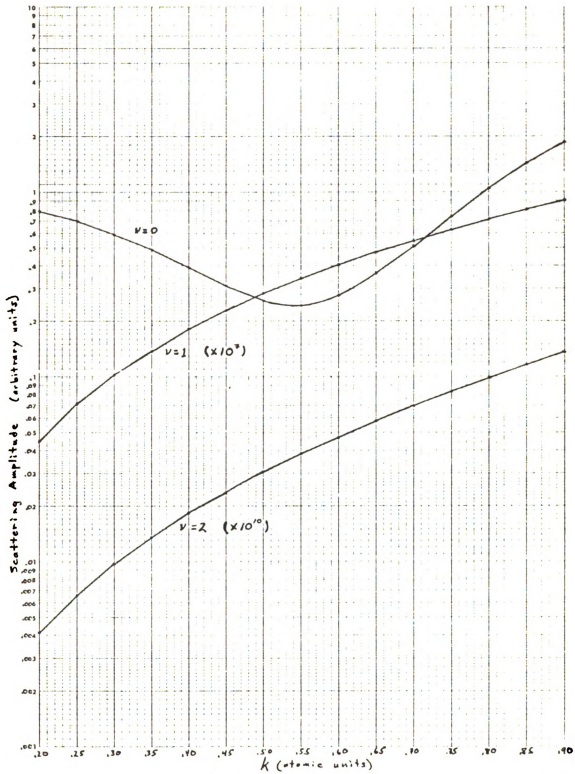

FIGURE 1: SCATTERING AMPLITUDE AS A FUNCTION OF ENERGY

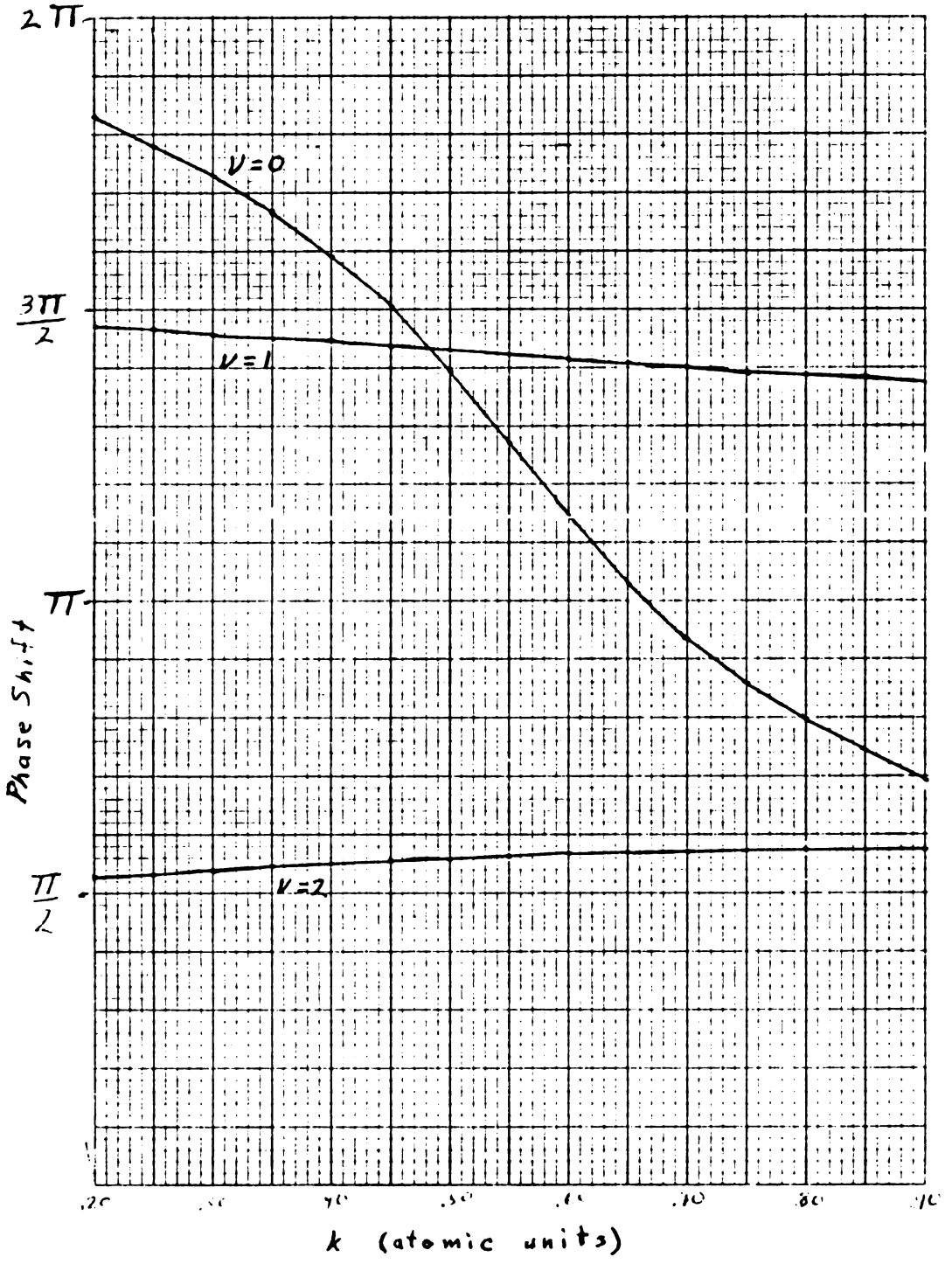

FIGURE 2: PHASE SHIFT AS A FUNCTION OF ENERGY

[1] Rose, op. cit., p. 39.

[2] G. Herzberg, Molecular Spectra and Molecular Structure, pp. 98 & 532, VanNostrand, New York, (1961).

[3] Schulz, op. cit.

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APPENDICES

APPENDIX A

Determinant and Minors of the Matrix of Overlap Integrals

I. Expansion of determinants.

Let U be an N×N matrix. The (N^{th} order) determinant of this matrix is designated by $\|U\|$. I can write $\|U\|$ in terms of N-1^{st} order determinants by expanding along a row or column of the matrix. Expanding along the i^{th} row will give

$$\|U\| = \sum_{j=1}^{N} (-1)^{i+j} U_{ij} \|U\|_M^{ij} \quad . \tag{A.1}$$

$\|U\|_M^{ij}$ is a first order unsigned minor of $\|U\|$, and is the (N-1^{st} order) determinant of the matrix obtained by deleting the i^{th} row and j^{th} column from U. The minor with the sign term included is the signed minor, $\|U\|^{ij}$. Minors are henceforth assumed to be signed minors unless stated otherwise.

$$\|U\|^{ij} = (-1)^{i+j} \|U\|_M^{ij} \tag{A.2}$$

$$\|U\| = \sum_{j=1}^{N} U_{ij} \|U\|^{ij} \quad . \tag{A.3}$$

The first order minor can itself be expanded:

$$\|U\|^{ij} = (-1)^{i+j} \left[\sum_{\ell=1}^{j-1} (-1)^{k+\ell} U_{k\ell} \| \|U\|_M^{ij} \|_M^{k\ell} + \sum_{\ell=j}^{N-1} (-1)^{k+\ell} U_{k,\ell+1} \| \|U\|_M^{ij} \|_M^{k\ell} \right]$$

if $k<i$ or,

$$\|U\|^{ij} = (-1)^{i+j} \left[\sum_{\ell=1}^{j-1} (-1)^{k+\ell} U_{k+1,\ell} \| \|U\|_M^{ij} \|_M^{k\ell} + \sum_{\ell=j}^{N-1} (-1)^{k+\ell} U_{k+1,\ell+1} \| \|U\|_M^{ij} \|_M^{k\ell} \right]$$

if $k>i$. (A.4)

These expressions can be simplified by substituting the second order unsigned minors for the first order minors of the first order minors. The second order minors are defined analogously to the first order minors but with two rows and two columns removed. The distinction is that k and ℓ in equation (A.4), where used as superscripts on the minors, refer to the row and column numbers in the first order minors, not the original determinant.

$$\|U\|^{ij} = (-1)^{i+j} \left[\sum_{\ell=1}^{j-1} (-1)^{k+\ell} U_{k\ell} \|U\|_{MM}^{ik,j\ell} + \sum_{\ell=j+1}^{N} (-1)^{k+\ell-1} U_{k\ell} \|U\|_{MM}^{ik,j\ell} \right]$$

if $i>k$ or

$$\|U\|^{i,j} = (-1)^{i+j} \left[\sum_{\ell=1}^{j-1} (-1)^{k-1+\ell} U_{k\ell} \|U\|_{MM}^{ik,j\ell} + \sum_{\ell=j+1}^{N} (-1)^{k-1+\ell-1} U_{k\ell} \|U\|_{MM}^{ik,j\ell} \right]$$

if $i<k$. (A.5)

In equation (A.5) all indices refer to the row and column numbers in the original matrix. I can simplify this equation further by using P( ) operators, where P("statement") = +1 if "statement" is true and -1 if "statement" is false:

$$\|U\|^{i,j} = (-1)^{i+j} \sum_{\ell \neq j}^{N} (-1)^{k+\ell} P(i>k)P(j>\ell)\, U_{k\ell} \|U\|_{MM}^{ik,j\ell}$$

(A.6)

But the signed second order minor is

$$\|U\|^{ik,j\ell} = (-1)^{i+j+k+\ell}\, P(i>k)P(j>\ell)\, \|U\|_{MM}^{ik,j\ell}$$

so

$$\|U\|^{i,j} = \sum_{\ell \neq j}^{N} U_{k\ell} \|U\|^{ik,j\ell} \quad . \tag{A.7}$$

and

$$\|U\| = \sum_{j=1}^{N} \sum_{\ell \neq j}^{N} U_{ij} U_{k\ell} \|U\|^{ik,j\ell} \quad . \tag{A.8}$$

II. The determinant of the matrix of overlap integrals.

The matrix of overlap integrals is

$$D = \begin{bmatrix} 1 & 0 & 0 & \cdots & D_{1,N+1} \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & D_{3,N+1} \\ \vdots & \vdots & \vdots & & \vdots \\ D_{N+1,1} & 0 & D_{N+1,3} & \cdots & D_{N+1,N+1} \end{bmatrix} \tag{A.9}$$

Expanding along row 1,

$$\|D\| = \|D\|^{1,1} + D_{1,N+1} \|D\|^{1,N+1} \tag{A.10}$$

Expanding $\|D\|^{1,N+1}$ along column 1,

$$\|D\|^{1,N+1} = D_{N+1,1} \|D\|^{1,N+1;N+1,1} = -D_{N+1,1} \|D\|^{1,N+1;1,N+1}$$

but $\|D\|^{1,N+1;1,N+1} = 1$ so

$$\|D\| = \|D\|^{1,1} - D_{N+1,1}D_{1,N+1} \tag{A.11}$$

Expanding $\|D\|^{1,1}$ along row 3

$$\|D\|^{1,1} = \|D\|^{1,3;1,3} + D_{3,N+1}\|D\|^{1,3;1,N+1} \tag{A.12}$$

and $\|D\|^{1,3;1,N+1} = D_{N+1,3}\|D\|^{1,3,N+1;1,N+1,3} = -D_{N+1,3}$

so $$\|D\| = \|D\|^{1,3;1,3} - D_{N+1,1}D_{1,N+1} - D_{N+1,3}D_{3,N+1}$$

(A.13)

Continuing this process, I eventually obtain

$$\|D\| = \|D\|^{1,3,..N-1;1,3,..N-1} - \sum_{\substack{i=1 \\ \text{odd}}}^{N-1} D_{N+1,i}D_{i,N+1}$$

(A.14)

where

$$\|D\|^{1...N-1;1...N-1} = \begin{vmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & D_{N+1,N+1} \end{vmatrix}$$

$$= D_{N+1,N+1} \tag{A.15}$$

and

$$\|D\| = D_{N+1,N+1} - \sum_{i}^{N} D_{N+1,i}\, D_{i,N+1} \tag{A.16}$$

The terms in the above summation with i even are all zero, so that the restriction can be dropped without affecting the result.

III. The first order minors.

The first order minors can be divided into three classes. In the first, both indices are less than N+1; in the second, one is N+1; and in the last, both are N+1.

Class 1: $\|D\|^{i,j}$ $i,j<N+1$

If $i=j$ then $\|D\|^{i,j} = \|D\|^{i,i}$. To evaluate $\|D\|^{i,i}$ compare it to $\|D\|$ and note that performing a series of expansions analogous to those in section II produces the same result except for the term $-D_{N+1,i}\, D_{i,N+1}$ which is missing.

$$\|D\|^{i,i} = D_{N+1,N+1} - \sum_{j\neq i}^{N} D_{N+1,i}\, D_{i,N+1} \tag{A.17}$$

Note that if i is even the missing term is zero and then $\|D\|^{i,i} = \|D\|$.

If $i \neq j$, deleting the i^{th} row will leave $D_{N+1,i}$ as the only non-zero element in the i^{th} column, and expanding $\|D\|^{i,j}$ gives

$$\|D\|^{i,j} = D_{N+1,i} \|D\|^{i,N+1;j,i} \tag{A.18}$$

Deleting the j^{th} column likewise leaves $D_{j,N+1}$ as the only non-zero element in the j^{th} row, so that

$$\|D\|^{i,j} = D_{N+1,i}\, D_{j,N+1}\, \|D\|^{i,N+1,j;j,i,N+1} \,. \tag{A.19}$$

Now $\|D\|^{i,N+1,j;j,i,N+1} = -\|D\|^{i,j,N+1;j,i,N+1}$

$$= +\|D\|^{i,j,N+1;i,j,N+1} = 1 \quad \text{so}$$

$$\|D\|^{i,j} = D_{N+1,i}\, D_{j,N+1} \,. \tag{A.20}$$

Note that if either i or j is even $\|D\|^{i,j} = 0$.

Class 2: $\|D\|^{i,N+1}$ and $\|D\|^{N+1,i}$

Deleting the i^{th} row or column leaves $D_{N+1,i}$ or $D_{i,N+1}$, respectively, as the only non-zero element in the i^{th} column or row, so that

$$\|D\|^{i,N+1} = D_{N+1,i}\, \|D\|^{i,N+1;N+1,i}$$

and $\|D\|^{N+1,i} = D_{i,N+1}\|D\|^{N+1,i;i,N+1}$. (A.21)

Now $\|D\|^{N+1,i;i,N+1} = \|D\|^{i,N+1;N+1,i} = -\|D\|^{i,N+1;i,N+1}$

$= -1$ so that

$$\|D\|^{i,N+1} = -D_{N+1,i}$$

and $\|D\|^{N+1,i} = -D_{i,N+1}$. (A.22)

Note that if i is even $\|D\|^{i,N+1} = \|D\|^{N+1,i} = 0$.

Class 3: $\|D\|^{N+1,N+1}$

By inspection

$$\|D\|^{N+1,N+1} = 1 \qquad (A.23)$$

Section IV: The second-order minors.

The second-order minors can be grouped according to the number of distinct numbers represented by the four indices. It is meaningless to write a second-order minor with both row indices the same or with both column indices the same, since the same row or column cannot be deleted twice. With this restriction, the four indices may represent two, three, or four distinct numbers.

For the second-order minors, $\|D\|^{\mu\nu,k\ell}$, I will need to consider only those minors for which $\mu>\nu$ and $k>\ell$. In the evaluation of these I will sometimes need to use minors not obeying this convention, but will always end up with expressions using only minors which do obey it.

A. Suppose that the four indices represent three distinct numbers.

Case I: all indices are less than N+1.

$$\|D\|^{\mu\nu,k\ell} = \|D\|^{\mu\nu,\mu\ell} ,$$

$$\|D\|^{\mu\nu,k\mu} ,$$

$$\|D\|^{\mu\nu,\nu\ell} , \text{ or}$$

$$\|D\|^{\mu\nu,k\nu} \qquad (A.24)$$

To evaluate $\|D\|^{\mu\nu,\mu\ell}$, I expand it along the ℓ^{th} row. The only non-zero element in the ℓ^{th} row is $D_{\ell,N+1}$ so

$$\|D\|^{\mu\nu,\mu\ell} = D_{\ell,N+1}\|D\|^{\mu\nu\ell,\mu\ell N+1} \qquad (A.25)$$

Next, expand the third order minor along the ν^{th} column, which has $D_{N+1,\nu}$ as its only non-zero element:

$$\|D\|^{\mu\nu\ell,\mu\ell N+1} = D_{N+1,\nu}\|D\|^{\mu\nu\ell N+1,\mu\ell N+1\nu} \tag{A.26}$$

and $$\|D\|^{\mu\nu\ell N+1,\mu\ell N+1\nu} = 1 \tag{A.27}$$

so that

$$\|D\|^{\mu\nu,\mu\ell} = D_{N+1,\nu}\, D_{\ell,N+1} \tag{A.28}$$

To evaluate $\|D\|^{\mu\nu,k\mu}$, expand successively along the k^{th} row and ν^{th} column giving:

$$\|D\|^{\mu\nu,k\mu} = D_{k,N+1}\|D\|^{\mu\nu k,k\mu N+1}$$

$$= D_{k,N+1}\, D_{N+1,\nu}\|D\|^{\mu\nu kN+1,k\mu N+1\nu} \tag{A.29}$$

$$= - D_{N+1,\nu}\, D_{k,N+1} \tag{A.30}$$

Similarly, for $\|D\|^{\mu\nu,\nu\ell}$;

$$\|D\|^{\mu\nu,\nu\ell} = D_{\ell,N+1}\, D_{N+1,\mu}\|D\|^{\mu\nu\ell N+1,\nu\ell N+1\mu}$$

$$= - D_{N+1,\mu}\, D_{\ell,N+1} \tag{A.31}$$

And for $\|D\|^{\mu\nu,k\nu}$;

$$\|D\|^{\mu\nu,k\nu} = D_{k,N+1}D_{N+1,\mu}\|D\|^{\mu\nu kN+1,k\nu N+1\mu}$$

$$= D_{N+1,\mu}\, D_{k,N+1} \qquad \text{(A.32)}$$

Case II: one index is N+1.

$$\|D\|^{\mu\nu,k\ell} = \|D\|^{N+1\nu,k\nu}\ ,$$

$$\|D\|^{N+1\nu,\nu\ell}\ ,$$

$$\|D\|^{\mu\nu,N+1\nu}\ , \text{ or}$$

$$\|D\|^{\mu\nu,N+1\mu}\ . \qquad \text{(A.33)}$$

To evaluate $\|D\|^{N+1\nu,k\nu}$, expand along the k^{th} row, which has $D_{k,N+1}$ as its only non-zero element:

$$\|D\|^{N+1\nu,k\nu} = D_{k,N+1}\|D\|^{N+1\nu k,k\nu N+1} \qquad \text{(A.34)}$$

but $\|D\|^{N+1\nu k,k\nu N+1} = -\|D\|^{N+1\nu k,N+1\nu k} = -1$, since $k\nu N+1$ is an odd permutation of $N+1\nu k$, and

$$\|D\|^{N+1\nu,k\nu} = -D_{k,N+1}\ . \qquad \text{(A.35)}$$

The other three cases can be evaluated similarly:

$$\|D\|^{N+1\nu,\nu\ell} = D_{\ell,N+1}\|D\|^{N+1\nu\ell,\nu\ell N+1} = D_{\ell,N+1} \qquad \text{(A.36)}$$

$$\|D\|^{\mu\nu,N+1\nu} = D_{N+1,\mu}\|D\|^{\mu\nu N+1,N+1\nu\mu} = -D_{N+1,\mu} \quad (A.37)$$

$$\|D\|^{\mu\nu,N+1\mu} = D_{N+1,\nu}\|D\|^{\mu\nu N+1,N+1\mu\nu} = D_{N+1,\nu} \quad (A.38)$$

Case III: two indices are N+1.

The only example of case III is $\|D\|^{N+1\nu,N+1\ell}(\nu\neq\ell)$. The N+1,N+1 minor, however, is the determinant of the N×N unit matrix so

$$\|D\|^{N+1\nu,N+1\ell} = \delta_{\nu,\ell} = 0 \quad (A.39)$$

B. Suppose the four indices represent only two distinct numbers.

Case I: $\mu\neq N+1$.

$$\|D\|^{\mu\nu,k\ell} = \|D\|^{\mu\nu,\mu\nu} \quad (A.40)$$

Now $\|D\|^{\mu,\mu} = D_{N+1,N+1} - \sum_{i\neq\mu} D_{N+1,i}\, D_{i,N+1}$. Deleting the ν^{th} row and column from this minor removes the $D_{N+1,\nu}\, D_{\nu,N+1}$ term leaving

$$\|D\|^{\mu\nu,\mu\nu} = D_{N+1,N+1} - \sum_{i\neq\mu,\nu} D_{N+1,i}\, D_{i,N+1} \quad (A.41)$$

Case II: $\mu=N+1$.

Then

$$\|D\|^{\mu\nu,k\ell} = \|D\|^{N+1\nu,N+1\nu} = \delta_{\nu,\nu} = 1 \quad (A.42)$$

C. The remaining case which must be considered is that $\mu\nu,k\ell$ may all be different.

Deleting the μ^{th} and ν^{th} rows from the matrix leaves $D_{N+1,\mu}$ as the only non-zero element in the μ^{th} column (which is not deleted) and $D_{N+1,\nu}$ as the only non-zero element in the ν^{th} column (which also is not deleted). Expanding along the μ^{th} column,

$$\|D\|^{\mu\nu,k\ell} = D_{N+1,\mu}\|D\|^{\mu\nu N+1,k\ell\mu} \quad . \tag{A.43}$$

The minor $\|D\|^{\mu\nu N+1,k\ell\mu}$ still contains the ν^{th} column, but the $N+1^{st}$ row has been deleted, including $D_{N+1,\nu}$, and the ν^{th} column now has no non-zero elements. Thus

$$\|D\|^{\mu\nu N+1,k\ell\mu} = 0$$

$$\text{and} \quad \|D\|^{\mu\nu,k\ell} = 0 \qquad (\mu,\nu,k,\ell \text{ all different}) \tag{A.44}$$

The results of the above derivations are compiled in Table I and Table II on pages 23 and 24.

APPENDIX B

A One Determinant Approximation to a Two Determinant Function

The two determinant function I wish to approximate is

$$\Psi(N+1,\vec{R}) = \sum_{\nu j m_j} \left(\Psi^M(N)\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j} \Psi^P(N)\chi^B_{\nu j m_j}(1)\right) \chi_\nu(R)Y_{j m_j}(\theta_R,\phi_R). \tag{B.1}$$

The undistorted ground state function is written

$$\Psi^M(N) = \mathcal{A}\chi_1(1)\chi_2(2)\ldots\chi_N(N) \tag{B.2}$$

where the χ_i are the various normalized Hartree-Fock orbitals. The distorted function can be written

$$\Psi^P(N) = \mathcal{A}\chi'_1(1)\chi'_2(2)\ldots\chi'_N(N) \tag{B.3}$$

where the χ_i' are the distorted orbitals. Let

$$\delta\chi_i \equiv \chi_i' - \chi_i \tag{B.4}$$

represent the distortion. Then

$$\Psi^P(N) = \mathcal{A}(\chi_1(1)+\delta\chi_1(1))(\chi_2(2)+\delta\chi_2(2))\ldots$$

$$(\chi_N(N)+\delta\chi_N(N))$$

$$= \mathcal{A}\prod_{i=1}^{N}(\chi_i(i)+\delta\chi_i(i)) \tag{B.5}$$

$$= \mathcal{A}\prod_{i=1}^{N}\chi_i(i) + \mathcal{A}\sum_{j=1}^{N}\delta\chi_j(j)\prod_{i\neq j}(\chi_i(i)$$

$$+\delta\chi_i(i)) \tag{B.6}$$

The first term is the same as $\Psi^M(N)$, so that

$$\Psi(N+1,\vec{R}) = \sum_{\nu j m_j}\Big[\mathcal{A}\Psi^M(N)(\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1)$$

$$+ C_{\nu j m_j}\chi_{\nu j m_j}(1)) + C_{\nu j m_j}\mathcal{A}\sum_{j=1}^{N}\delta\chi_j(j)\prod_{i\neq j}^{N}$$

$$(\chi_i(i)+\delta\chi_i(i))\chi^B_{\nu j m_j}(1)\Big]\underline{\chi}_\nu(R)Y_{jm_j}(\theta_R,\phi_R)$$

$$\tag{B.7}$$

$$\text{Let } \Psi^{\varepsilon}(N) \equiv \mathcal{A} N_{\varepsilon} \prod_{i=1}^{N} (\chi_i(i)+\varepsilon\delta\chi_i(i)) \tag{B.8}$$

where $0 \leq \varepsilon \leq 1$, and N_{ε} is the necessary renormalization constant. Then $\Psi^{1}(N) = \Psi^{P}(N)$ and $\Psi^{0}(N) = \Psi^{M}(N)$. If I write

$$\Psi^{\varepsilon}(N+1,\vec{R}) = \sum_{\nu j m_j} \mathcal{A} \Psi^{\varepsilon}(N)(\chi^{S}_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j} \chi^{B}_{\nu j m_j}(1))\underline{\chi}_{\nu}(R)Y_{j m_j}(\theta_R,\phi_R) \tag{B.9}$$

the error which I have introduced is the difference between the original two-determinant function and the new one-determinant function. This difference is

$$\Psi(N+1,\vec{R}) - \Psi^{\varepsilon}(N+1,\vec{R}) = \sum_{\nu j m_j} \Big\{ \mathcal{A} \Big\{ (1-N_{\varepsilon})\Psi^{M}(N) - \varepsilon N_{\varepsilon} \sum_{j=1}^{N} \delta\chi_j(j) \prod_{i\neq j}^{N} (\chi_i(i)+\varepsilon\delta\chi_i(i)) \Big\}$$

$$(\chi^{S}_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j} \chi_{\nu j m_j}(1)) + C_{\nu j m_j}$$

$$\mathcal{A} \sum_{j=1}^{N} \delta\chi_j(j) \prod_{i\neq j}^{N} (\chi_i(i)+\delta\chi_i(i))\chi^{B}_{\nu j m_j}(1)$$

$$\Big\} \underline{\chi}_{\nu}(R)Y_{j m_j}(\theta_R,\phi_R) \tag{B.10}$$

This can also be written:

$$\Psi(N+1,\vec{R}) - \Psi^{\varepsilon}(N+1,\vec{R}) = \sum_{\nu j m_j} \Big\{ \mathcal{A}\Big\{ (1-N_\varepsilon)\Psi^M(N) - \varepsilon N_\varepsilon \sum_{j=1}^{N} \delta\chi_j(j) \prod_{j=1}^{N} (\chi_i(i)+\varepsilon\delta\chi_i(i)) \Big\}$$

$$\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j} \mathcal{A}\Big\{ (1-N_\varepsilon)\Psi^M(N) + (1-\varepsilon N_\varepsilon) \sum_{j=1}^{N} \delta\chi_j(j) \prod_{i\neq j}^{N} \chi_i(i) + (1-\varepsilon^2 N_\varepsilon) \sum_{j=1}^{N} \sum_{k\neq j}^{N} \delta\chi_j(j)\delta\chi_k(k) \prod_{i\neq j,k}^{N} \chi_i(i) + \ldots \Big\}$$

$$\chi^B_{\nu j m_j}(1) \Big\} \chi_\nu(R) Y_{j m_j}(\theta_R,\phi_R) \qquad \text{(B.11)}$$

For an optimal one-determinant approximation epsilon could be included as a variational parameter. This, however, still requires obtaining the distortions $\delta\chi_i$ and once these are obtained we might as well use the two-determinant function, since finding the $\delta\chi_i$ is the major part of that problem. Thus, I will set $\varepsilon=0$ and obtain

$$\Psi(N+1,\vec{R}) = \Psi^0(N+1,\vec{R}) = \sum_{\nu j m_j} \mathcal{A}\Psi^M(N)(\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j}\chi^B_{\nu j m_j}(1))\chi_\nu(R)Y_{j m_j}(\theta_R,\phi_R) \qquad \text{(B.12)}$$

$$= \mathcal{A}\Psi^M(N) \sum_{\nu j m_j} (\chi^S_{\nu_0 j_0 m_{j_0},\nu j m_j}(1) + C_{\nu j m_j}\chi^B_{\nu j m_j}(1)) \chi_\nu(R)Y_{j m_j}(\theta_R,\phi_R) \qquad \text{(B.13)}$$

APPENDIX C

Evaluation of $P^{JMj\ell}\,\psi$

I wish to obtain

$$\psi^{JMj\ell}(N+1,\vec{R}) = P^{JMj\ell}\ \psi^{M}(N) \sum_{\nu j' m_j} \left(\chi^{S}_{\nu,j,m_j,,\nu j' m_j}(1) + C_\nu \chi^{B}_\nu(1)\right)\chi_\nu(R) Y_{j' m_j}(\theta_R,\phi_R)$$

$$= P^{JMj\ell}\psi^{M}(N) \sum_{\nu j' m_j} \left(\chi^{S}_{\nu,j,m_j,,\nu j' m_j}(1) + C_\nu \chi^{B}_\nu(1)\right)\chi_\nu(R) Y_{j' m_j}(\theta_R,\phi_R) \qquad (C.1)$$

where

$$P^{JMj\ell} = \sum_{m_\ell m_j} |C(j\ell J, m_j m_\ell M)|^2\ |Y_{\ell m_\ell}(\theta,\phi) Y_{j m_j}(\theta_R,\phi_R)\rangle \langle Y_{\ell m_\ell}(\theta,\phi) Y_{j m_j}(\theta_R,\phi_R)| \ . \qquad (C.2)$$

To do so I must evaluate the integral

$$I \equiv \langle Y_{\ell m}(\theta,\phi) Y_{j m_j}(\theta_R,\phi_R)|\psi^{M}(N) \sum_{\nu j' m_j,}$$

$$\left(\chi^{S}_{\nu_0 j_0 m_{j_0},\nu j' m_{j'}}(1) + C_\nu \chi^{B}_\nu(1)\right)\chi_\nu(R)Y_{j'm_{j'}}(\theta_R,\phi_R)$$

$$= \langle Y_{\ell m_\ell}(\theta,\phi)Y_{jm_j}(\theta_R,\phi_R)|\Psi^M(N) \sum_{\nu j' m_{j'}} \Bigg[\sum_{\ell'=0}^{\infty}$$

$$\left(i^{\ell'}\sqrt{4\pi(2\ell'+1)}\,j_{\ell'}(k_0 r)Y_{\ell' 0}(\theta,\phi)\delta_{\nu\nu_0}\delta_{j'j_0}\right.$$

$$\delta_{m_{j'},m_{j_0}} + e^{ik_{\nu j'}r} \sum_{m'=-\ell'}^{+\ell'} f_{\ell' m',\nu_0 j_0 m_{j_0},\nu j m_j}(r)$$

$$\left.Y_{\ell' m'}(\theta,\phi)\right)\alpha(1) + C_\nu \chi^{B}_\nu(1) \Bigg]$$

$$\chi_\nu(R)Y_{j'm_{j'}}(\theta_R,\phi_R) \quad . \tag{C.3}$$

Most parts of this expression may be evaluated immediately, giving

$$I = \Psi^M(N) \sum_\nu \Bigg[\Big(i^\ell\sqrt{4\pi(2\ell+1)}\; j_\ell(k_0 r)\delta_{\nu\nu_0}\delta_{jj_0}\delta_{m_j m_{j_0}}$$

$$\delta_{m_\ell 0} + e^{ik_{\nu j}r} f_{\ell m_\ell,\nu_0 j_0 m_{j_0},\nu j m_j}(r)\Big)\alpha(1)$$

$$+ \sum_{j' m_{j'}} \langle Y_{\ell m_\ell}(\theta,\phi)Y_{jm_j}(\theta_R,\phi_R)|C_\nu\chi^{B}_\nu(1)$$

$$Y_{j'm_{j'}}(\theta_R,\phi_R)\rangle \Bigg] \chi_\nu(R) \tag{C.4}$$

To evaluate the remaining integral, I expand $\chi^{B}_\nu(1)$ in spherical harmonics starting with $Y_{\ell_0 m_0}$ where ℓ_0 and m_0 are determined by the symmetry of the orbital.

An arbitrary function, $f(r,\theta,\phi)$, with the same angular symmetry as the spherical harmonic $Y_{\ell_0 m_0}(\theta,\phi)$ can be expanded as

$$f(r,\theta,\phi) = \sum_{i=0}^{\infty} f_i(r) Y_{\ell_0+2i,m_0}(\theta,\phi) \qquad (C.5)$$

I arbitrarily take $m_0 \geq 0$. Since I am summing over m_ℓ states of the scattering electron this will not affect the results.

$$C_\nu \chi_\nu^B(1) = \sum_i C_{\nu i} f_{\nu i}(r) Y_{\ell_0+2i,m_0}(\tilde{\theta},\tilde{\phi})\alpha(1) \qquad (C.6)$$

The tilda on $\tilde{\theta}$ and $\tilde{\phi}$ indicates angles relative to the molecular axis. I now have to write these functions in terms of functions of the angles of the external coordinate system.

$$Y_{\ell_0+2i,m_0}(\tilde{\theta},\tilde{\phi}) = \sum_{m'} D^{\ell_0+2i}_{m'm_0}(-\phi_R,\theta_R,\phi_R) Y_{\ell_0+2i,m'}(\theta,\phi)^1$$

$$(C.7)$$

The last term of equation (C.4) can now be rewritten as

$$\sum_{j'm_j'} \sum_{im'} C_{\nu i} f_{\nu i}(r)\alpha(1) \langle Y_{\ell m_\ell}(\theta,\phi) Y_{jm_j}(\theta_R,\phi_R) |$$

$$D^{\ell_0+2i}_{m'm}(-\phi_R,\theta_R,\phi_R) Y_{\ell_0+2i,m'}(\theta,\phi) Y_{j'm_j'}(\theta_R,\phi_R) \rangle$$

$$= \sum_{ij',m_j',m'} C_{\nu i} f_{\nu i}(r)\alpha(1)\delta_{mm'}\delta_{\ell,\ell_0+2i}$$

$$\langle Y_{jm_j}(\theta_R,\phi_R)|D^{\ell}_{mm_0}(-\theta_R,\phi_R,\theta_R)Y_{j',m_j'}(\theta_R,\phi_R)\rangle$$

(C.8)

$$= \sum_{m_j,j'} \sum_{i} \delta_{i,(\ell-\ell_0)/2} C_{\nu i} f_{\nu i}(r)\alpha(1) \left[\frac{2j+1}{4\pi}\right]^{1/2}$$

$$\left[\frac{2j'+1}{4\pi}\right]^{1/2} \int D^{j}_{m_j 0}(\phi_R,\theta_R,0)D^{\ell}_{mm_0}(-\phi_R,\theta_R,\phi_R)$$

$$D^{j',*}_{m_j 0}(\phi_R,\theta_R,0)d\phi_R \sin\theta_R d\theta_R \quad . \qquad (C.9)$$

Since $D^{j}_{m0}(\alpha,\beta,0) = D^{j}_{m0}(\alpha,\beta,\gamma)$ (C.10)

and $D^{\ell}_{m',m}{}^{*}(\alpha,\beta,\gamma) = D^{\ell}_{m',m}(-\alpha,\beta,-\gamma)$, (C.11)

I can rewrite the right side of equation (C.9) as

$$\sum_{m_j,m'} \sum_{i} \delta_{i,(\ell-\ell_0)/2} C_{\nu i} f_{\nu i}(r)\alpha(1)\frac{((2j+1)(2j'+1))^{1/2}}{4\pi}$$

$$\int D^{j'}_{m_j 0}(-\phi_R,\theta_R,\phi_R)D^{\ell}_{mm_0}(-\phi_R,\theta_R,\phi_R)D^{j,*}_{m_j 0}(-\phi_R,\theta_R,\phi_R)$$

$$d\phi_R \sin\theta_R d\theta_R \qquad (C.12)$$

$$= \sum_{m_j,j'} \sum_{i} \delta_{i,(\ell-\ell_0)/2} C_{\nu i} f_{\nu i}(r)\alpha(1)\frac{((2j+1)(2j'+1))^{1/2}}{4\pi}$$

$$\sum_{j_1} C(j'\ell j_1, m_j' m_\ell m_j'+m) C(j'\ell j_1, m_0 0 m_0)$$

$$\int D^{j_1}_{m_j'+m_\ell, m_0}(-\phi_R, \theta_R, \phi_R) D^{j}_{m_j 0}{}^{*}(-\phi_R, \theta_R, \phi_R) d\phi_R \sin\theta_R d\theta_R \quad . \quad ^2$$

(C.13)

This integral can be written

$$\int_0^\pi d\theta_R \sin\theta_R \; d^{j_1}_{m_j'+m_\ell, m_0}(\theta_R) d^{j}_{m_j 0}(\theta_R) \int_0^{2\pi} d\phi_R \; e^{-im_0\phi_R}$$

$$e^{i(m_j'+m_\ell)\phi_R} \; e^{-im_j\phi_R}$$

$$= 2\pi\delta_{(m_j'+m_\ell)(m_j+m_0)} \int_0^\pi d\theta_R \sin\theta_R \; d^{j_1}_{m_j'+m_\ell, m_0}(\theta_R)$$

$$d^{j}_{m_j 0}(\theta_R) \; . \qquad \text{(C.14)}$$

Now, $d^{j_1}_{m_j'+m_\ell, m_0}(\theta_R) d^{j}_{m_j 0}(\theta_R) =$

$$\{(j_1+m_0)!(j_1-m_0)!(j_1+m_j'+m_\ell)!(j_1-m_j-m_\ell)!(j+m_j)!$$

$$(j-m_j)!j!j!\}^{1/2} \sum_{k_1 k_2} (-1)^{k_1+k_2}$$

$$\{(j_1-m_j'-m_\ell-k_1)!(j_1+m_0-k_1)!(k_1+m_j'+m_\ell-m_0)!k_1!$$

$$(j-m_j-k_2)!(j-k_2)!(k_2+m_j)!k_2!\}^{-1} \left[\sin(\theta_R/2)\right]^{2k_1+2k_2}$$

$$\left(\cos(\theta_R/2)\right)^{2j_1+m_0-m_j'-m_\ell-2k_1+2j-m_0+m_j'+m_\ell-2k_2} \quad ,$$

(C.15)

So that

$$\int_0^\pi d\theta_R \sin\theta_R \, d^{j_1}_{m_j'+m_\ell m_0}(\theta_R) d^{j}_{m_j 0}(\theta_R) =$$

$$\{(j!)^2(j_1+m_0)!(j_1-m_0)!(j_1+m_j+m_0)!(j_1-m_j-m_0)!$$

$$(j+m_j)!(j-m_j)!\}^{1/2} \sum_{k_1 k_2} (-1)^{k_1+k_2}$$

$$\{(j_1-m_j-m_0-k_1)!(j_1+m_0-k_1)!(k_1+m_j)!k_1!$$

$$(j-m_j-k_2)!(j-k_2)!(k_2+m_j)!k_2!\}^{-1}$$

$$\int_0^\pi d\theta_R \sin\theta_R (\cos\theta_R/2)^{2(j_1+j-k_1-k_2)} (\sin\theta_R/2)^{2(k_1+k_2)}$$

(C.16)

Integrating by parts

$$\int_0^\pi d\theta_R \sin\theta_R (\cos\theta_R/2)^{2(j_1+j-k_1-k_2)} (\sin\theta_R/2)^{2(k_1+k_2)}$$

$$= 2 \frac{(j_1+j-k_1-k_2)!(k_1+k_2+2)!}{(j_1+j+2)!(k_1+k_2+1)} \qquad \text{(C.17)}$$

Equation (C.16) becomes

$$\int_0^{\pi} d\theta_R \sin\theta_R d^{j_1}_{m_j', +m_\ell, m_0}(\theta_R) d^{j}_{m_j 0}(\theta_R) = \{(j_1+m_0)!$$

$$(j_1-m_0)!(j_1+m_j+m_0)!(j_1-m_j-m_0)!(j+m_j)!(j-m_j)!\}^{1/2}$$

$$j! \sum_{k_1 k_2} (-1)^{k_1+k_2} 2(j_1+j-k_1-k_2)!(k_1+k_2+2)!$$

$$\{(j_1-m_j-m_0-k_1)!(j_1+m_0-k_1)!(k_1+m_j)!k_1!(j-m_j-k_2)!$$

$$(j-k_2)!(k_2+m_j)!k_2!(j_1+j+2)!(k_1+k_2+1)\}^{-1}$$

(C.18)

I can now replace (C.8) with

$$\sum_{j' m_j'} \sum_{i m'} C_{\nu i} f_{\nu i}(r)\alpha(1) \langle Y_{\ell m_\ell}(\theta,\phi) Y_{j m_j}(\theta_R,\phi_R) |$$

$$D^{\ell_0+2i}_{m' m_0}(-\phi_R,\theta_R,\phi_R) Y_{\ell_0+2i, m'}(\theta,\phi) Y_{j' m_j'}(\theta_R,\phi_R) \rangle$$

$$= \sum_{j' m_j'} \sum_{i} \delta_{i,(\ell-\ell_0)/2} C_{\nu i} f_{\nu i}(r)\alpha(1)$$

$$\frac{(2j+1)^{1/2}(2j'+1)^{1/2}}{2} \sum_{j_1} C(j'\ell j_1, m_j'\ m_\ell\ m_j'+m_\ell)$$

$$C(j'\ell j_1, m_0 0 m_0)\delta_{(m_j'+m_\ell)(m_j+m_0)} \{(j_1+m_0)!$$

$$(j_1-m_0)!(j_1+m_j+m_0)!(j_1-m_j-m_0)!(j+m_j)!$$

$$(j-m_j)!\}^{1/2}\ j!/(j_1+j+2)!\ \sum_{k_1k_2} 2(-1)^{k_1+k_2}$$

$$(j_1+j-k_1-k_2)!(k_1+k_2+2)!\ \{(j_1-m_j-m_0-k_1)!$$

$$(j_1+m_0+k_1)!(k_1+m_j)!k_1!(j-m_j-k_2)!(j-k_2)!$$

$$(k_2+m_j)!k_2!(k_1+k_2+1)\}^{-1} \qquad \text{(C.19)}$$

$$\equiv \sum_i \delta_{i,(\ell-\ell_0)/2}\ C_{\nu i} f_{\nu i}(r)\alpha(1)I(jm_j\ell m_\ell m_0) \qquad \text{(C.20)}$$

So that

$$\langle Y_{\ell m_\ell}(\theta,\phi)Y_{jm_j}(\theta_R,\phi_R)|\Psi^M(N) \sum_{\nu jm_j} \{\chi^S_{\nu_0 j_0 m_{j_0},\nu j' m_j}(1)$$

$$+ C_\nu \chi^B_\nu(1)\}\chi_\nu(R)Y_{j'm_j}(\theta_R,\phi_R)\rangle = \Psi^M(N) \sum_\nu \Big\{ i^\ell$$

$$\sqrt{4\pi(2\ell+1)}\ j_\ell(k_0 r)\delta_{m_j m_{j_0}}\delta_{m_\ell 0}\delta_{\nu\nu_0}\delta_{jj_0}$$

$$+ e^{ik_{\nu j}r} f_{\ell m_\ell,\nu_0 j_0 m_{j_0},\nu j m_j}(r) + \sum_i \delta_{i,(\ell-\ell_0)/2}$$

$$C_{\nu i} f_{\nu i}(r)I(jm_j\ell m_\ell m_0)\Big\}\ \alpha(1)\chi_\nu(R) \qquad \text{(C.21)}$$

Thus the desired wave function is

$$\psi^{JMj\ell}(N+1,\vec{R}) = \sum_{m_\ell m_j} C(j\ell J, m_j m_\ell M)\, {}^2Y_{\ell m_\ell}(\theta,\phi)$$

$$Y_{jm_j}(\theta_R,\phi_R)\psi^M(N) \sum_\nu \Big\{ i^\ell \sqrt{4\pi(2\ell+1)}\; j_\ell(k_\nu r)$$

$$\delta_{m_j m_{j_0}} \delta_{m_\ell 0} \delta_{\nu\nu_0} \delta_{jj_0} + e^{ik_{\nu j} r} f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j m_j}(r)$$

$$+ \sum_i \delta_{i,(\ell-\ell_0)/2}\, C_{\nu i} f_{\nu i}(r) I(jm_j \ell m_\ell m_0) \Big\}$$

$$\alpha(1)\chi_\nu(R)$$

$$= \psi^M(N) \sum_{\nu m_\ell m_j} C(j\ell J, m_j m_\ell M)^2 \Big\{ i^\ell \sqrt{4\pi(2\ell+1)}$$

$$j_\ell(k_\nu r)\delta_{m_j m_{j_0}} \delta_{m_\ell 0} \delta_{\nu\nu_0} \delta_{jj_0} + e^{ik_{\nu j} r}$$

$$f_{\ell m_\ell, \nu_0 j_0 m_{j_0}, \nu j m_j}(r) + \sum_i \delta_{i,(\ell-\ell_0)/2}\, C_{\nu i} f_{\nu i}(r)$$

$$I(jm_j \ell m_\ell m_0) \Big\} Y_{\ell m_\ell}(\theta,\phi) Y_{jm_j}(\theta_R,\phi_R)\alpha(1)\chi_\nu(R) \,. \qquad \text{(C.23)}$$

[1] Rose, op. cit., p.60.

[2] ibid., p.58.

[3] ibid., p.52.

APPENDIX D

Listing of Computer Programs

I. The program used to find the H_2 wave function was:

```
      PROGRAM ENMAP2
      EN1 = 1.23   $   Z1 = 1.22
      R=1.25
      DO 10,K=1,2
      ALPHA=1.896+.001*K
      PRINT 30,R
      DO 10,I=1,5
      EN2=1.84+I*.01
      PRINT 40
      DO 10,J=1,7
      Z2=J*.01 +1.2
      E=EDEL(EN1,EN2,Z1,Z2,R,ALPHA)
 10   PRINT 20,E,Z2,EN2,ALPHA
 20   FORMAT(10X,F20.8,3F15.3)
 30   FORMAT(*1*21X*ENERGY*13X*Z2*13X*EN2*11X*ALPHA*10X*R=*F8.3)
 40   FORMAT ( X)
      END
      FUNCTION EDEL(EN1,EN2,Z1,Z2,R,ALPHA)
      TYPE REAL INBETA
      ENS=EN1+EN2   $   ZS=Z1+Z2   $   RHO1=Z1*R $ RHO2=Z2*R   $ A1=2*EN1
      A2=2*EN2   $   B2=A2+1   $   C2=A2-2   $   D2=A2+2   $   E3=A2+3 $B1=A1+1
      GENS=GAMIN(ENS-1.0,)$GB2=GAMIN(B2,0.)$BS=(ENS+1)*ENS*(ENS-1)*GENS
      EONE = Z2*Z2*(EN2+4)/(A2*(A2-1))
      ETWOA = GAMIN(A2,RHO2)/GB2
      ETWOB = (1-GAMIN(B2,RHO2)/GB2)/RHO2
      ETWOC = RHO2*RHO2*GAMIN(C2,RHO2)/(2.5*GB2)
      ETWOD = .4*(D2*B2-GAMIN(E3,RHO2)/GB2)/RHO2**3
      ETHREE = 2*Z1*INBETA(Z2/ZS,B2,A1)/EN1
      EFOUR = 2*Z2*INBETA(Z1/ZS,B1,A2)/EN2
      EFIVE=(2*Z1)**B1*(2*Z2)**B2*GENS*BS*INBETA(.5,ENS+2,ENS-1)/(GAMIN(
     CB1,0.)*GB2*ZS**(2*ENS+1)*1.5)
      ETWO = 4*Z2*(ETWOA+ETWOB+ETWOC+ETWOD)   $   CREP = ETHREE+EFOUR
      EDEL = EONE        +ALPHA*(CREP-ETWO-EFIVE)
      END
      REAL FUNCTION INBETA (X,P,Q)
      B=0 $ N=0
    1 PN=P+N $ CN=N
      IF(Q-N,EQ.0.) GO TO 2
      BA=(-1)**N*X**PN/(PN*GAMIN (Q-N,0.)*GAMIN (CN+1,0.))
      B=B+BA $ N=N+1 $ S=BA*10.**8/B   $ IF (S*S.GT.1.) 1,2
    2 INBETA=B*GAMIN (P+Q,0.)/GAMIN (P,0.)
      END
```

II. The program used to find the H_2^- wave function was:

```
      PROGRAM ENFIND
      TYPE DOUBLE 7
      COMMON /1/C(2,4),EN(2,4)
      COMMON / 2 / EDELA,EDELREAL,ALPHA,R
      COMMON / 3 / EINT,EKINETIC,M
      COMMON / 4 / I,J,M3
      COMMON / FIX / Z(2,4)
      ENN(I,J,K,L)=EN(I,J)+EN(K,L),                                    STF
      ZZ(I,J,K,L)=Z(I,J)+Z(K,L)                                        STF
      R=1.25  $  M=0
      I3=0
      M3=0
      DO 10, II=1,4                                                    10
      DO 10,JJ=1,2                                                     10
      EN(JJ,II)=C(JJ,II)=Z(JJ,II)=0
10    CONTINUE
      EN(1,1)=1.23  $  Z(1,1)=1.22  $  C(1,1)=1.
      EN(2,1)=1.572 $  Z(2,1)=0.527
      EN(2,2)=2.959  $ Z(2,2)=2.655
      EN(2,3)=10.618$ Z(2,3)=8.268
      C(2,1)=.749179 $ C(2,2)=.439276 $ C(2,3)=-.058261
      ALPHA=1.818
      J=2
      J=3
      I=2  $J=1
      FF=FACTOR(I)
      C(I,1)=FF*C(I,1)     $  C(I,2)=FF*C(I,2)
      C(I,3)=FF*C(I,3)     $  C(I,4)=FF*C(I,4)
      CALL ENERGY3
      D2=EDELA
5     M2=M
      M5=M3
      J=J-1
      IF(J.EQ.0) J=3
      FF=FACTOR(I)
      C(I,1)=FF*C(I,1)     $  C(I,2)=FF*C(I,2)
      C(I,3)=FF*C(I,3)     $  C(I,4)=FF*C(I,4)
      CALL ENERGY3
      D=EDELA
      PRINT 500
      IF (I5.LT.2) PRINT 100,EDELREAL,EDELA,ALPHA,R,((C(K,L),L=1,4),K=1,      100
     2 2),((EN(K,L),L=1,4),K=1,2),((Z(K,L),L=1,4),K=1,2)
      I5=1                                                             $$$ I5
      I4=0
86    NE=1




      IF (J.EQ.1) NE=2
40    M1=M
      M4=M3
      CALL ENERGY3
      I1=0
15    D1=EDELA
      EN(I,J) = EN(I,J)+.1**NE
      Z(I,J)=Z(I,J)+.1**NE
      CALL COPT
      I1=I1+1
      IF (EDELA.LT.D1) GO TO 15                                        15
      EDELA=D1
      EN(I,J)=EN(I,J)-.1**NE
      Z(I,J)=Z(I,J)-.1**NE
      IF (I1.EQ.1) GO TO 20                                            20
      GO TO 29                                                         29
20    D1=EDELA
      EN(I,J)=EN(I,J)-.1**NE
      Z(I,J)=Z(I,J)-.1**NE
      CALL COPT
      IF (EDELA.LT.D1) GO TO 20                                        20
      EDELA=D1
      EN(I,J) = EN(I,J)+.1**NE
      Z(I,J)=Z(I,J)+.1**NE
29    I2=0
```

```
30    D1=EDELA
      EN(I,J) = EN(I,J)+.1**NE
      Z(I,J)=Z(I,J)-.1**NE
      CALL COPT
      I2=I2+1
      IF (EDELA.LT.D1) GO TO 30                                          30
      EDELA=D1
      EN(I,J)=EN(I,J)-.1**NE
      Z(I,J)=Z(I,J)+.1**NE
      IF (I2.EQ.1) GO TO 50                                              50
      GO TO 60                                                           60
50    D1=EDELA
      EN(I,J)=EN(I,J)-.1**NE
      Z(I,J)=Z(I,J)+.1**NE
      CALL COPT
      IF (EDELA.LT.D1) GO TO 50                                          50
      EN(I,J) = EN(I,J)+.1**NE
      Z(I,J)=Z(I,J)-.1**NE
60    CALL COPT
      PRINT 300,M,M1,NE,I3,I4                                                300


      M1=M-M1
      M4=M3-M4
      IF((M4.GT.9).OR.(I2.GT.1).OR.(I1.GT.1)) GO TO 40
      NE=NE+1
      IF (NE.LT.4) GO TO 40                                              40
      M2=M-M2
      M5=M3-M5
      PRINT 200,M,M2,M3,M5                                                   200
      PRINT 500                                                              500
      CALL PSIGRAPH
      I3=I3+1
      PRINT 400,I3                                                       $$$$$400
      IF(D2.GT.EDELA) I3=0
      IF(D2.GT.EDELA) D2=EDELA
      PRINT 400,I3                                                       $$$$$400
      IF(I3.LT.2) GO TO 5                                                5
      PRINT 400,I3                                                       $$$$$400
100   FORMAT(/* TRUE ENERGY = *F15.8,10X*ADJUSTED ENERGY = *F12.8 ,10X
     2*ALPHA = *F7.4,10X*R = *F6.3//*     C(I,J)  = *8F15.6/*     EN(I,J)
     3= *8F15.6/*     Z(I,J)  = *8F15.6//)
200   FORMAT (* ENERGY3 CALLED *I5*  TIMES (TOTAL)*/* ENERGY3 CALLED *I5
     2*  TIMES (THIS TIME)*/* COPT    CALLED *I5*  TIMES (TOTAL)*/* COPT
     3    CALLED *I5*  TIMES (THIS TIME)*)
300   FORMAT (* M=*I5,7X*M1=*I5,10X*NE=*I5,10X*I3=*I5,7X*I4=*I5/*1*)
400   FORMAT (I15)                                                       $$$$$$$$
500   FORMAT (*1*)
999   CONTINUE                                                           $$$$$$$$
      END
      SUBROUTINE COPT
      TYPE DOUBLE Z
      COMMON /1/C(2,4),EN(2,4)
      COMMON / 2 / EDELA,EDELREAL,ALPHA,R
      COMMON / 4 / I,J,M3
      COMMON / FIX / Z(2,4)
      DIMENSION CR1(5)
      M3=M3+1
      FF=FACTOR(1)
      C(1,1)=FF*C(1,1)     $  C(1,2)=FF*C(1,2)
      C(1,3)=FF*C(1,3)     $  C(1,4)=FF*C(1,4)
      CALL ENERGY3
      D1=EDELA
      I1=0
      I2=0
      NC=2
      CR1(1)=1.




      CR1(2)=C(1,2)/C(1,1)
      CR1(3)=C(1,3)/C(1,1)
      CR1(4)=C(1,4)/C(1,1)
10    D=D1
      CR1(5)=CR1(J)
      IF (I2.EQ.0) CR1(J)=CR1(J)+.1**NC
      IF (I2.EQ.1) CR1(J)=CR1(J)-.1**NC
      C(1,1)=CR1(1) $ C(1,2)=CR1(2) $ C(1,3)=CR1(3) $ C(1,4)=CR1(4)
      FF=FACTOR(1)
      C(1,1)=FF*C(1,1)     $  C(1,2)=FF*C(1,2)
      C(1,3)=FF*C(1,3)     $  C(1,4)=FF*C(1,4)
      CALL ENERGY3
      D1=EDELA
```

```
      I1=I1+1
      IF(D1.LT.D) GO TO 10                                                  1/
      D1=D
      CR1(J)=CR1(5)
      I2=I1
      IF(I1.EQ.1) GO TO 10                                                  10
      C(I,1)=CR1(1) $ C(I,2)=CR1(2) $ C(I,3)=CR1(3) $ C(I,4)=CR1(4)
      FF=FACTOR(I)
      C(I,1)=FF*C(I,1)     $  C(I,2)=FF*C(I,2)
      C(I,3)=FF*C(I,3)     $  C(I,4)=FF*C(I,4)
      CALL ENERGY3
      NC=NC+1
      I1=0 $ I2=0
      IF(NC.LT.6) GO TO 10                                                  10
      PRINT 100,EDELREAL,EDELA,ALPHA,R,((C(K,L),L=1,4),K=1,2),((EN(K,L),    100
     2L=1,4),K=1,2),((Z(K,L),L=1,4),K=1,2)
100   FORMAT(/* TRUE ENERGY = *F15.8,10X*ADJUSTED ENERGY = *F12.9 ,10X
     2*ALPHA = *F7.4,10X*R = *F6.3//*     C(I,J)  = *8F15.6/*     EN(I,J)
     3= *8F15.6/*     Z(I,J)  = *8F15.6//)
      END
      SUBROUTINE PSIGRAPH
      TYPE DOUBLE Z
      DIMENSION OLD(73),ROLD(73)
      COMMON /1/C(2,4),EN(2,4)
      COMMON / FIX / Z(2,4)
      A(B,C)=C**(.5*B+.5)/GAMIN(B+1.0,)**.5                                 STF
      A1=A(2*EN(2,1),2*Z(2,1))
      A2=A(2*EN(2,2),2*Z(2,2))
      A3=A(2*EN(2,3),2*Z(2,3))
      SUM1=SUM2=SUM12=SUM3=0.
      SUM13=SUM23=SUM4=0.
      DO 10,I=1,73                                                          10

      R3=(I-11)*.2
      DELTA=.2
      IF(I.LT.22) R3=(I-1)*.1
      IF(I.LT.22) DELTA=.1
      IF(I.GE.32) R3=(I-23)*.5
      IF(I.GE.32) DELTA=.5
      PSI1=A1*R3**(EN(2,1)-1)*EXP(-R3*Z(2,1))
      PSI2=A2*R3**(EN(2,2)-1)*EXP(-R3*Z(2,2))
      PSI3=A3*R3**(EN(2,3)-1)*EXP(-R3*Z(2,3))
      RP1=PSI1*R3
      RP2=PSI2*R3
      RP3=PSI3*R3
      SUM1=SUM1+DELTA*RP1*RP1
      SUM2=SUM2+DELTA*RP2*RP2
      SUM3=SUM3+DELTA*RP3*RP3
      SUM12=SUM12+DELTA*RP1*RP2
      SUM13=SUM13+DELTA*RP1*RP3
      SUM23=SUM23+DELTA*RP2*RP3
      PSI4=C(2,1)*PSI1+C(2,2)*PSI2+C(2,3)*PSI3
      RP4=PSI4*R3
      SUM4=SUM4+DELTA*RP4*RP4
      DIFF=PSI4-OLD(I)
      RDIFF=RP4-ROLD(I)
      OLD(I)=PSI4
      ROLD(I)=RP4
10    PRINT 100,R3,PSI1,RP1,PSI2,RP2,PSI3,RP3,PSI4,RP4,DIFF,RDIFF           100
      PRINT 200,R3,SUM1,SUM2,SUM3,SUM4                                      200
      PRINT 300,SUM12,SUM13,SUM23                                           300
100   FORMAT (F7.3,5(F12.5,F10.5))
200   FORMAT(/F7.3,4(12X,F10.5))
300   FORMAT (/*      SUM12=*F10.5/*      SUM13=*F10.5/*      SUM23=*F10.5)
      END
      SUBROUTINE ENERGY3
      TYPE DOUBLE Z
      COMMON /1/C(2,4),EN(2,4)
      COMMON / 2 / EDELA,EDELREAL,ALPHA,R
      COMMON / 3 / EINT,FKINETIC,M
      COMMON / FIX / Z(2,4)
      ZZ(I,J,K,L)=Z(I,J)+Z(K,L)                                             STF
      RHO(I,J,K,L)=.5*R*ZZ(I,J,K,L)                                         STF
      ENN(I,J,K,L)=EN(I,J)+EN(K,L)                                          STF
      A(B,C)=C**(.5*B+.5)/GAMIN(B+1.0,)**.5                                 STF
      M=M+1
      EINT=0
      DO 10,K=1,4
```

```
      IF ( C(2,K).EQ.0.) GO TO 10
      DO 10 L=1,4
      IF ( C(2,L).EQ.0.) GO TO 10
      REPSUM      =0
      DO 20 I=1,4
      IF (C(1,I).EQ.0.) GO TO 20
      DO 20 J=1,4
      IF (C(1,J).EQ.0.) GO TO 20
      REPSUM      =REPSUM      +C(1,I)*C(1,J)*A(ENN(1,I,1,I),ZZ(1,I,1,I))
     2*A(ENN(1,J,1,J),ZZ(1,J,1,J))*REP(I,J,K,L)
20    CONTINUE
      EINT=EINT+C(2,K)*C(2,L)*A(ENN(2,K,2,K),ZZ(2,K,2,K))*A(ENN(2,L,2,L)
     2,ZZ(2,L,2,L))*(REPSUM-ATTR(K,L))
10    CONTINUE
      EKINETIC=0
      DO 30 K1=1,4
      IF (C(2,K1).EQ.0.) GO TO 30
      DO 30 L1=1,4
      IF (C(2,L1).EQ.0.) GO TO 30
      PART1 = Z(2,L1)*Z(2,L1)*EN(2,K1)*(EN(2,K1)-1)-2*Z(2,L1)*Z(2,K1)
     2*EN(2,L1)*EN(2,K1)+Z(2,K1)*Z(2,K1)*EN(2,L1)*(EN(2,L1)-1)-2*ZZ(2,K1  PART1 2
     3,2,L1)**2                                                           PART1 3
      PART2 = A(ENN(2,K1,2,L1),ZZ(2,K1,2,L1))**2*2*ENN(2,K1,2,L1)*(ENN(2  PART2 1
     2,K1,2,L1)-1)                                                        PART2 2
      PART3 = C(2,K1)*C(2,L1)*A(ENN(2,K1,2,K1),ZZ(2,K1,2,K1))*A(ENN(2,L1  PART3 1
     2,2,L1),ZZ(2,L1,2,L1))                                               PART3 2
      EKINETIC = EKINETIC-PART3/PART2*PART1
30    CONTINUE
      EDELREAL =EKINETIC+EINT
      EDELA = EKINETIC+ALPHA*EINT
      END
      FUNCTION REP(I,J,K,L)
      TYPE DOUBLE Z
      COMMON /1/C(2,4),EN(2,4)
      COMMON / FIX / Z(2,4)
      TYPE REAL INBETA
      ZZ(A,B,C,D)=Z(A,B)+Z(C,D)                                          STF
      RHO(A,B,C,D)=.5*B*ZZ(A,B,C,D)                                      STF
      ENN(A,B,C,D)=EN(A,B)+EN(C,D)                                       STF
      ENC(I,J,K,L) = ENN(I,J,K,L)                                        STF
      BETA(I,J,K,L) = INBETA(ZZ(I,J,K,L)/ZZ,ENN(I,J,K,L)+1,ENC(I,J,K,L))STF
      BETA3(I,J,K,L)=INBETA(ZZ(I,J,K,L)/ZZ,ENN(I,J,K,L)+2,ENC(I,J,K,L)-1)STF
      A(B,C)=C**(.5*B+.5)/GAMIN(B+1.0.)**.5                              STF
      ENS = EN(I,I)+EN(I,J)+EN(2,K)+EN(2,L)
      ZS = Z(I,I)+Z(I,J)+Z(2,K)+Z(2,L)
      REP1 = 2*BETA(2,K,2,L)        /(A(ENN(I,I,I,J)-1,ZZ(I,I,I,J))*       F REP1
                                                                             REP1
     2A(ENN(2,K,2,L),ZZ(2,K,2,L)))**2                                        REP1
      REP2  =  2*BETA(I,I,I,J)     /(A(ENN(2,K,2,L)-1,ZZ(2,K,2,L))*       S REP2
                                                                             REP2
     2A(ENN(I,I,I,J),ZZ(I,I,I,J)))**2                                        REP2
      REP3  =  -1./3*BETA3(2,K,I,J)  /(A(ENN(I,I,2,L)-2,ZZ(I,I,2,L))*        REP3
                                                                             REP3
     2A(ENN(2,K,I,J)+1,ZZ(2,K,I,J)))**2                                      REP3
      REP4  =  -1./3*BETA3(I,I,2,L)  /(A(ENN(2,K,I,J)-2,ZZ(2,K,I,J))*        REP4
                                                                             REP4
     2A(ENN(I,I,2,L)+1,ZZ(I,I,2,L)))**2
      REP=REP1+REP2+REP3+REP4
      END
      FUNCTION ATTR(K,L)
      TYPE DOUBLE Z
      COMMON /1/C(2,4),EN(2,4)
      COMMON / 2 / EDELA,EDELREAL,ALPHA,R
      COMMON / FIX / Z(2,4)
      ZZ = Z(2,K)+Z(2,L)
      RHO = .5*R*ZZ
      ENN = EN(2,K)+EN(2,L)
      ATTR = 2/ZZ**ENN*(GAMIN(ENN,RHO)+1/RHO*(GAMIN(ENN+1.0.)-GAMIN(ENN+  ATTR 1
     21,RHO))+.4*RHO**2*GAMIN(ENN-2,RHO)+.4/RHO**3*(GAMIN(ENN+3.0.)-GAMI  ATTR 2
     3N(ENN+3,RHO)))                                                      ATTR 3
      END
      FUNCTION FACTOR(I)
      TYPE DOUBLE Z
      COMMON /1/C(2,4),EN(2,4)
      COMMON / FIX / Z(2,4)
      ENN(I,J,K,L)=EN(I,J)+EN(K,L)                                       STF
      ZZ(I,J,K,L)=Z(I,J)+Z(K,L)                                          STF
      A(B,C)=C**(.5*B+.5)/GAMIN(B+1.0.)**.5                              STF
      CC(J,K)=C(I,J)*C(I,K)                                              STF
      IF(CC(1,2).EQ.0) GO TO 2                                           2
```

```
1     FACT1=C(I,1)*C(I,2)*A(ENN(I,1,I,1),ZZ(I,1,I,1))*A(ENN(I,2,I,2),ZZ(
     2I,2,I,2))/(A(ENN(I,1,I,2),ZZ(I,1,I,2))**2)                          1
2     IF(CC(1,3).EQ.0) GO TO 3                                             3
      FACT2=C(I,1)*C(I,3)*A(ENN(I,1,I,1),ZZ(I,1,I,1))*A(ENN(I,3,I,3),ZZ(
     2I,3,I,3))/(A(ENN(I,1,I,3),ZZ(I,1,I,3))**2)                          2
3     IF(CC(1,4).EQ.0) GO TO 4                                             4
      FACT3=C(I,1)*C(I,4)*A(ENN(I,1,I,1),ZZ(I,1,I,1))*A(ENN(I,4,I,4),ZZ(
     2I,4,I,4))/(A(ENN(I,1,I,4),ZZ(I,1,I,4))**2)                          3
4     IF(CC(2,3).EQ.0) GO TO 5                                             5
      FACT4=C(I,2)*C(I,3)*A(ENN(I,2,I,2),ZZ(I,2,I,2))*A(ENN(I,3,I,3),ZZ(
     2I,3,I,3))/(A(ENN(I,2,I,3),ZZ(I,2,I,3))**2)                          4
5     IF(CC(2,4).EQ.0) GO TO 6                                             6
      FACT5=C(I,2)*C(I,4)*A(ENN(I,2,I,2),ZZ(I,2,I,2))*A(ENN(I,4,I,4),ZZ(
     2I,4,I,4))/(A(ENN(I,2,I,4),ZZ(I,2,I,4))**2)                          5




6     IF(CC(3,4).EQ.0) GO TO 7                                             7
      FACT6=C(I,3)*C(I,4)*A(ENN(I,3,I,3),ZZ(I,3,I,3))*A(ENN(I,4,I,4),ZZ(
     2I,4,I,4))/(A(ENN(I,3,I,4),ZZ(I,3,I,4))**2)                          6
7     FACT7=C(I,1)**2+C(I,2)**2+C(I,3)**2+C(I,4)**2
      FACT8=2*(FACT1+FACT2+FACT3+FACT4+FACT5+FACT6)
      FACTOR=(FACT7+FACT8)**(-.5)
      END
```

III.The program used to find the scattering amplitudes and phase shifts was:

```
      PROGRAM NU1
      TYPE COMPLEX SUM,PART2,INC,X,PSI1,PS12,PSI3,VR,A,EXCH,COUL
      RR,R,R,R                                                        STF
      NU=2
      NU=1
      NU=0
      RR=1.4
      R=1R.3851
      BSQ=4.2R778
      BSQR=6.002R9
      BSQR2=36.034R
      BSQR3=216.313
      P2=.9641R96
      P22=.39R9423
      BSQR4=BSQR2**2
      BSQR5=BSQR2*BSQR3
      BSQR6=BSQR3**2
      BSQR7=BSQR3*BSQR4
      DO 30,I=1,15
      R=0.
      WN=.15+.05*I
      SUM=0.
      C1= 0.3R0803R9
      C2= 5.29565747
      C4= 0.07611600
      C7=1.772453R*1.7320508
10    CONTINUE
      IF(R.LT.10) EPS=.01
      IF (R.LT..0991) EPS=.001
      R=R+EPS
      RK=WN*R
      SR=SIN(RK)
      CR=COS(RK)
      T1=SR/RK-CR
      J1=T1/RK
      J2=SR-J1*2
      J3=(2-RK**2)*J1-2*J2
      IF (NU.EQ.0) GO TO 60
      IF(NU.EQ.1.) GO TO 40
      IF (NU.EQ.2.) GO TO 50
60    IF(R.GT. .7) GO TO 61
      TERM=BSQ*P2*(1/(2*R)*GI(1,R)+1/RR*(2*G(1)-GI(1,R)-1/BSQR*GI(2,R)+1
     2/BSQR2*(2*G(3)-GI(3,R))-1/BSQR3*GI(4,R)+1/BSQR4*(2*G(5)-GI(5,R))-1
     3/BSQR5*GI(6,R)+1/BSQR6*(2*G(7)-GI(7,R))-1/BSQR7*GI(8,R)))
      GO TO 80



61    IF(R.GT.1.4) GO TO 62
      TERM=BSQ*P2*(1/(R*2)*(2*G(1)-GI(1,R))+1/RR*(GI(1,R)-1/BSQR*GI(2,R)
     2+1/BSQR2*GI(3,R)-1/BSQR3*GI(4,R)+1/BSQR4*GI(5,R)-1/BSQR5*GI(6,R)+1
     3/BSQR6*GI(7,R)-1/BSQR7*GI(8,R)))
      GO TO 80
62    CONTINUE
      TERM=BSQ*P2*G(1)/2
      GO TO 80
40    IF(R.GT. .7) GO TO 41
      TERM=BSQ*P22*(-GI(2,R)/R+2/RR*(GI(2,R)-1/BSQR*(2*G(3)-GI(3,R))+1/B
     2SQR2*GI(4,R)-1/BSQR3*(2*G(5)-GI(5,R))+1/BSQR4*GI(6,R)-1/BSQR5*(2*G
     3(7)-GI(7,R))+1/BSQR6*GI(8,R)-1/BSQR7*(2*G(9)-GI(9,R))))
      GO TO 70
41    IF(R.GT.1.4) GO TO 42
      TERM=BSQ*P22*(-GI(2,R)/R+2/RR*(GI(2,R)-1/BSQR*GI(3,R)+1/BSQR2*GI(4
     2,R)-1/BSQR3*GI(5,R)+1/BSQR4*GI(6,R)-1/BSQR5*GI(7,R)+1/BSQR6*GI(8,R
     3)-1/BSQR7*GI(9,R)))
      GO TO 70
42    CONTINUE
      TERM=0
      GO TO 70
```

```
50    IF(R.GT. .7) GO TO 51
      TERM=.5*BSQ*P22*(1/R*(2*GI(3,R)-GI(1,R))+2/RR*(4*G(3)-2*GI(3,R)+GI
     2(1,R)-2*G(1)-1/BSQR*(2*GI(4,R)-GI(2,R))+1/BSQR2*(4*G(5)-2*GI(5,R)+
     3GI(3,R)-2*G(3))-1/BSQR3*(2*GI(6,R)-GI(4,R))+1/BSQR4*(4*G(7)-2*GI(7
     4,R)+GI(5,R)-2*G(5))-1/BSQR5*(2*GI(8,R)-GI(6,R))+1/BSQR6*(4*G(9)-2*
     5GI(9,R)+GI(7,R)-2*G(7))-1/BSQR7*(2*GI(10,R)-GI(8,R))))
      GO TO 70
51    IF(R.GT.1.4) GO TO 52
      TERM=.5*BSQ*P22*(1/R*(4*G(3)-2*GI(3,R)+GI(1,R)-2*G(1))+2/RR*(2*GI(
     23,R)-GI(1,R)-1/BSQR*(2*GI(4,R)-GI(2,R))+1/BSQR2*(2*GI(5,R)-GI(3,R)
     3)-1/BSQR3*(2*GI(6,R)-GI(4,R))+1/BSQR4*(2*GI(7,R)-GI(5,R))-1/BSQR5*
     4(2*GI(8,R)-GI(6,R))+1/BSQR6*(2*GI(9,R)-GI(7,R))-1/BSQR7*(2*GI(10,R
     5)-GI(8,R))))
      GO TO 70
52    CONTINUE
      TERM=0
      GO TO 70
80    CONTINUE
      X=(0.,1.)*PK
      PSI1=(0.,2.)*C7*J1+3*C4*(C1*R**.6R2*EXP(-.607*R)+C2*R**1.852*EXP(-
     22.752*R))
      PSI2=(0.,2.)*C7*J2+3*C4*(C1*R**.6R2*EXP(-.607*R)*(.6R2-.607*R)+C2*
     2R**1.852*EXP(-2.752*R)*(1.852-2.752*R))
      PSI3=(0.,1.)*C7*J3+3*C4*(C1*R**.6R2*EXP(-.607*R)*(-.6R2*.718/2-.60
     2*.6R2*R+(.607*R)**2)+C2*(1.852*.852/2-2.752*1.852*R+(2.752*R)**2)
     3)
      VR=(PSI3+PSI2)
      EXC2=3*C4*(1/R **2*(C1*1.827**(-2.912)*(GAMIN(2.912,0.)-GAMIN(2.91
     22,1.827*R))+C2*3.272**(-4.0R2)*(GAMIN(4.0R2,0.)-GAMIN(4.0R2,3.272*
     3R)))+R *(C1*1.827**(.0R0)*GAMIN(.0R0,1.827*R)+C2*3.272**(-1.0R2)*G
     4AMIN(1.0R2,3.272*R)))
      A=EXCH(R,WN)
      COUL=1/R*(2.44**(-1.46)*(GAMIN(1.46,0.)-GAMIN(1.46,2.44*R))+2.44**
     2(-.46)*GAMIN(.46,2.44*R))*PSI1-A/6-EXC2/6
      INC=(COUL+(1/(3.141592653**1.772453R)*TERM+1.-.5*RK**2)*PSI1-VR)*C
     2EXP(-X)*EPS
      GO TO 90
70    CONTINUE
      X=(0.0,-1.)*WN*R
      FR=C1*R**.6R2*EXP(-.607*R)+C2*R**1.852*EXP(-2.752*R)
      INC = C4*FR*CEXP(X)*P22*TERM/3.141592654*EPS
      IF(NU.EQ.1) INC=4*INC
90    CONTINUE
      SUM=SUM+INC
      IF(R.LT.3.01) GO TO 10
20    CONTINUE
      PART2=SUM*WN*(0.,1.)/(4*3.141592654*1.7724538)
      IF (NU.EQ.0.) PART2=PART2+1
      AMP=CABS(PART2)
      PART2=(0.,1.)*CLOG(AMP/PART2)/3.141592654
      AMP=AMP**2
      PRINT 400,NU,WN,AMP,PART2
400   FORMAT (6H   NU=,I2,10X,3HWN=,F5.2,10X,4HAMP=,E15.7,10X,*PHASE SHI
     2FT=*,2(F10.5,F10.5),10H  TIMES PI//)
30    CONTINUE
      END
      FUNCTION G(N)
      G=GAMIN(.5*N,0.)
      END
      FUNCTION GI(N,X)
      GI=GAMIN(.5*N,18.3851 *(1.4-2*X)**2)
      END
      COMPLEX FUNCTION EXCH (RP,WN)
      TYPE REAL LARGE
      R=.0001
      EXCH=(0.,0.)
10    CONTINUE
      RK=R*WN
      SR=SIN(RK)/RK-COS(RK)
      C=2*1.772453R*1.7320508
      EX=EXP(-1.22*R)
      IF (R.LE.RP) SMALL= R**.23*SR*C/RP**2
      IF (R.GT.RP) SMALL= R**(-2.77)*SR*C*RP
      LARGE=EX*SMALL*.001/WN
      IF (R.GT..1) LARGE=10*LARGE
      IF (R.LT..03)LARGE=.1*LARGE
      EXCH=EXCH+LARGE*(0.,1.)
      IF (R.LT..03)GO TO 20
      IF (R.GT..09999) R=R+.01
      IF (R.LT..1) R=R+.001
      IF (R.LT.9) GO TO 10
20    CONTINUE
      IF (R.LT..03)R=R+.0001
      IF (R.LT..03001) GO TO 10
      END
```

IV. GAMIN(ALPHA,X): In the above programs variables of the form GAMIN(ALPHA,X) are in fact calls to a library subroutine which calculates and returns the value of $\Gamma(\alpha,x)$, the incomplete gamma function. The same subroutine can be, and is, used with x=0 to calculate the gamma function wherever it is needed.

V. Data: The original output, listing the scattering amplitudes and phase shifts, is here reproduced:

NU	WN	AMP	PHASE SHIFT		
NU= 0	WN= 0.20	AMP= 7.9841363-001	PHASE SHIFT= -0.17266	0.00000	TIMES PI
NU= 0	WN= 0.25	AMP= 6.9993081-001	PHASE SHIFT= -0.22162	0.00000	TIMES PI
NU= 0	WN= 0.30	AMP= 5.9344594-001	PHASE SHIFT= -0.27550	-0.00000	TIMES PI
NU= 0	WN= 0.35	AMP= 4.8737900-001	PHASE SHIFT= -0.33699	0.00000	TIMES PI
NU= 0	WN= 0.40	AMP= 3.8982051-001	PHASE SHIFT= -0.40937	0.00000	TIMES PI
NU= 0	WN= 0.45	AMP= 3.1028002-001	PHASE SHIFT= -0.49733	-0.00000	TIMES PI
NU= 0	WN= 0.50	AMP= 2.5841382-001	PHASE SHIFT= -0.60468	-0.00000	TIMES PI
NU= 0	WN= 0.55	AMP= 2.4393852-001	PHASE SHIFT= -0.72086	0.00000	TIMES PI
NU= 0	WN= 0.60	AMP= 2.7633771-001	PHASE SHIFT= -0.85001	0.00000	TIMES PI
NU= 0	WN= 0.65	AMP= 3.6456923-001	PHASE SHIFT= -0.96961	0.00000	TIMES PI
NU= 0	WN= 0.70	AMP= 5.1678043-001	PHASE SHIFT= 0.93672	0.00000	TIMES PI
NU= 0	WN= 0.75	AMP= 7.4003882-001	PHASE SHIFT= 0.86059	-0.00000	TIMES PI
NU= 0	WN= 0.80	AMP= 1.0400851+000	PHASE SHIFT= 0.79720	0.00000	TIMES PI
NU= 0	WN= 0.85	AMP= 1.4211151+000	PHASE SHIFT= 0.74277	-0.00000	TIMES PI
NU= 0	WN= 0.90	AMP= 1.8855967+000	PHASE SHIFT= 0.69453	0.00000	TIMES PI

NU= 1 WN= 0.20 AMP= 4.9689490-009 PHASE SHIFT= -0,52000 0,00000 TIMES PI

NU= 1 WN= 0.25 AMP= 7.1247944-009 PHASE SHIFT= -0,53510 -0,00000 TIMES PI

NU= 1 WN= 0.30 AMP= 1.0251249-008 PHASE SHIFT= -0,54213 0,00000 TIMES PI

NU= 1 WN= 0.35 AMP= 1.3939499-008 PHASE SHIFT= -0,54915 0,00000 TIMES PI

NU= 1 WN= 0.40 AMP= 1.8186231-008 PHASE SHIFT= -0,55617 -0,00000 TIMES PI

NU= 1 WN= 0.45 AMP= 2.2987630-008 PHASE SHIFT= -0,56319 0,00000 TIMES PI

NU= 1 WN= 0.50 AMP= 2.8339384-008 PHASE SHIFT= -0,57021 -0,00000 TIMES PI

NU= 1 WN= 0.55 AMP= 3.4236690-008 PHASE SHIFT= -0,57724 0,00000 TIMES PI

NU= 1 WN= 0.60 AMP= 4.0674256-008 PHASE SHIFT= -0,58426 0,00000 TIMES PI

NU= 1 WN= 0.65 AMP= 4.7646305-008 PHASE SHIFT= -0,59128 -0,00000 TIMES PI

NU= 1 WN= 0.70 AMP= 5.5146586-008 PHASE SHIFT= -0,59831 -0,00000 TIMES PI

NU= 1 WN= 0.75 AMP= 6.3168378-008 PHASE SHIFT= -0,60533 -0,00000 TIMES PI

NU= 1 WN= 0.80 AMP= 7.1704493-008 PHASE SHIFT= -0,61236 -0,00000 TIMES PI

NU= 1 WN= 0.85 AMP= 8.0747289-008 PHASE SHIFT= -0,61938 -0,00000 TIMES PI

NU= 1 WN= 0.90 AMP= 9.0288473-008 PHASE SHIFT= -0,62641 -0,00000 TIMES PI

NU= 2 WN= 0.20 AMP= 4.1682781-013 PHASE SHIFT= 0,52065 -0,00000 TIMES PI

NU= 2 WN= 0.25 AMP= 6.0238521-013 PHASE SHIFT= 0,53285 0,00000 TIMES PI

NU= 2 WN= 0.30 AMP= 8.7498181-013 PHASE SHIFT= 0,53876 -0,00000 TIMES PI

NU= 2 WN= 0.35 AMP= 1.3610285-012 PHASE SHIFT= 0,54433 0,00000 TIMES PI

NU= 2 WN= 0.40 AMP= 1.8287820-012 PHASE SHIFT= 0,54953 -0,00000 TIMES PI

NU= 2 WN= 0.45 AMP= 2.3877310-012 PHASE SHIFT= 0,55433 -0,00000 TIMES PI

NU= 2 WN= 0.50 AMP= 3.0485792-012 PHASE SHIFT= 0,55871 -0,00000 TIMES PI

NU= 2 WN= 0.55 AMP= 3.8232271-012 PHASE SHIFT= 0,56264 0,00000 TIMES PI

NU= 2 WN= 0.60 AMP= 4.7247515-012 PHASE SHIFT= 0,56614 -0,00000 TIMES PI

NU= 2 WN= 0.65 AMP= 5.7673824-012 PHASE SHIFT= 0,56917 -0,00000 TIMES PI

NU= 2 WN= 0.70 AMP= 6.9664786-012 PHASE SHIFT= 0,57176 -0,00000 TIMES PI

NU= 2 WN= 0.75 AMP= 8.3385089-012 PHASE SHIFT= 0,57390 0,00000 TIMES PI

NU= 2 WN= 0.80 AMP= 9.9109838-012 PHASE SHIFT= 0,57560 0,00000 TIMES PI

NU= 2 WN= 0.85 AMP= 1.1672504-011 PHASE SHIFT= 0,57687 0,00000 TIMES PI

NU= 2 WN= 0.90 AMP= 1.3672650-011 PHASE SHIFT= 0,57773 0,00000 TIMES PI