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CORRECTIONS TO THE BORN-OPPENHEIMER APPROXIMATION

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Part II

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VI. ADIABATIC CORRECTIONS TO LONG-RANGE BO POTENTIALS

In the previous section the electronic wavefunctions for large R were expressed in terms of products of atomic wavefunctions, $\phi(c)$, characterized by definite atomic parity, $\mathcal{P}_c$, and angular momenta, L_c, S_c, J_c, and M_c. The large R expansion of the BO electronic Hamiltonian was also expressed at Eq. (5-13) in terms of atomic irreducible spherical tensors of definite atomic parity. In this section the adiabatic corrections are similarly expressed, and parity and the Wigner-Eckart theorem[83] are used to find selection rules on the corrections. More detail on the procedure is given in Appendix D. It should be noted that some of the corrections allowed to be non-zero by these selection rules may still contain equal terms of opposite signs that cancel each other and leave the correction zero. Everything in this section is diagonal in the good quantum numbers Ω, $\bar{p}$, and $\bar{\mathcal{P}}_e$, and they will not be explicitly written. The "resonant" and "non-resonant" cases introduced at Eq. (5-72) are considered in order, and at the end of the section the meaning and importance of the corrections are discussed.

A. The "Resonant" Case

In this subsection it is assumed that the system consists of identical atoms in states of different energies; that is, with $k_a \neq k_b$. The true resonance case is a subcase of this and is defined below. In order to more clearly see the relative importance of the corrections obtained, the selection rules on the static or BO potential are reviewed first, and then the selection rules on the corrections are obtained.

1. The BO Potential

The selection rules on the long range BO potential have been treated in detail by Knipp[84], Fontana[85], and Chang[80]. They are only sketched here. The coefficients $\mathcal{E}_{js}^{(n)}$, for n = 3, 4, and 5 are given by Eq. (5-25), which now becomes

$$\mathcal{E}_{js}^{(n)} = \sum_{J_a' J_b'} \sum_{M_a' M_b'} \sum_{J_a J_b} \sum_{M_a M_b} \sum_{\ell=1}^{n-2} \sum_{m} G(n\ell m) \langle ' | \Psi_{js}^{(0)} \rangle^{*} \langle \; | \Psi_{js}^{(0)} \rangle \, [\;] , \tag{6-1}$$

where $[\;]$ can be written in the form,

$$\begin{aligned}[\;] = {} & \langle \phi(a;a') | \mathcal{M}_{\ell}^{m}(a) | \phi(a;a) \rangle \langle \phi(b;b') | \mathcal{M}_{n-1-\ell}^{-m}(b) | \phi(b;b) \rangle \; + \\ & (-1)^{8} \langle \phi(a;a') | \mathcal{M}_{\ell}^{m}(a) | \phi(a;b) \rangle \langle \phi(b;b') | \mathcal{M}_{n-1-\ell}^{-m}(b) | \phi(b,a) \rangle .\end{aligned} \tag{6-2}$$

The notation is explained in connection with Eq. (5-69). One has here $k_a' = k_a$ and $k_b' = k_b$ because only the energy degenerate quantum numbers are included in the summation. The first product of integrals in (6-2) will be called the "diagonal part" of (6-2); the second product of integrals will be called the "off-diagonal part" of (6-2).

Now let us first consider

$$\mathcal{E}_{js}^{(3)} = \langle \Psi_{js}^{(0)} | \mathcal{H}_{s}^{(3)} | \Psi_{js}^{(0)} \rangle \quad . \qquad \text{(6-3)}$$

The atomic tensors $\mathcal{M}_{\ell}^{m}$ have atomic parity $(-1)^{\ell}$, and in this sum only the odd parity $\mathcal{M}_{1}^{m}$ appear. All of the diagonal parts of (6-2) vanish for this case, and from the Wigner-Eckart theorem (Appendix D), the off-diagonal parts of (6-2) also vanish unless

$$\begin{gathered} \mathcal{P}_a \neq \mathcal{P}_b , \\ |J_b - 1| \leq J_a \leq J_b + 1 , \\ |L_b - 1| \leq L_a \leq L_b + 1 , \text{ and} \\ S_a = S_b . \end{gathered} \qquad \text{(6-4)}$$

The last two restrictions hold because the $\mathcal{M}_{\ell}^{m}$ only act on configuration space. If (6-4) holds, then one has

$$\mathcal{E}_{js}^{(3)} \neq 0 , \qquad \text{(6-5)}$$

which is the true <u>resonance</u> interaction.

To consider $\mathcal{E}_{is}^{(4)}$ one observes that for even n the product $\mathcal{M}_{\ell}^{m}(a)\mathcal{M}_{n-1-\ell}^{-m}(b)$ always consists of one tensor of <u>even</u> parity and one tensor of <u>odd</u> parity. This makes one of the integrals in each term in (6-2) always vanish and leads to the result that, for <u>even</u> n ,

$$\langle \psi_{is}^{(0)} | \mathcal{H}_s^{(n)} | \psi_{js}^{(0)} \rangle = 0, \quad \text{all } i,j \leq g_\Omega . \tag{6-6}$$

Thus, one always has

$$\mathcal{E}_{js}^{(4)} = 0. \tag{6-7}$$

In Eq. (6-1) for $\mathcal{E}_{js}^{(5)}$, examination of the possible tensors shows that one can have

$$\mathcal{E}_{js}^{(5)} \neq 0, \tag{6-8}$$

if either

$$\begin{gathered} \wp_a = \wp_b, \\ |J_a - J_b| \leq 2 \leq J_a + J_b, \\ |L_a - L_b| \leq 2 \leq L_a + L_b, \text{ and} \\ S_a = S_b, \end{gathered} \tag{6-9}$$

or else

$$\begin{gathered} \wp_a \neq \wp_b, \\ |J_a - J_b| \leq 1 \leq 3 \leq J_a + J_b, \\ |L_a - L_b| \leq 1 \leq 3 \leq L_a + L_b, \text{ and} \\ S_a = S_b. \end{gathered} \tag{6-10}$$

The first integral in Eq. (5-26) for $\mathcal{E}_{js}^{(6)}$ vanishes from (6-7). The second one is

$$\mathcal{E}_{js}^{(6)} = \langle \Psi_{js}^{(0)} | \mathcal{H}_s^{(3)} | \Psi_{js}^{(0)} \rangle , \tag{6-11}$$

$$= \sum_{k}^{g_\Omega}{}' \langle \Psi_{ks}^{(0)} | \Psi_{js}^{(3)} \rangle \langle \Psi_{js}^{(0)} | \mathcal{H}_s^{(3)} | \Psi_{ks}^{(0)} \rangle - \sum_{\ell > g} \frac{| \langle \Phi_\ell^J | \mathcal{H}_s^{(3)} | \Psi_{js}^{(0)} \rangle |^2}{\mathcal{E}_{\ell s}^{(0)} - \mathcal{E}_{js}^{(0)}} . \tag{6-12}$$

The first term vanishes if $\mathcal{H}_s^{(3)}$ is fully diagonal in the set of degenerate zeroth-order wavefunctions. The second term is the van der Waals coefficient and never vanishes.

2. The Mass Polarization Corrections

The mass polarization correction to the electronic Hamiltonian is given by Eq. (5-30),

$$\mathcal{H}_\mu^{(0)}(m) = \frac{\mu}{2m_a} \underset{\sim}{P}_a^2 + \frac{\mu}{2m_b} \underset{\sim}{P}_b^2 . \tag{6-13}$$

$\mathcal{H}_\mu^{(0)}(m)$ contributes even at $R = \infty$. Had it been included in the separated atom Hamiltonian and that solved exactly, the $\mathcal{E}_{j\mu}^{(k)}(m)$ would not appear; hence, they simply correct for the fact that we used fixed-nucleus atomic wavefunctions rather than exact atomic wavefunctions.

Before considering the energy corrections, Eq. (5-35 to 38), let us consider the more general matrix element,

$$\langle \psi_{is}^{(0)} | \mathcal{H}_{\mu}^{(1)}(m) | \psi_{js}^{(0)} \rangle , \tag{6-14}$$

where $i, j \leq g_{\Omega}$. Substituting into this, one gets a sum similar to Eq. (6-1) and matrix elements similar to Eq. (6-2) with one $\mathcal{M}_{\ell}^{m}$ replaced by $\underset{\sim}{P}_{c}^{2}$, the other replaced by unity. Because $k_a \neq k_b$, orthogonality makes the off-diagonal parts vanish. Also $\underset{\sim}{P}_{c}^{2}$ is a zero rank, even parity atomic tensor depending only on the configuration space. Using the Wigner-Eckart theorem (see Appendix D) the equivalent of Eq. (6-2) becomes

$$[\,] = \frac{1}{4} \delta_{b'b} \delta_{a'a} \left[\langle \phi(a;a) \| \underset{\sim}{P}_{a}^{2} \| \phi(a;a) \rangle + \langle \phi(b;b) \| \underset{\sim}{P}_{b}^{2} | \phi(b;b) \rangle \right] , \tag{6-15}$$

where $\mu/2m_a = \mu/2m_b = 1/4$ for like atoms. These reduced matrix elements $\langle \| \, \| \rangle$ depend only on k_a and k_b . They can be factored out of the (6-1)-type sum, and from Eq. (5-73) one obtains

$$\langle \psi_{is}^{(0)} | \mathcal{H}_{\mu}^{(0)}(m) | \psi_{js}^{(0)} \rangle = \delta_{ij} [\,] . \tag{6-16}$$

Thus, $\mathcal{H}_{\mu}^{\prime(0)}(m)$ is always diagonal no matter what linear combination (5-70) is chosen for $\psi_{js}^{(0)}$. Furthermore, it has the same value over the whole degenerate set. It shifts all zeroth order energies but splits none of them. Hence, the energy correction $\mathcal{E}^{(0)}_{j\mu}(m)$ is given by Eq. (6-16). Its value is often made easier to calculate if one makes use of sum rules[52,68]. It is positive definite and always nonzero,

$$\mathcal{E}^{(0)}_{j\mu}(m) \neq 0. \tag{6-17}$$

For k = 3, 4, or 5, Eq. (5-37) for $\mathcal{E}^{(k)}_{j\mu}(m)$ becomes

$$\mathcal{E}^{(k)}_{j\mu}(m) = -2\sum_{\ell>g} \frac{\langle \Psi^{(0)}_{js} | \mathcal{H}^{(0)}_{\mu}(m) | \Phi^{J}_{\ell}\rangle \langle \Phi^{J}_{\ell} | \mathcal{H}^{(k)}_{s} | \Psi^{(0)}_{js}\rangle}{\mathcal{E}^{(0)}_{\ell s} - \mathcal{E}^{(0)}_{js}} \, , \tag{6-18}$$

Let us now replace the energy denominator by an average value $\Delta^{(0)}_{js}$. If one tries to estimate $\Delta^{(0)}_{js}$, this becomes Unsöld's approximation. However, for selection rule purposes, all one need assert is that for <u>some</u> $\Delta^{(0)}_{js}$,

$$\mathcal{E}^{(k)}_{j\mu}(m) = -\frac{2}{\Delta^{(0)}_{js}} \sum_{\ell>g} \langle \Psi^{(0)}_{js} | \mathcal{H}^{(0)}_{\mu}(m) | \Phi^{J}_{\ell}\rangle \langle \Phi^{J}_{\ell} | \mathcal{H}^{(k)}_{s} | \Psi^{(0)}_{js}\rangle . \tag{6-19}$$

This assertion is equivalent to the mean value theorem[86]. Using the completeness relation and (6-16) this becomes

$$\mathcal{E}^{(k)}_{j\mu}(m) = \frac{-2}{\Delta^{(0)}_{js}} \left[\langle \Psi^{(0)}_{js} | \mathcal{H}^{(0)}_{\mu}(m) \mathcal{H}^{(k)}_{s} | \Psi^{(0)}_{js}\rangle - \langle \Psi^{(0)}_{js} | \mathcal{H}^{(0)}_{\mu}(m) | \Psi^{(0)}_{js}\rangle \langle \Psi^{(0)}_{js} | \mathcal{H}^{(k)}_{s} | \Psi^{(0)}_{js}\rangle \right] . \tag{6-20}$$

Because $\mathcal{H}^{(0)}_{\mu}(m)$ contains only even parity zero rank tensors, both integrals in (6-20) are subject to just exactly the same selection rules as $\mathcal{H}_s^{(k)}$. One therefore has

$$\mathcal{E}_{j\mu}^{(0)}(m) \neq 0 \Leftrightarrow \mathcal{E}_{ks}^{(k)} \neq 0 \text{ , for } k=3,4, \text{ and } 5. \qquad (6\text{-}21)$$

Furthermore, from the simple symmetry of $\mathcal{H}_\mu^{(0)}(m)$ and Eq. (5-38), it is clear that one always has

$$\mathcal{E}_{j\mu}^{(6)}(m) \neq 0 . \qquad (6\text{-}22)$$

This $\mathcal{E}_{j\mu}^{(6)}(m)$ represents a small correction to the BO van der Waals coefficient $\mathcal{E}_{js}^{(6)}$. For most atoms $\mathcal{E}_{js}^{(6)}$ is not presently known to sufficient accuracy make $\mathcal{E}_{j\mu}^{(6)}(m)$ contribute to its significant figures, but $\mathcal{E}_{j\mu}^{(6)}(m)$ will be treated in more detail in Section VII for a special case in which it is significant.

We thus see that $\mathcal{H}_\mu^{(0)}(m)$ contributes nothing new to the potential but is just a small correction to each non-zero term in the BO potential and is due to our choice of atomic wavefunctions.

3. Corrections to the Centrifugal Potential

Dalgarno and McCarroll[10] calculated corrections to the centrifugal potential, but their formulas have limited meaning and validity because they used the products Φ rather than the linear combinations necessary to form the correct zeroth order wavefunctions. We now consider those corrections in more detail.

Let us first discuss $\mathcal{E}_{j\mu}^{(2)}(c)$. From Eq. (5-39) and (5-41), it is

$$\mathcal{E}^{(2)}_{j\mu}(c) = \frac{1}{2} \langle \Psi^{(0)}_{js} | (\mathcal{J}^2 - \Omega^2) | \Psi^{(0)}_{js} \rangle . \qquad (6\text{-}23)$$

The operator here is positive definite. Therefore,

$$\mathcal{E}^{(2)}_{j\mu}(c) \geq 0 , \qquad (6\text{-}24)$$

and the equality holds only if $\Psi^{(0)}_{js}$ is an eigenfunction of $\mathcal{J}^2$ with eigenvalue 0 . This $\mathcal{E}^{(2)}_{j\mu}(c)$ appears in the effective potential as a term of $\mathcal{O}(1/\mu R^2)$. For sufficiently large R , $\mathcal{H}^{(2)}_{\mu c}$ is the largest perturbation in (5-2) and the zeroth order wavefunctions are chosen to diagonalize it. This diagonalization simply implies that for large enough R the static interaction is small enough that $\underset{\sim}{L}^2$ and $\mathcal{J}^2$ can be simultaneously quantized. In such cases, (6-23) is easily evaluated. For smaller R , when $\mathcal{J}^2$ is not always diagonal, Eq. (6-23) can still be readily evaluated by writing $\mathcal{J}^2 = (\mathcal{J}_a + \mathcal{J}_b)^2$ as

$$\mathcal{J}^2 = \mathcal{J}_a^2 + \mathcal{J}_b^2 + (\mathcal{J}_a)_+(\mathcal{J}_b)_- + (\mathcal{J}_a)_-(\mathcal{J}_b)_+ + 2(\mathcal{J}_a)_z(\mathcal{J}_b)_z . \qquad (6\text{-}25)$$

The first two terms in (6-25) are zero rank tensors, the other three are products of first rank tensors. All have even atomic parity. Their actions on $\phi(a)$ and $\phi(b)$ are well known. To evaluate (6-23) one just substitutes (5-72) and (6-25) into it and adds up the results.

The higher corrections $\mathcal{E}^{m}_{j\mu}(c)$ for m = 5,6 are obtained from (5-43),

$$\mathcal{E}_{j\mu}^{(m)}(c) = \langle \Psi_{js}^{(0)} | (\mathcal{J}^2 - \Omega^2) | \Psi_{js}^{(m-2)} \rangle . \tag{6-26}$$

The Ω^2 term vanishes from the normalization conditions (C-48). If $\Psi_{js}^{(0)}$ is an eigenfunction of $\mathcal{J}^2$, then $\mathcal{E}_{j\mu}^{(m)}(c)$ completely vanishes for the same reason. Using Eq. (5-74) and the mean value theorem (6-19), Eq. (6-26) becomes

$$\mathcal{E}_{j\mu}^{(m)}(c) = \sum_{k}^{g_\Omega}{}' \langle \Psi_{ks}^{(0)} | \Psi_{js}^{(m-2)} \rangle \langle \Psi_{js}^{(0)} | \mathcal{J}^2 | \Psi_{ks}^{(0)} \rangle - \frac{1}{\Delta_{js}^{(0)}} \Big[\langle \Psi_{js}^{(0)} | \mathcal{H}_s^{(m-2)} \mathcal{J}^2 | \Psi_{js}^{(0)} \rangle -$$

$$\sum_{k}^{g_\Omega} \langle \Psi_{js}^{(0)} | \mathcal{J}^2 | \Psi_{ks}^{(0)} \rangle \langle \Psi_{ks}^{(0)} | \mathcal{H}_s^{(m-2)} | \Psi_{js}^{(0)} \rangle \Big] . \tag{6-27}$$

For any specified set of zeroth order functions the $\mathcal{J}^2$ integrals can be performed using (6-25). Because all the terms in (6-25) have even atomic parity, $\mathcal{H}_s^{(m-2)} \mathcal{J}^2$ has the parities of $\mathcal{H}_s^{(m-2)}$. Therefore, the second term in (6-27) vanishes for m = 6,

$$\frac{1}{\Delta}[\;] = 0, \quad m = 6 . \tag{6-28}$$

For m = 5, one has $\mathcal{H}_0^{(3)}$ in the second term of (6-27) and parity arguments lead to

$$\frac{1}{\Delta}[\;] = 0 , \quad \text{for} \quad m = 5, \quad \text{unless} \quad p_a \neq p_b . \tag{6-29}$$

If $\mathcal{P}_a \neq \mathcal{P}_b$, there are many different atomic tensors which can be formed from $\mathcal{H}_S^{(3)} \mathcal{J}^2$ through the Clebsch-Gordan theorem (Appendix D), indicating that the second integral will not usually vanish.

In actual practice Eq. (6-27) is usually easy to evaluate or estimate, and we do not consider these general forms any further.

4. The Cross Derivative Corrections

To get selection rules on the corrections that come from the cross derivatives, let us first look at $\mathcal{H}_\mu^{(1)}(X)$, Eq. (5-47),

$$\mathcal{H}_\mu^{(1)}(X) = \frac{i}{\sqrt{2}} \left(P_1^{-1} \mathcal{J}_+ + P_1^{1} \mathcal{J}_- \right). \tag{6-30}$$

This can be written in terms of atomic tensors,

$$\mathcal{H}_\mu^{(1)}(X) = \frac{i}{\sqrt{2}} \left\{ \left[\frac{\mu}{m_a} P_1^{-1}(a) - \frac{\mu}{m_b} P_1^{-1}(b) \right] \left[(\mathcal{J}_a)_+ + (\mathcal{J}_b)_+ \right] + \left[\frac{\mu}{m_a} P_1^{1}(a) - \frac{\mu}{m_b} P_1^{1}(b) \right] \left[(\mathcal{J}_a)_- + (\mathcal{J}_b)_- \right] \right\}. \tag{6-31}$$

When multiplied out, each term consists of a product of an odd parity function ($P_1^{\pm 1}$ or $P_1^{\pm 1} \mathcal{J}_\mp$) on one atom and an even parity function ($\mathcal{J}_\pm$ or unity) on the other. Therefore, from Eq. (6-6),

$$\langle \psi_{iS}^{(0)} | \mathcal{H}_\mu^{(1)}(X) | \psi_{jS}^{(0)} \rangle = 0, \quad \text{all } i, j \leq g_\Omega . \tag{6-32}$$

And Eq. (5-51) is always

$$\mathcal{E}_{j\mu}^{(1)}(X) = 0 . \tag{6-33}$$

To obtain the corrections in (5-53) we observe that

$$P_z = \frac{\mu}{m_a} P_z(a) - \frac{\mu}{m_b} P_z(b) \qquad (6\text{-}34)$$

also consists only of odd tensors $(P_z = P_1^0)$ on one atom times even tensors (unity) on the other. Using these results and the mean value theorem on Eq. (5-53) one obtains for k = 4,5, and 6,

$$\mathcal{E}^{(k)}_{j\mu}(x) = -\frac{1}{\Delta^{(0)}_{js}} \langle \psi^{(0)}_{js} | [2\mathcal{H}^{(1)}_{\mu}(x) + i(k-1) P_z] \mathcal{H}^{(k-1)}_{s} | \psi^{(0)}_{js} \rangle . \qquad (6\text{-}35)$$

If k = 4 or 6, then $\mathcal{H}^{(k-1)}_{s}$ consists only of products of tensors with the same parity on each atom and the integrand in (6-35) will again consist only of products of an even function on one atom times an odd function on the other. Thus, from Eq. (6-6), one always has

$$\mathcal{E}^{(k)}_{j\mu}(x) = 0 , \quad \text{for} \quad k = 4 \text{ and } 6. \qquad (6\text{-}36)$$

However, for k = 5, $\mathcal{H}^{(4)}_{s}$ appears and the resulting product contains functions with the same parity on each atom. If one uses the Clebsch-Gordan theorem (Appendix D) to write this product in terms of irreducible tensors on each atom, he obtains

$$[2\mathcal{H}^{(1)}_{\mu}(x) + i(k-1) P_z] \mathcal{H}^{(4)}_{s} \sim \sum_{q,n=0}^{3} \sum_{p} T^{m}_{q}(a;p)\, T^{-m}_{n}(b;p) . \qquad (6\text{-}37)$$

The ranks q and n each run through all values shown except the combinations $q = 3$, $n = 3$ and $q = 0$, $n = 0$, which do not occur. Hence, it appears that the only essential requirement in order to have

$$\mathcal{E}_{j\mu}^{(5)}(X) \neq 0 \qquad (6\text{-}38)$$

is that at least one of L_a, L_b is non zero. However, in this case of identical atoms, the expectation values of some of the terms in (6-31) may tend to cancel other similar terms of opposite sign.

This concludes the discussion of selection rules for the "resonant" case. After discussing selection rules in the "non-resonant" case, all the results will be summarized and discussed.

B. The "Non-Resonant" Case

Let us assume that the system now either consists of unlike atoms in any states or like atoms in states of the same energy $(k_a = k_b)$. This case is considerably simpler than the resonance case discussed above. The major difference is that the $\bar{O}_I$ in (5-70) is redundant and is to be left out. Then, in equations like (6-2), only the first product (diagonal part) appears.

1. The BO Potential

As first shown by Knipp[84] and as pointed out in the discussion of Eq. (6-3) to (6-7), when the second term in (6-2) is no longer included, one has

$$\mathcal{E}_{js}^{(k)} = 0 \,, \quad k = 3 \text{ and } 4. \qquad (6\text{-}39)$$

The next term in the series can be nonzero,

$$\mathcal{E}_{js}^{(5)} \neq 0, \tag{6-40}$$

only if

$$\begin{aligned} &1 \leq J_a \quad , \quad 1 \leq J_b \text{ , and} \\ &1 \leq L_a \quad , \quad 1 \leq L_b . \end{aligned} \tag{6-41}$$

$\mathcal{E}_{js}^{(6)}$ is also simplified. Because of parity restrictions $\langle \Psi_{is}^{(0)} | \mathcal{H}_s^{(3)} | \Psi_{js}^{(0)} \rangle = 0$, all $i, j \leq g_\Omega$, and

$$\mathcal{E}_{js}^{(6)} = - \sum_{\ell > q} \frac{|\langle \Phi_\ell^J | \mathcal{H}_s^{(3)} | \Psi_{js}^{(0)} \rangle|^2}{\mathcal{E}_{\ell s}^{(0)} - \mathcal{E}_{js}^{(0)}} . \tag{6-42}$$

This never vanishes.

2. The Mass Polarization Corrections

The mass polarization corrections are not affected by the off-diagonal part of (6-2). Eq. (6-16) becomes

$$\langle \Psi_{is}^{(0)} | \mathcal{H}_\mu^{(0)}(m) | \Psi_{js}^{(0)} \rangle = \delta_{ij} \left[\frac{\mu}{2m_a} \langle \phi(a;a) \| \underset{\sim}{P}_a^2 \| \phi(a;a) \rangle + \frac{\mu}{2m_b} \langle \phi(b;b) \| \underset{\sim}{P}_b^2 \| \phi(b;b) \rangle \right], \tag{6-43}$$

for $i, j \leq g_\Omega$. One always has

$$\mathcal{E}_{j\mu}^{(0)}(m) \neq 0, \tag{6-44}$$

as before. The procedure leading to (6-21) now leads to

$$\mathcal{E}^{(k)}_{j\mu}(m) = 0 \,, \quad k = 3 \text{ and } 4 \,, \tag{6-45}$$

and

$$\mathcal{E}^{(5)}_{j\mu}(m) \neq 0 \quad \Longleftrightarrow \quad \mathcal{E}^{(5)}_{js} \neq 0 \,. \tag{6-46}$$

And as in the resonance case one again always has

$$\mathcal{E}^{(6)}_{j\mu}(m) \neq 0 \,. \tag{6-47}$$

3. Corrections to the Centrifugal Potential

These corrections are also very similar to the resonant case. The result of Eq. (6-24),

$$\mathcal{E}^{(2)}_{j\mu}(c) \geq 0 \,, \tag{6-48}$$

still holds as before. However, by parity arguments, instead of Eq. (6-29), one now has

$$\frac{1}{\Delta}[\;] = 0 \,, \quad \text{for} \quad m = 5 \text{ and } 6 \,, \tag{6-49}$$

simplifying the expressions for $\mathcal{E}^{(m)}_{j\mu}(c)$.

4. The Cross Derivative Corrections

The odd-even parity combinations of $\mathcal{H}^{(1)}_{\mu}(x)$ and P_z again yield

$$\mathcal{E}_{j\mu}^{(k)}(x) = 0, \quad \text{for} \quad k = 1, 4, \quad \text{and} \quad 6. \tag{6-50}$$

Now, the terms of odd parity in (6-37) do not contribute to $\mathcal{E}_{j\mu}^{(5)}(x)$. However, it still appears that if at least one of L_a , L_b is non zero, one will obtain

$$\mathcal{E}_{j\mu}^{(5)}(x) \neq 0, \tag{6-51}$$

which completes the selection rules needed. We next discuss the effective potential and the relative importance of the corrections:

C. Discussion. The Nonrelativistic Effective Potential.

From the results of this section the nonrelativistic effective potential of Eq. (5-6), correct through $\mathcal{O}(\mu^{-1})$ is

$$\mathcal{E}_j(R;\text{eff}) = \sum_{n=0}^{\infty} R^{-n} \mathcal{E}_j^{(n)}(\text{eff}). \tag{6-52}$$

The coefficients for $n \leq 6$ which can sometimes be nonzero for neutral atoms are

$$\begin{aligned}
\mathcal{E}_j^{(0)}(\text{eff}) &= \mathcal{E}_{js}^{(0)} + \mu^{-1}\,\mathcal{E}_{j\mu}^{(0)}(m), \\
\mathcal{E}_j^{(1)}(\text{eff}) &= 0, \\
\mathcal{E}_j^{(2)}(\text{eff}) &= \mu^{-1}\,\mathcal{E}_c^{(2)} + \mu^{-1}\,\mathcal{E}_{j\mu}^{(2)}(c), \\
\mathcal{E}_j^{(3)}(\text{eff}) &= \mathcal{E}_{js}^{(3)} + \mu^{-1}\,\mathcal{E}_{j\mu}^{(3)}(m), \\
\mathcal{E}_j^{(4)}(\text{eff}) &= 0, \\
\mathcal{E}_j^{(5)}(\text{eff}) &= \mathcal{E}_{js}^{(5)} + \mu^{-1}\left(\mathcal{E}_{j\mu}^{(5)}(m) + \mathcal{E}_{j\mu}^{(5)}(c) + \mathcal{E}_{j\mu}^{(5)}(x)\right), \text{ and} \\
\mathcal{E}_j^{(6)}(\text{eff}) &= \mathcal{E}_{js}^{(6)} + \mu^{-1}\left(\mathcal{E}_{j\mu}^{(6)}(m) + \mathcal{E}_{j\mu}^{(6)}(c)\right).
\end{aligned} \tag{6-53}$$

And for any given system, some of these terms will usually vanish.

One sees that in most orders of R^{-1}, the corrections are $\mathcal{O}(\mu^{-1})$ smaller than an already nonzero term. However, <u>all</u> the terms in the centrifugal potential are of $\mathcal{O}(\mu^{-1})$, and the corrected centrifugal potential is

$$\mathcal{E}_j^{(2)}(\text{eff}) = \frac{\mu^{-1}}{2}\left[J(J+1) - 2\Omega^2 + \langle \Psi_{js}^{(0)} | \mathcal{L}^2 | \Psi_{js}^{(0)} \rangle\right]. \tag{6-54}$$

The first term is the BO result. The other two are corrections. Grouping one Ω^2 with the BO result produces the symmetric top result used here as the uncorrected centrifugal potential, Eq. (5-5). If J is large, it is clear from Eq. (3-9) that these correction terms have little importance, but if J is small, they are of the same order of magnitude, and due to their R^{-2} dependence in (6-52), they can have considerable effect on the long range effective potential.

In discussing these corrections to the centrifugal potential it is important to emphasize the fact that <u>they are part of the effective potential</u> and not connected with the <u>static</u> potential. They arise solely because of the motion of the nuclei and are present in the equation for relative motion of any two particles having internal structure. For example, due to their spins, the equation for the relative motion of two neutrons has terms equivalent to these corrections, even though the neutrons really have negligible interaction at these R values. Thus, while the correction terms are mathematically significant in the equations for nuclear motion, they have limited physical significance. Failure to make this distinction led Dalgarno and McCarroll[10] into the difficulty of an infinite elastic scattering cross section.

Because of the selection rules on $\mathcal{E}^{(k)}_{j\mu}(m)$, the only situation in which the $\mathcal{E}^{(k)}_{j\mu}$, for k ≥ 3, might be significant at long range would be a case in which $\mathcal{E}^{(3)}_{js} = \mathcal{E}^{(5)}_{js} = 0$, so that $\mathcal{E}^{(6)}_{js}$ is the first static term, but in which either $\mathcal{E}^{(5)}_{j\mu}(c)$ or $\mathcal{E}^{(5)}_{j\mu}(X)$ did not vanish. One can find a number of cases in which the selection rules will provide this behavior. However, many of these cases are also those for which Meath[20] has shown that there is a relativistic and magnetic correction of $\mathcal{O}(\alpha^2/R^3)$, which would dominate the $\mathcal{O}(1/\mu R^5)$ term for all large R. One of the cases in which the $\mathcal{O}(\alpha^2/R^3)$ also vanishes but in which the $\mathcal{O}(1/\mu R^5)$ term does not vanish is the interaction of two unlike atoms, one of which is in a ${}^1S$ state, but the other is in any state of non-zero orbital angular momentum, L. Then $\mathcal{E}^{(3)}_{js} = \mathcal{E}^{(5)}_{js} = \mathcal{E}^{(3)}_{j\alpha} = 0$, and most of the correction terms also vanish, but one may still have $\mathcal{E}^{(5)}_{j\mu}(x) \neq 0$. The nonrelativistic effective potential assumes the form

$$\mathcal{E}_j(R;\mathrm{eff}) - \mathcal{E}_j(\infty;\mathrm{eff}) = \frac{J(J+1) - 2\Omega^2 + \langle \mathcal{J}^2 \rangle}{2\mu R^2} + \frac{\mathcal{E}^{(5)}_{j\mu}(x)}{\mu R^5} + \frac{\mathcal{E}^{(6)}_{js} + \mu^{-1}\mathcal{E}^{(6)}_{j\mu}(x)}{R^6} + \cdots \tag{6-55}$$

A specific example in which the effective potential could have this sort of behavior is the interaction of the ground state boron (${}^2P$) and helium (${}^1S$) atoms.

However, even if (6-55) holds, the importance of the $\mathcal{O}(1/\mu R^5)$ term is minimized by the fact that there is always a relativistic correction of $\mathcal{O}(\alpha^2/R^4)$. In addition, it should be noted that $\mathcal{O}(1/\mu R^5)$ will not become appreciable compared to $\mathcal{O}(R^{-6})$ until R is so large that retardation effects have to be considered and the whole development breaks down.

VII. EXAMPLE. TWO 1S-HYDROGEN ATOMS

In this section the interaction of ground state hydrogen atoms is considered. This is a very simple problem, and some of the corrections discussed are unimportant, but they serve to illustrate the kinds of terms encountered. The corrections to the long range potentials and the nuclear equations of motion are discussed.

A. The Zeroth-order Wavefunctions

In the LSJM coupling terminology of Section V, the ground state hydrogen atom wavefunctions can be written as

$$\phi(c; k_c, J_c, M_c) = \phi(r_{ic}; k_c, \tfrac{1}{2}, \pm\tfrac{1}{2}) \equiv \phi(c; \pm\tfrac{1}{2}) \,, \tag{7-1}$$

where i is the electron associated with the atom c, and

$$k_c = (n_c, p_c, L_c, S_c) = (1, 0, 0, \tfrac{1}{2}) \,. \tag{7-2}$$

From these atomic functions one can form four degenerate products $\Phi^J = \phi(a)\,\phi(b)$. In this case the correct zeroth order wavefunctions are uniquely determined just by projecting out eigenfunctions of J_z and $\bar{\sigma}_{yz}$. This is a non-resonant interaction, and the functions automatically have g or u symmetry. They can be labeled by $\Psi^{(0)}(\Omega, \bar{p}, p_e)$, according to (5-67) and (4-33), or else labeled by the spectroscopic notation,

$$ {}^{S}[\Lambda]^{+/-}_{g/u,\,\Omega}\,. $$

The zeroth-order functions are easily shown to be

$$ \Psi_s^{(0)}(0,J+1,g) = \Psi_s^{(0)}({}^1\Sigma^+_{g,0}) = \frac{1}{\sqrt{2}}\left[\phi(a;\tfrac12)\phi(b;-\tfrac12) - \phi(a;-\tfrac12)\phi(b;\tfrac12)\right], \tag{7-3} $$

$$ \Psi_s^{(0)}(\pm1,\bar{p},u) = \Psi_s^{(0)}({}^3\Sigma^+_{u,\pm1}) = \phi(a;\pm\tfrac12)\phi(b;\pm\tfrac12), \text{ and} \tag{7-4} $$

$$ \Psi_s^{(0)}(0,J,u) = \Psi_s^{(0)}({}^3\Sigma^+_{u,0}) = \frac{1}{\sqrt{2}}\left[\phi(a;\tfrac12)\phi(b;-\tfrac12) + \phi(a;-\tfrac12)\phi(b;\tfrac12)\right]. \tag{7-5} $$

The $\bar{p}$ in (7-4) implies that the functions are not to be eigenfunctions of $\bar{\sigma}_{yz}$. The reason that the parities under $\bar{\sigma}_{yz}$ of the two $\Omega = 0$ functions differ, even though they are both classified as + states, is that the reflection operator σ_{yz} includes spins, but the + refers only to space reflection.

It should be noted that these correct zeroth order wavefunctions also happen to be eigenfunctions of the total electronic angular momentum. One has

$$ j^2\,\Psi_s^{(0)} = j(j+1)\,\Psi_s^{(0)}, \tag{7-6} $$

where $j = 0$ for the ${}^1\Sigma$ and 1 for the ${}^3\Sigma$ states.

B. The Long Range Effective Potentials

From the selection rules given in Section VI, one readily finds that most of the correction terms vanish here, and the long range, nonrelativistic effective potential is just

$$\mathcal{E}(R;\mathrm{eff}) = \mathcal{E}_s^{(0)} + \mu^{-1}\mathcal{E}_\mu^{(0)}(m) + \frac{J(J+1)-2\Omega^2+j(j+1)}{2\mu R^2} + \frac{\mathcal{E}_s^{(6)}+\mu^{-1}\mathcal{E}_\mu^{(6)}(m)}{R^6} + \cdots \tag{7-7}$$

Here $\mathcal{E}_s^{(0)}$ is the energy of the separated atoms, and $\mathcal{E}_s^{(6)}$ is essentially the van der Waals coefficient.

The mass polarization corrections, $\mathcal{E}_\mu^{(0)}(m)$ and $\mathcal{E}_{\mu m}^{(6)}$, could be obtained from Eq.(5-35 and 38). However, it is much easier in this special case to follow Dalgarno and McCarroll[10] and use the virial theorem,[87]

$$\langle \Psi_s | T_e | \Psi_s \rangle = -\mathcal{E}_s(R) - R\,\frac{\partial \mathcal{E}_s(R)}{\partial R}, \tag{7-8}$$

which in this case becomes

$$\langle \Psi_s | T_e | \Psi_s \rangle = -\mathcal{E}_s^{(0)} + \frac{5\,\mathcal{E}_s^{(6)}}{R^6} + \cdots \tag{7-9}$$

For the interaction of any isotopes of the hydrogen atom, one has

$$T_e = \frac{1}{2}p_{1a}^2 + \frac{1}{2}p_{2b}^2, \tag{7-10}$$

and

$$\mathcal{H}_\mu(m) = \frac{\mu}{2m_a} p_{1a}^2 + \frac{\mu}{2m_b} p_{2b}^2 . \qquad (7\text{-}11)$$

Using the fact that $\mathcal{H}_s$ and Ψ_s are independent of m_a and m_b, one can easily show from symmetry that

$$\langle \Psi_s | p_{1a}^2 | \Psi_s \rangle = \langle \Psi_s | p_{2b}^2 | \Psi_s \rangle , \qquad (7\text{-}12)$$

and therefore,

$$\mathcal{E}_\mu(R;m) = \langle \Psi_s | \mathcal{H}_\mu(m) | \Psi_s \rangle = \frac{1}{2} \langle \Psi_s | T_e | \Psi_s \rangle . \qquad (7\text{-}13)$$

From (7-7) and (7-9) one sees immediately that

$$\mathcal{E}_\mu^{(0)}(m) = -\frac{1}{2} \mathcal{E}_S^{(0)} , \text{ and} \qquad (7\text{-}14)$$

$$\mathcal{E}_\mu^{(6)}(m) = \frac{5}{2} \mathcal{E}_S^{(6)} . \qquad (7\text{-}15)$$

Let us now list the potentials for the states (7-3 to 5). Adding in the relativistic corrections obtained by Meath[20], we have as the long range effective potentials correct to μ^{-1}, α^2, and R^{-6};

$$\mathcal{E}(\mathrm{eff};{}^1\Sigma^+_{g,0}) = \mathcal{E}_s^{(0)}\left(1-\frac{1}{2\mu}\right) + \frac{J(J+1)}{2\mu R^2} + \frac{0.40\alpha^2}{R^4} + \frac{\mathcal{E}_s^{(6)}\left(1+\frac{5}{2\mu}\right)}{R^6}\,, \tag{7-16}$$

$$\mathcal{E}(\mathrm{eff};{}^3\Sigma^+_{u,\pm 1}) = \mathcal{E}_s^{(0)}\left(1-\frac{1}{2\mu}\right) + \frac{J(J+1)}{2\mu R^2} - \frac{\alpha^2}{2R^3} + \frac{0.40\,\alpha^2}{R^4} + \frac{\mathcal{E}_s^{(6)}\left(1+\frac{5}{2\mu}\right)}{R^6}\,, \tag{7-17}$$

$$\mathcal{E}(\mathrm{eff};{}^3\Sigma^+_{u,0}) = \mathcal{E}_s^{(0)}\left(1-\frac{1}{2\mu}\right) + \frac{J(J+1)+2}{2\mu R^2} + \frac{\alpha^2}{R^3} + \frac{0.40\alpha^2}{R^4} + \frac{\mathcal{E}_s^{(6)}\left(1+\frac{5}{2\mu}\right)}{R^6}\,. \tag{7-18}$$

The constant term is usually subtracted off, leaving the effective interaction potentials, $\mathcal{E}(\mathrm{int}) = \mathcal{E}(R;\mathrm{eff}) - \mathcal{E}(\infty;\mathrm{eff})$.

The numerical values (in atomic units) of the constants in these potentials are as follows. The energy of the separated hydrogen atoms is

$$\mathcal{E}_s^{(0)} = -\tfrac{1}{2} - \tfrac{1}{2} = -1\,, \tag{7-19}$$

the square of the fine structure constant is

$$\alpha^2 = 5.32492 \times 10^{-5},$$

and the van der Waals coefficient has been accurately calculated to be[88]

$$\mathcal{E}_s^{(6)} = -C_6 = -6.499026 \tag{7-20}$$

Let us now tabulate the corrected van der Waals coefficients for some of the isotopes of hydrogen.

Isotope	μ (a.u.)	$-\mathcal{E}_s^{(6)}(1+\frac{\xi}{3\mu})$ (a.u.)
H_2	918.06	6.516723
HD	1223.87	6.512330
D_2	1835.22	6.507879
T_2	2748.37	6.504938

Here $\mu = m_a m_b/(m_a + m_b)$ expressed in atomic units, and we have used $m_H = 1836.12$, $m_D = 3670.44$, and $m_T = 5496.74$. One sees that the corrections to $\mathcal{E}_s^{(6)}$ are very small even for these light atoms.

The most important long range adiabatic correction to these potentials is thus seen to be the 2 in the centrifugal potential in (7-18). For $R \geq 9a_0$ (for H_2) it contributes more to the effective potential than the van der Waals term does. Hence, for small J and large R, this correction to the centrifugal potential should not be neglected in the nuclear equations of motion.

It should also be noted from the accurate potentials of Kolos and Wolniewicz[11] that these long range representations of the potential are accurate only for $R > 10a_0$, due to our neglect of electron exchange. Kolos and Wolniewicz's accurate potentials only extend to $10\, a_0$, and there is still sufficient exchange contribution at that point to prevent matching our potential and theirs.

C. The Bound $^1\Sigma^+_{g,0}$ State of the H_2 Molecule

Let us now consider a hydrogen molecule with insufficient energy to dissociate to the atoms. For this case it can be shown from the secular equation (4-37) that the first contribution of the Ω coupling to the energy is of $\mathcal{O}(\mu^{-2})$. Hence, one can combine the extended adiabatic and adiabatic treatments of Section IV and write the nuclear equations of motion for the bound state hydrogen molecule complete to order α^2 and μ^{-2} in the form

$$(h_{00} - E_{0\nu})\, \chi(0) + 2 h_{01}\, \chi(1) = 0 , \tag{7-21}$$

where $\chi(\Omega) = \chi(R; J, \Omega, p = J+1, j = 0, \nu)$, and

$$h_{00} = \frac{1}{2\mu} p_R^2 + \frac{J(J+1)}{2\mu R^2} + \mathcal{E}_s(R) + \alpha^2 \mathcal{E}_\alpha(R) + \mu^{-1}\mathcal{E}_\mu(R) + \mu^{-2}\mathcal{E}_{\mu\mu}(R) + U^{nad}(R). \tag{7-22}$$

Here p_R is given by (2-49), $\mathcal{E}_{\mu\mu}(R)$ is given by (5-10), $U^{nad}(R)$ is given by Eq. (4-22), and h_{01} is given by (4-29) and (3-3). The first order corrections have been discussed.

Eq. (7-21) needs to be solved accurately. Since h_{01} and contribute to the energy only in $\mathcal{O}(\mu^{-2})$, they could be calculated to sufficient accuracy using BO wavefunctions. Kolos and Wolniewicz[11] have calculated accurate BO wavefunctions and also the relativistic and first order adiabatic corrections to the potential, and their results could be used. The nonadiabatic corrections, U^{nad}, have been estimated by Van Vleck[5], Fisk and Kirtman[14], and Poll and Karl[15], but they need to be estimated more accurately. The $\mathcal{E}_{\mu\mu}$ term has usually been neglected but could readily be estimated. The h_{01} terms need further study. (For the ground rotational state, which is of the most interest, J = 0 and $h_{01} = 0$.) When all these corrections are included, Eq. (7-21) should give extremely accurate results. However, it is expected to increase the calculated dissociation energy and thus not improve agreement with the experimental dissociation energy of H_2.

Let us now restrict Eq. (7-21) to the large R region. Since the $\mathcal{O}(\mu^{-2})$ corrections are small, we keep only their lead term. The Ω coupling term is

$$h_{01} = \frac{[J(J+1)]^{1/2}}{\mu R} \langle \Psi_s(0,J+1,g) | \frac{\mp 1}{2R} \ell_{\mp} + \frac{1}{\sqrt{2}\, i} P_1^{\mp 1} | \Psi_s(1,\bar{p},g) \rangle . \qquad (7\text{-}23)$$

The unique identification of the state $\Psi_s(1,\bar{p},g)$ may not be possible. The energetically nearest candidates are the ${}^3\Sigma^+_{g\pm 1}$ ${}^1\Pi_g$, and ${}^3\Pi_g$ states which come from one 1s-hydrogen atom and one 2s- or 2p- hydrogen atom. Because of Eq. (7-6) the $\ell_{\mp}$ term in (7-23) does not contribute until at least $\mathcal{O}(1/\mu R^5)$, and its large R energy effect is negligible. The $P_1^{\mp 1}$ term <u>can</u> contribute and make $h_{01} \sim \mathcal{O}(1/\mu R)$. The resulting effect on the energy is of $\mathcal{O}(1/\mu^2 R^2)$ and is negligible unless one wants extremely high accuracy.

At large R, the $\mathcal{E}_{\mu\mu}(R)$ correction can be approximated from

$$\mathcal{E}_{j\mu\mu}^{(\infty)} = -\sum_i{}' \frac{|\langle \psi_{is}^{(0)} | \mathcal{H}_{\mu m}^{(0)} | \psi_{js}^{(0)} \rangle|^2}{E_{is}^{(0)} - E_{js}^{(0)}} . \tag{7-24}$$

But these are equivalent to the second order mass polarization corrections at $R=\infty$. They can be found instead by using (7-10), solving the separated atom equation exactly in reduced mass atomic units, and writing the result in Hartree atomic units again. One finds that

$$\begin{aligned} \mathcal{E}_s^{(0)}(\text{exact}) &= \mathcal{E}_s^{(0)}(a)\left(\frac{1}{1+1/m_a}\right) + \mathcal{E}_s^{(0)}(b)\left(\frac{1}{1+1/m_b}\right) \\ &= \mathcal{E}_s^{(0)}\left[1 - \frac{1}{2\mu} + \frac{1}{2}\left(\frac{1}{m_a^2} + \frac{1}{m_b^2}\right)\right] . \end{aligned} \tag{7-25}$$

The first order correction is that obtained at (7-14). Thus, the dominant contribution to $\mathcal{E}_{\mu\mu}(R)$ at large R is

$$\mathcal{E}_{\mu\mu}(R) = -\frac{\mu^2}{2}\left(\frac{1}{m_a^2} + \frac{1}{m_b^2}\right) \sim \mathcal{O}(1) , \tag{7-26}$$

and its energy contribution is negligible for most purposes. It could also be subtracted off along with $\mathcal{E}_s^{(0)}$ and $\mathcal{E}_\mu^{(0)}(m)$.

In estimating the lead term of $\mathcal{U}^{nad}$ at large R, we take $\tilde{\Delta}_{j\nu} = \frac{1}{2}$, the transition energy from the ground ${}^1\Sigma_g^+$ state to the first excited ${}^1\Sigma_g^+$ state of H_2, as a reasonable "guesstimate"[14] of $\Delta_{j\nu}$. Then,

$$\mathcal{U}^{nad} \approx -\frac{2}{\mu^2} \langle \Psi_s^{(0)} | P_z^2 \Psi_s^{(0)} \rangle p_R^2 , \tag{7-27}$$

$$\approx -\frac{1}{2\mu^2} \langle \Psi_s^{(0)} | (P_a)_z^2 + 2(P_a)_z (P_b)_z + (P_b)_z^2 | \Psi_s^{(0)} \rangle p_R^2 .$$

The cross term vanishes because of parity, and because of the spherical symmetry of the atoms,

$$\langle (P_a)_z^2 + (P_b)_z^2 \rangle \doteq \frac{2}{3} \langle T_e \rangle . \tag{7-28}$$

From Eq. (7-9) this is

$$\mathcal{U}^{nad} \approx -\frac{1}{3\mu^2} p_R^2 , \tag{7-29}$$

which will also generally be negligible.

Neglecting these tiny corrections, the equation for nuclear motion at large R becomes

$$\left[\frac{1}{2\mu}p_R^2 + \frac{J(J+1)}{2\mu R^2} + \frac{0.40\alpha^2}{R^4} + \frac{\mathcal{E}_S^{(6)}(1+\frac{5}{2\mu})}{R^6} - E_{0\nu}\right]\chi(0) = 0. \tag{7-30}$$

Thus, neither the adiabatic nor the nonadiabatic corrections have much effect on the long range effective potential of the bound H_2 molecule.

D. The $^3\Sigma_u^+$ States of the H_2 System.

Let us now consider the nuclear equations of motion for the $^3\Sigma_u^+$ states. For simplicity, we neglect all second order and nonadiabatic terms except the Ω coupling. Assuming also that the relative kinetic energy is in the thermal range (considerably less than the first excitation energy of an H atom, $\frac{3}{8}\frac{e^2}{a_0} \approx 10\,e.v.$), one can also neglect the Ω coupling with higher states and only include coupling between the three states of the triplet. The resulting equations are

$$\left[\frac{1}{2\mu}p_R^2 + \mathcal{E}(\text{eff}; {}^3\Sigma_{u,0}^+) - E\right]\chi(0,J) + 2h_{01}\,\chi(1,J) = 0, \tag{7-31}$$

$$h_{10}\chi(0,J) + \left[\frac{1}{2\mu}p_R^2 + \mathcal{E}(\text{eff}; {}^3\Sigma_{u,1}^+) - E\right]\chi(1,J) = 0,$$

where $\chi = \chi(\Omega, p)$. The third nuclear function has opposite parity, $p = J+1$, in Eq. (4-36) and only has Ω coupling to distant excited states. Neglecting that coupling, its equation is just

$$\left[\frac{1}{2\mu}p_R^2 + \mathcal{E}(\mathrm{eff}; {}^3\Sigma^+_{u,1}) - E\right]\chi(1,J+1) = 0. \tag{7-32}$$

At large R, one can use Eq. (7-6) and atomic parity to show that the leading term of h_{01} and h_{10} is

$$h_{01} = h_{10} \simeq \frac{[2J(J+1)]^{1/2}}{2\mu R^2}. \tag{7-33}$$

and with Eq. (7-17 and 18) the three equations become

$$\left[\frac{1}{2\mu}p_R^2 + \frac{J(J+1)+2}{2\mu R^2} + \frac{\alpha^2}{R^3} + \frac{0.40\alpha^2}{R^4} + \frac{\mathcal{E}_S^{(6)}(1+\frac{5}{2\mu})}{R^6} - E\right]\chi(0,J) + \frac{[2J(J+1)]^{1/2}}{\mu R^2}\chi(1,J) = 0, \tag{7-34}$$

$$\frac{[2J(J+1)]^{1/2}}{2\mu R^2}\chi(0,J) + \left[\frac{1}{2\mu}p_R^2 + \frac{J(J+1)}{2\mu R^2} - \frac{\alpha^2}{2R^3} + \frac{0.40\alpha^2}{R^4} + \frac{\mathcal{E}_S^{(6)}(1+\frac{5}{2\mu})}{R^6} - E\right]\chi(1,J) = 0, \tag{7-35}$$

$$\left[\frac{1}{2\mu}p_R^2 + \frac{J(J+1)}{2\mu R^2} - \frac{\alpha^2}{2R^3} + \frac{0.40\,\alpha^2}{R^4} + \frac{\mathcal{E}_S^{(6)}(1+\frac{5}{2\mu})}{R^6} - E\right]\chi(1,J+1) = 0, \tag{7-36}$$

where the constant terms in the potential have been subtracted off.

These are examples of the kinds of equations one encounters in this formalism.

VIII. APPENDICES

Appendix A. Relative Coordinate Systems

In this appendix, we transform the Breit-Pauli Hamiltonian for a system of N electrons and two nuclei (a and b) from laboratory-fixed coordinates into three different relative coordinate systems. The directional axes are kept space-fixed here. They are rotated in Appendix B.

1. The Hamiltonian in Laboratory-fixed Coordinates

In the laboratory coordinates the Breit-Pauli Hamiltonian of our system is

$$\mathcal{H}_\tau = T_\tau + V + \alpha^2 \mathcal{H}_\alpha , \tag{A-1}$$

where τ stands for "total", and the total kinetic energy is

$$T_\tau = \frac{1}{2m_a}\not{p}_a^2 + \frac{1}{2m_b}\not{p}_b^2 + \frac{1}{2}\sum_{i=1}^{N}\not{p}_i^2 , \tag{A-2}$$

where $\not{p}_g = \frac{1}{i}\underset{\sim}{\nabla}_g , \; g = a, b, 1 \cdots N$. Here everything is in the Hartree atomic units discussed in Section II, and m_a and m_b are the masses of the nuclei a and b . The electrostatic potential energy V is

$$V = \frac{Z_a Z_b}{r_{ba}} - \sum_{i=1}^{N}\frac{Z_b}{r_{ib}} - \sum_{i=1}^{N}\frac{Z_a}{r_{ia}} + \sum_{j>i=1}^{N}\frac{1}{r_{ij}} . \tag{A-3}$$

$\alpha = (137.037)^{-1}$ is the fine structure constant and $\mathcal{H}_\alpha$ contains the magnetic and relativistic corrections. We use the form of $\mathcal{H}_\alpha$ given by Meath and Hirschfelder[20].

This Hamiltonian is written in terms of the laboratory-fixed coordinates,

$$\underset{\sim}{r}_a, \underset{\sim}{r}_b, \underset{\sim}{r}_i, \underset{\sim}{s}_i, \quad 1 \le i \le N, \tag{A-4}$$

where $\underset{\sim}{s}_i$ is the spin operator of electron i, and the rest of the set are vectors from some point in the laboratory to the particles.

The Hamiltonian has the following set of constants of the motion,

$$\underset{\sim}{J}_\tau^2, (\underset{\sim}{J}_\tau)_{z'}, \mathcal{I}, \mathcal{P}_{ij}, \bar{\mathcal{P}}_{ab}. \tag{A-5}$$

They are respectively, the square of the total angular momentum, $\underset{\sim}{J}_\tau$ The component of $\underset{\sim}{J}_\tau$ along the space-fixed (primed) z axis, the inversion of the coordinate system, the exchange of any two electrons i and j, and the interchange of the nuclei a and b. The bar over $\mathcal{P}_{ab}$ implies that $\mathcal{P}_{ab}$ is only a constant of the motion if the nuclei are identical $(m_a = m_b, Z_a = Z_b)$. If

$$\mathbf{x}'_g = \begin{pmatrix} x'_g \\ y'_g \\ z'_g \end{pmatrix}$$

represents the components of $\underset{\sim}{r}_g$ along the laboratory fixed axes, then the actions of the operators on these coordinates are as follows.

$$\mathcal{I}\,\Psi_\tau(\mathbf{x}'_g) = \Psi_\tau(-\mathbf{x}'_g), \quad g = a, b, 1, \cdots N, \tag{A-6}$$

$$\mathcal{P}_{ij}\,\Psi_\tau(\mathbf{x}'_i, \mathbf{x}'_j) = \Psi_\tau(\mathbf{x}'_j, \mathbf{x}'_i), \quad 1 \le i, j \le N, \tag{A-7}$$

$$\mathcal{P}_{ab}\,\Psi_\tau(\mathbf{x}'_a, \mathbf{x}'_b) = \Psi_\tau(\mathbf{x}'_b, \mathbf{x}'_a), \tag{A-8}$$

$$\underset{\sim}{J}_\tau = \underset{\sim}{\ell}_a + \underset{\sim}{\ell}_b + \underset{\sim}{\mathcal{L}} + \underset{\sim}{S}, \tag{A-9}$$

$$\underset{\sim}{\mathcal{L}} = \sum_i^N \underset{\sim}{\ell}_i, \quad \underset{\sim}{S} = \sum_i^N \underset{\sim}{s}_i, \quad \text{and} \tag{A-10}$$

$$\underset{\sim}{\ell} = \underset{\sim}{r}_i \times \underset{\sim}{p}_i . \tag{A-11}$$

Here we have suppressed all coordinates in Ψ_τ that are not affected by a particular operator. $\underset{\sim}{\mathcal{L}}$ and $\underset{\sim}{S}$ are clearly the electronic orbital and spin angular momenta.

2. The Separated Atom Relative Coordinates

We now transform the operators of the previous subsection into the "separated atom" coordinate system. This system is discussed in the main body of the paper. The "separated atom" relative coordinates are the set $\underset{\sim}{C}$, $\underset{\sim}{R}$, $\underset{\sim}{r}_{ia}$, $\underset{\sim}{r}_{jb}$ defined by (see Figure 1a):

$$\begin{aligned}
\underset{\sim}{r}_{ia} &= \underset{\sim}{r}_i - \underset{\sim}{r}_a , \qquad 1 \le i \le N_a , \\
\underset{\sim}{r}_{ib} &= \underset{\sim}{r}_i - \underset{\sim}{r}_b , \qquad N_a+1 \le i \le N, \\
\underset{\sim}{R} &= \underset{\sim}{r}_b - \underset{\sim}{r}_a , \quad \text{and} \\
\underset{\sim}{C} &= \frac{1}{M}\left(m_a \underset{\sim}{r}_a + m_b \underset{\sim}{r}_b + \sum_{i=1}^{N} \underset{\sim}{r}_i\right).
\end{aligned} \tag{A-12}$$

In atomic units,

$$M = m_a + m_a + N \tag{A-13}$$

is the total mass of the system, and $\underset{\sim}{C}$ is the center of mass of the entire system.

The momentum operators are readily transformed into the new coordinates by use of the chain rule[89].

$$\underset{\sim}{p}_q = \frac{1}{i}\underset{\sim}{\nabla}_q = \sum_{k=1}^{3} \frac{\hat{e}_k'}{i}\frac{\partial}{\partial X_{gk}'} ,$$

$$\begin{aligned}
\underset{\sim}{p}_q = \frac{1}{i}\sum_{k=1}^{3} \hat{e}_k' \Bigg\{ & \frac{\partial C_k'}{\partial X_{gk}'}\frac{\partial}{\partial C_k'} + \frac{\partial \ast_k'}{\partial X_{gk}'}\frac{\partial}{\partial \ast_k'} + \sum_{i=1}^{N_a} \frac{\partial (X_{ia}')_k}{\partial X_{gk}'}\frac{\partial}{\partial (X_{ia}')_k} + \\
& \sum_{i=N_a+1}^{N} \frac{\partial (X_{ib}')_k}{\partial X_{gk}'}\frac{\partial}{\partial (X_{ib}')_k} \Bigg\}.
\end{aligned} \tag{A-14}$$

Using (A-5) it is clear that

$$
\begin{aligned}
\mathbf{p}_a &= \frac{m_a}{M}\mathbf{p}_c - \mathbf{p}_R - \sum_{i=1}^{N_a} \mathbf{p}_{ia}, \\
\mathbf{p}_b &= \frac{m_b}{M}\mathbf{p}_c - \mathbf{p}_R - \sum_{i=N_a+1}^{N} \mathbf{p}_{ib}, \\
\mathbf{p}_i &= \frac{1}{M}\mathbf{p}_c + \mathbf{p}_{ia}, \quad 1 \le i \le N_a, \text{ and} \\
\mathbf{p}_i &= \frac{1}{M}\mathbf{p}_c + \mathbf{p}_{ib}, \quad N_a+1 \le i \le N.
\end{aligned}
\tag{A-15}
$$

It is also convenient to have the inverse of Eq. (12). It is easily found and is

$$
\begin{aligned}
\mathbf{r}_a &= \mathbf{C} - \frac{M_b}{M}\mathbf{R} - \frac{1}{M}\left\{ \sum_{i=1}^{N_a} \mathbf{r}_{ia} + \sum_{i=N_a+1}^{N} \mathbf{r}_{ib} \right\}, \\
\mathbf{r}_b &= \mathbf{C} + \frac{M_a}{M}\mathbf{R} - \frac{1}{M}\left\{ \sum_{i=1}^{N_a} \mathbf{r}_{ia} + \sum_{i=N_a+1}^{N} \mathbf{r}_{ib} \right\}, \\
\mathbf{r}_i &= \mathbf{r}_{ia} + \mathbf{C} - \frac{M_b}{M}\mathbf{R} - \frac{1}{M}\left\{ \sum_{i=1}^{N_a} \mathbf{r}_{ia} + \sum_{i=N_a+1}^{N} \mathbf{r}_{ib} \right\}, \quad 1 \le i \le N_a, \\
\mathbf{r}_i &= \mathbf{r}_{ib} + \mathbf{C} + \frac{M_b}{M}\mathbf{R} - \frac{1}{M}\left\{ \sum_{i=1}^{N_a} \mathbf{r}_{ia} + \sum_{i=N_a+1}^{N} \mathbf{r}_{ib} \right\}, \quad N_a+1 \le i \le N.
\end{aligned}
\tag{A-16}
$$

Here $M_a = M_a + N_a$ and $M_b = M_b + (N-N_a)$ are the total masses of the "atoms" a and b .

To transform $\mathcal{H}_\tau$ into these coordinates, we note that V is trivially written in terms of them and is independent of $\underset{\sim}{C}$, and $\mathcal{H}_\alpha$ depends only on relative vectors[20] (which are independent of $\underset{\sim}{C}$) and on the electronic momenta[50]. But in Eq. (A-15),

$$\wp_i = \wp_{i\alpha} + \mathcal{O}(\tfrac{1}{M}), \quad 1 \leq i \leq N \text{ and } a \leq \alpha \leq b, \tag{A-17}$$

so that the change in $\mathcal{H}_\alpha$ is of $\mathcal{O}(\frac{\alpha^2}{M})$ and hence negligible. Hence, in $\mathcal{H}_\alpha$ we just let $\wp_i \rightarrow \wp_{i\alpha}$ to express it in this relative coordinate system. To transform T_τ into these coordinates, we just substitute in Eq. (A-15). The result is:

$$T_\tau = \frac{1}{2M}\wp_c^2 + \frac{1}{2\mu}\wp_R^2 + \frac{1}{\mu}\underset{\sim}{P}\cdot\wp_R + T_e + \frac{1}{2m_a}\underset{\sim}{P}_a^2 + \frac{1}{2m_b}\underset{\sim}{P}_b^2, \tag{A-18}$$

where μ is the reduced mass of the nuclei, $\mu = m_a m_b/(m_a + m_b)$,

$$\underset{\sim}{P} = \frac{\mu}{m_a}\underset{\sim}{P}_a - \frac{\mu}{m_b}\underset{\sim}{P}_b, \tag{A-19}$$

$$\underset{\sim}{P}_a = \sum_{i=1}^{N_a} \wp_{ia}, \tag{A-20}$$

$$\underset{\sim}{P}_b = \sum_{i=N_a+1}^{N} \wp_{ib}, \tag{A-21}$$

and

$$T_e = \frac{1}{2}\sum_{i=1}^{N_a} p_{ia}^2 + \frac{1}{2}\sum_{i=N_a+1}^{N} p_{ib}^2 . \qquad \text{(A-21)}$$

T_e is the electronic kinetic energy operator in the BO approximation. $\underset{\sim}{P}_a^2$ and $\underset{\sim}{P}_b^2$ are the mass polarization[52] operators of the separated atoms. They are often split into their diagonal and nondiagonal parts,

$$\frac{1}{2m_d}\underset{\sim}{P}_d^2 = \frac{1}{2m_d}\Big\{\sum_i^{N_d} p_{id}^2 + 2\sum_{i<j}^{N_d} p_{id}\cdot p_{jd}\Big\} , \quad d=a,b . \qquad \text{(A-22)}$$

The diagonal parts are just

$$\frac{1}{2m_d}\sum_i^{N_d} p_{id}^2 = \frac{1}{m_d} T_d , \qquad \text{(A-23)}$$

where T_d is the atomic kinetic energy operator. They simply shift the energy slightly and give rise to the normal mass effect in atoms. The off diagonal terms produce the special mass effect, which is usually smaller. It is convenient for us to keep them together and be able to use the BO wavefunctions.

We now have $\mathcal{H}_\tau$ expressed in the separated atom coordinate system. The only dependence of $\mathcal{H}_\tau$ on $\underset{\sim}{C}$ is contained in the first term of Eq. (A-18),

$$T_c = \frac{1}{2M} p_c^2 . \qquad \text{(A-24)}$$

By setting $\Psi_T = \Psi \psi_c$ and appropriately choosing the zero of energy, we can exactly separate off the uninteresting motion of the center of mass and leave as the equation for relative motion,

$$\mathcal{H} \Psi = i \frac{\partial \Psi}{\partial t} , \tag{A-25}$$

where

$$\mathcal{H} = T + V + \alpha^2 \mathcal{H}_\alpha \tag{A-26}$$

and from Eq. (A-18),

$$T = T_T - T_c \tag{A-27}$$

Now let us determine the operators of (A-5) in this relative coordinate system. From Eq. (A-12) and Eq. (A-6 and 8), it is clear that

$$\mathcal{I} \Psi(\mathbf{X}'_{ia}, \mathbf{X}'_{jb}, \mathbf{X}') = \Psi(-\mathbf{X}'_{ia}, -\mathbf{X}'_{jb}, -\mathbf{X}') , \quad \text{and} \tag{A-28}$$

$$\mathcal{P}_{ab} \Psi(\mathbf{X}'_{ia}, \mathbf{X}'_{jb}, \mathbf{X}) = \Psi(\mathbf{X}'_{ib}, \mathbf{X}'_{ja}, -\mathbf{X}'), \tag{A-29}$$

where $1 \le i \le N_a$, $N_a + 1 \le j \le N$, and $\mathbf{X}' = \mathbf{X}'_R$. Also

$$\mathcal{P}_{ij} \Psi(\mathbf{X}'_{ic}, \mathbf{X}'_{jd}) = \Psi(\mathbf{X}'_{jc}, \mathbf{X}'_{id}) , \tag{A-30}$$

where $i \neq j;\ 1 \leq i, j \leq N;$ and $a \leq c, d \leq b$. Substituting Eq. (A-15) and (A-16) into Eq. (A-9) and rearranging, we get

$$\underset{\sim}{J}_{\tau} = \underset{\sim}{L}_{c} + \underset{\sim}{L}_{R} + \sum_{i=1}^{N_a} \underset{\sim}{\ell}_{ia} + \sum_{j=N_a+1}^{N} \underset{\sim}{\ell}_{jb} + \underset{\sim}{S}\,, \qquad \text{(A-31)}$$

where $\underset{\sim}{\ell}_{ia} = \underset{\sim}{r}_{ia} \times \underset{\sim}{p}_{ia}$, etc.. $\underset{\sim}{S}$ is a formal operator, invariant under the transformation. When the center of mass motion is separated off, the conserved angular momentum we are interested in is

$$\underset{\sim}{J} = \underset{\sim}{J}_{\tau} - \underset{\sim}{L}_{c}\,. \qquad \text{(A-32)}$$

3. The Center of Mass of the Nuclei System

The second relative coordinate system to which we transform $\mathcal{H}_{\tau}$ is the "center of mass of the nuclei" (CMN) system. It avoids the nuclear-electronic cross derivatives[40] which appeared in the other system. It is convenient for bound state molecules[90] and also for short range potentials because it goes smoothly to the united atom Hamiltonian[91]. In this system the electronic coordinates are taken relative to the center of mass of the nuclei as follows: (See Figure 1b)

$$\underset{\sim}{r}_{in} = \underset{\sim}{r}_i - \frac{1}{(m_a+m_b)}(m_a \underset{\sim}{r}_a + m_b \underset{\sim}{r}_b), \quad 1 \le i \le N,$$

$$\underset{\sim}{R} = \underset{\sim}{r}_b - \underset{\sim}{r}_a, \text{ and} \tag{A-33}$$

$$\underset{\sim}{C} = \frac{1}{M}(m_a \underset{\sim}{r}_a + m_b \underset{\sim}{r}_b + \sum_{i=1}^{N} \underset{\sim}{r}_i).$$

M , $\underset{\sim}{C}$, and $\underset{\sim}{R}$ are thus the same as in the previous system.

Using the chain rule as before, we find that

$$f_a = \frac{m_a}{M} f_c - f_R - \frac{m_a}{(m_a+m_b)} \sum_{i=1}^{N} f_{in},$$

$$f_b = \frac{m_b}{M} f_c + f_R - \frac{m_b}{(m_a+m_b)} \sum_{i=1}^{N} f_{in}, \text{ and} \tag{A-34}$$

$$f_i = f_{in} + \frac{1}{M} f_c, \quad 1 \le i \le N.$$

The inverse transformation is

$$\underset{\sim}{r}_b = \frac{m_a}{m_a+m_b}\underset{\sim}{R} + \frac{M}{(M+m_a+m_b)}\underset{\sim}{C} - \frac{1}{(M+m_a+m_b)} \sum_{i=1}^{N} \underset{\sim}{r}_{in},$$

$$\underset{\sim}{r}_a = \frac{-m_b}{m_a+m_b}\underset{\sim}{R} + \frac{M}{(M+m_a+m_b)}\underset{\sim}{C} - \frac{1}{(M+m_a+m_b)} \sum_{i=1}^{N} \underset{\sim}{r}_{in}, \text{and} \tag{A-35}$$

$$\underset{\sim}{r}_i = \underset{\sim}{r}_{in} + \frac{M}{(M+m_a+m_b)}\underset{\sim}{C} - \frac{1}{(M+m_a+m_b)} \sum_{i=1}^{N} \underset{\sim}{r}_{in}, \quad 1 \le i \le N.$$

Eq. (A-17) holds as before. The relative vectors in $\mathcal{H}_\alpha$ and V are easily written using (A-35). Substituting Eq. (A-34) into T_τ we obtain

$$T_\tau = \frac{1}{2M}\mathbf{p}_c^2 + \frac{1}{2\mu}\mathbf{p}_R^2 + \frac{1}{2}\sum_{i=1}^{N}\mathbf{p}_{in}^2 + \frac{1}{2(m_a+m_b)}\mathbf{P}_n^2, \qquad \text{(A-36)}$$

where μ is the nuclear reduced mass as before, and

$$\mathbf{P}_n = \sum_{i=1}^{N}\mathbf{p}_{in}, \qquad \text{(A-37)}$$

so that the $\mathbf{P}_n^2$ term is the united atom mass polarization operator. The center of mass motion separates just as in the separated atom system, so that if $T = T_\tau - T_c$, the relative Hamiltonian is given by Eq. (A-26) using Eq. (A-36) for T_τ.

The symmetry operations become

$$\mathcal{I}\,\Psi(\mathbf{x}'_{in},\mathbf{x}') = \Psi(-\mathbf{x}'_{in},-\mathbf{x}'), \qquad \text{(A-38)}$$

$$\mathcal{P}_{ij}\,\Psi(\mathbf{x}'_{in},\mathbf{x}'_{jn}) = \Psi(\mathbf{x}'_{jn},\mathbf{x}'_{in}), \quad 1 \le i,j \le N. \qquad \text{(A-39)}$$

If $m_a = m_b$,

$$\mathcal{P}_{ab}\, \Psi(\underset{\sim}{x}'_{in}, \underset{\sim}{X}') = \Psi(\underset{\sim}{x}'_{in}, -\underset{\sim}{X}') \, . \qquad \text{(A-40)}$$

The total angular momentum becomes

$$\underset{\sim}{J}_T = \underset{\sim}{L}_e + \underset{\sim}{L}_R + \sum_{i=1}^{N} \underset{\sim}{\ell}_{in} + \underset{\sim}{S} \, . \qquad \text{(A-41)}$$

where $\underset{\sim}{\ell}_{in} = \underset{\sim}{r}_{in} \times \underset{\sim}{p}_{in}$ and $\underset{\sim}{J} = \underset{\sim}{J}_T - \underset{\sim}{L}_e$ is again the interesting conserved angular momentum.

The removal of rotation from the Hamiltonian in this system is discussed at the end of Appendix B.

4. The "ρ" System (Joins Centers of Masses of Two "Atoms")

The third system into which we transform $\mathcal{H}_T$ was suggested by Jepsen and Hirschfelder[34,40]. In this system the vector ρ between the centers of masses of the "atoms" or subsystems is used as a coordinate rather than $\underset{\sim}{R}$. And in this system $\mathcal{H}$ goes smoothly to the separated atom limits but does not contain the bothersome nuclear-electronic cross derivatives. As a result the coupling terms are smaller and the nonadiabatic corrections go to zero at infinite separation, so that for sufficiently large distances it may well have more physical meaning than the separated atom system used in the text of this paper. However, its usefulness is severely limited by the fact that ρ is not invariant to exchange of electrons between the two atoms, and it becomes ill-defined and virtually impossible to use at any interatomic separations small enough that electron exchange must be included. Long range potentials and the adiabatic corrections are readily calculated in this system, but they would seem to be of limited value, since it is difficult to connect them accurately to the rest of the potential, which must be in terms of R . We do not use the system in this paper but present $\mathcal{H}_T$ in the system for use in interpreting our separated atom system results. The $\underset{\sim}{\rho}$ system is: (See Figure 1c)

$$\underset{\sim}{r}_{ia} = \underset{\sim}{r}_i - \underset{\sim}{r}_a , \quad 1 \leq i \leq N_a ,$$

$$\underset{\sim}{r}_{ib} = \underset{\sim}{r}_i - \underset{\sim}{r}_b , \quad N_a + 1 \leq i \leq N ,$$

$$\underset{\sim}{G} = \frac{1}{M}\left(m_a \underset{\sim}{r}_a + m_b \underset{\sim}{r}_b + \sum_{i=1}^{N} \underset{\sim}{r}_i\right), \text{ and} \qquad \text{(A-42)}$$

$$\underset{\sim}{\rho} = \frac{1}{M_b}\left(\sum_{i=N_a+1}^{N} \underset{\sim}{r}_i + m_b \underset{\sim}{r}_b\right) - \frac{1}{M_a}\left(\sum_{i=1}^{N_a} \underset{\sim}{r}_i + m_a \underset{\sim}{r}_a\right).$$

The mass symbols here are those used earlier. The only change from the separated atom set is the use here of $\underset{\sim}{\rho}$, the vector from the center of mass of "atom" a to that of "atom" b .

In these coordinates the momenta become

$$p_a = \frac{m_a}{M} p_c - \frac{m_a}{M_a} p_\rho - \sum_{i=1}^{N_a} p_{ia} ,$$

$$p_b = \frac{m_b}{M} p_c + \frac{m_b}{M_b} p_\rho - \sum_{i=N_a+1}^{N} p_{ib} , \qquad \text{(A-43)}$$

$$p_i = \frac{1}{M} p_c - \frac{1}{M_a} p_\rho + p_{ia} , \quad 1 \leq i \leq N_a , \quad \text{and}$$

$$p_i = \frac{1}{M} p_c + \frac{1}{M_b} p_\rho + p_{ib} , \quad N_a+1 \leq i \leq N .$$

The inverse transformations are

$$\underset{\sim}{r}_a = -\frac{M_b}{M} \rho + \underset{\sim}{c} - \frac{1}{M_a} \sum_{i=1}^{N_a} \underset{\sim}{r}_{ia} ,$$

$$\underset{\sim}{r}_b = \frac{M_a}{M} \rho + \underset{\sim}{c} - \frac{1}{M_b} \sum_{i=N_a+1}^{N} \underset{\sim}{r}_{ib} , \qquad \text{(A-44)}$$

$$\underset{\sim}{r}_i = \underset{\sim}{r}_{ia} - \frac{M_b}{M} \rho + \underset{\sim}{c} - \frac{1}{M_a} \sum_{j=1}^{N_a} \underset{\sim}{r}_{ja} , \quad 1 \leq i \leq N_a , \quad \text{and}$$

$$\underset{\sim}{r}_i = \underset{\sim}{r}_{ib} + \frac{M_a}{M} \rho + \underset{\sim}{c} - \frac{1}{M_b} \sum_{j=N_a+1}^{N} \underset{\sim}{r}_{jb} , \quad N_a+1 \leq i \leq N .$$

From Eq. (A-44) one sees that

$$\underset{\sim}{R} = \rho + \frac{1}{\mu_{at}} \underset{\sim}{y} , \qquad \text{(A-45)}$$

where $\mu_{at} = M_a M_b / (M_a + M_b)$ is the reduced mass of the <u>atoms</u>, and

$$\underset{\sim}{y} = \frac{\mu_{at}}{M_a} \sum_{i=1}^{N_a} \underset{\sim}{r}_{ia} - \frac{\mu_{at}}{M_b} \sum_{i=N_a+1}^{N} \underset{\sim}{r}_{ib} . \qquad \text{(A-46)}$$

In the BO approximation the distinction between $\underset{\sim}{R}$ and $\underset{\sim}{\rho}$ is negligible. Even here in $\mathcal{H}_{\alpha}$ the correction is negligible, and one just changes $\underset{\sim}{R}$ to $\underset{\sim}{\rho}$ in the separated atom form of $\mathcal{H}_{\alpha}$. To transform V to these coordinates we write it in terms of the separated atom coordinates and then use (A-45). It appears somewhat complicated, but for large $\underset{\sim}{\rho}$, it can be expanded as a Taylor series in μ_{at}^{-1},

$$V = [V]_{\underset{\sim}{\rho}=\underset{\sim}{R}} + \frac{1}{\mu_{at}} \underset{\sim}{y} \cdot \underset{\sim}{\nabla}_{\rho} [V]_{\underset{\sim}{\rho}=\underset{\sim}{R}} + O(\mu_{at}^{-2}) \, . \tag{A-47}$$

Each of these terms can be expanded in powers of ρ using methods developed by Rose,[74] and the interatomic potential and corrections can be calculated.

In this coordinate system,

$$T_{\tau} = \frac{1}{2M} \mathcal{P}_{c}^{2} + \frac{1}{2\mu_{at}} \mathcal{P}_{\rho}^{2} + T_{e} + \frac{1}{2m_a} \underset{\sim}{P}_{a}^{2} + \frac{1}{2m_b} \underset{\sim}{P}_{b}^{2} \, , \tag{A-48}$$

where T_e, $\underset{\sim}{P}_a$, $\underset{\sim}{P}_b$ have been given before, so that here T_{τ} differs from (A-18) only by $\mathcal{P}_{R} \rightarrow \mathcal{P}_{\rho}$ and the absence of nuclear electronic cross derivatives.

The center of mass motion separates as before. And in this system,

$$\underset{\sim}{J}_{\tau} = \underset{\sim}{L}_{c} + \underset{\sim}{L}_{\rho} + \sum_{i=1}^{N_a} \underset{\sim}{\ell}_{ib} + \sum_{i=N_a+1}^{N} \underset{\sim}{\ell}_{ib} + \underset{\sim}{S} \, . \tag{A-49}$$

The symmetry operations become

$$\mathcal{I}\,\Psi(\mathbf{x}'_{ia},\mathbf{x}'_{jb},\mathbf{x}'_{\rho}) = \Psi(-\mathbf{x}'_{ia},-\mathbf{x}'_{jb},-\mathbf{x}'_{\rho}), \quad \text{and} \qquad \text{(A-50)}$$

$$\mathcal{P}_{ij}\Psi(\mathbf{x}'_{ia},\mathbf{x}'_{ja},\mathbf{x}'_{\rho}) = \Psi(\mathbf{x}'_{ja},\mathbf{x}'_{ia},\mathbf{x}'_{\rho}) \qquad \text{(A-51)}$$

if i and j are in the same atom, but if i and j are in different atoms, ρ is neither invariant nor simply altered by $\mathcal{P}_{ij}$. The same is true of $\mathcal{P}_{ab}$. Hence, ρ can only be used for widely separated atoms and cannot be extended in to match with the other parts of the potential. For this reason we do not treat this system any further.

Appendix B. Removal of Rotation using Representations of the Rotation Group.

In this appendix the representations of the rotation group are used to obtain the results of Section II. There are four parts: 1) the separation of the rotational coordinates, 2) the transformation of the inversion operation to body-fixed coordinates, 3) a discussion of the double-valued representations of the rotation group encountered when the angular momentum is half-integral, and 4) a presentation of the results of Section II in the center of mass of the nuclei (CMN) coordinates.

1. Separation of Rotational Coordinates

The HWC series[42-46] is followed closely, and the reader is referred to those papers for more detail. The notation and conventions correspond more to the later papers[44-46] in the series.

a. Conventions

The notation and conventions are those of Section II. In addition it is convenient to list some of the conventions in more detail. Let us take

$$X' = \begin{pmatrix} X_1' \\ X_2' \\ X_3' \end{pmatrix} \qquad \text{(B-1)}$$

to be the components of $\underset{\sim}{R}$ relative to space-fixed axes. The space-fixed axes are denoted by the primed unit vectors,

$$\mathbb{e}' = (\hat{e}_1', \hat{e}_2', \hat{e}_3') . \qquad \text{(B-2)}$$

The body-fixed coordinates are given by $\mathbb{x}$, $\mathbb{X}$, where

$$\mathbb{x} = \mathbb{R}\mathbb{x}' , \quad \text{and}$$

$$\mathbb{X} = \mathbb{R}\mathbb{X}' \qquad \text{(B-3)}$$

The rotation matrix $\mathbb{R}$ is orthogonal,

$$\mathbb{R}^{-1} = \tilde{\mathbb{R}} \qquad \text{(B-4)}$$

We choose to rotate axes rather than vectors, so that $\underset{\sim}{r}$ is invariant to the rotation:

$$\underset{\sim}{r} = \mathbb{e}'\mathbb{x}' = \mathbb{e}\mathbb{x} . \qquad \text{(B-5)}$$

Then, it is clear that the body-fixed axes $\mathbb{e}$ are

$$\mathbb{e} = \mathbb{e}'\tilde{\mathbb{R}} . \qquad \text{(B-6)}$$

And scalar products are clearly invariant to rotations,

$$\underset{\sim}{r} \cdot \underset{\sim}{r} = \tilde{\mathbb{x}}'\mathbb{x}' = \tilde{\mathbb{x}}\mathbb{x} . \qquad \text{(B-7)}$$

The functional convention used in Section II,

$$\mathcal{R}^{-1}\Psi(\mathbf{x}',\mathbf{X}') \equiv \Psi(\mathbb{R}\mathbf{x}',\mathbb{R}\mathbf{X}') = \Psi(\mathbf{x},\mathbf{X}), \tag{B-8}$$

is the convention of HWC, Wigner[92], and Hamermesh[93], but is opposite the convention of Rose[94]. The wavefunctions are chosen to transform as basis functions of the irreducible representations of the rotation group,

$$\mathcal{R}\,\Psi(\mathbf{x}',\mathbf{X}';J,M) = \sum_{\Omega} D^{J}_{\Omega M}(\mathcal{R})\,\Psi(\mathbf{x}',\mathbf{X}';J,\Omega), \tag{B-9}$$

where the $D^{J}_{\Omega M}(\mathcal{R})$ form a representation of the group. Here J is the total angular momentum quantum number, and Ω and M $(-J \leq M, \Omega \leq J)$ are magnetic quantum numbers. It is clear from (B-9) that

$$D^{J}_{\Omega M}(\mathcal{R}) = \langle \Psi(\mathbf{x}',\mathbf{X}';J,\Omega)\,|\,\mathcal{R}\,|\,\Psi(\mathbf{x}',\mathbf{X}';J,M)\rangle. \tag{B-10}$$

Eq. (B-9) and (B-10) define $D^{J}_{\Omega M}(\mathcal{R})$ up to an arbitrary phase factor. The phase is fixed by requiring the spherical harmonics Y_{ℓ}^{m}, to transform according to (B-9). The spherical harmonics used for that purpose here are those of Condon and Shortley[95], Wigner[96], and Rose[97]. They differ by $(-1)^{m}$ from the Y_{ℓ}^{m} which HWC use[98],

$$Y_{\ell}^{m}(\text{here}) = (-1)^{m}\,Y_{\ell}^{m}(HWC)\,. \tag{B-11}$$

The choice made here allows one to use the ordinary raising and lowering operators which are defined by Eq. (2-22 to 24). Use of (B-11) in (B-9) shows that[99]

$$D^{J}_{\Omega M}(\text{here}) = (-1)^{\Omega - M} D^{J}_{\Omega M}(\text{HWC}). \tag{B-12}$$

The wavefunction used in the transformations is given by Eq. (2-37),

$$\Psi(x', X'; J, M) = \sum_{\Omega} D^{J}_{\Omega M}(\mathcal{R})\, \Psi(x, X, J, \Omega). \tag{2-37}$$

Here $\Psi(x, X, J, \Omega)$ is in body-fixed coordinates; hence, Ω is the component of the angular momentum along the body-fixed z axis.

b. The problem

To determine the equation satisfied by Ψ in the body-fixed coordinates we substitute Eq. (2-37) into the space-fixed relative Schrödinger equation,

$$\mathcal{H}\, \Psi(x', X'; J, M) = E_i\, \Psi(x', X'; J, M), \tag{B-13}$$

where $\mathcal{H}$ was obtained in Appendix A,

$$\mathcal{H} = \frac{1}{2\mu} \mathcal{P}_R^2 + \frac{1}{\mu} \mathbf{P} \cdot \mathcal{P}_R + \mathcal{H}_e, \tag{B-14}$$

and the $\mathbf{p}_q$ have the usual gradient representation in space-fixed coordinates.

Now let $\mathcal{R}$ be a rotation described by three Euler angles α, β, and γ, which are arbitrary, except that they are restricted to be independent of the electronic coordinates. Then $\mathcal{H}_e$ does not act on $D^J_{\Omega M}[\mathcal{R}(\alpha,\beta,\gamma)]$. Furthermore $\mathcal{H}_e$ consists only of scalar products which are invariant to rotation. Hence, we just drop the primes and $\mathcal{H}_e$ is prepared to act on $\Psi(\mathbf{x},\mathbf{X})$. However, for the other two operators, one needs to know

$$\frac{1}{i}\frac{\partial\Psi(\mathbf{x}',\mathbf{X}';J,M)}{\partial \mathbf{X}'_k} = \frac{1}{i}\sum_{\Omega}\left\{\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \mathbf{X}'_k}\Psi(\mathbf{x},\mathbf{X};J,\Omega) + D^J_{\Omega M}(\mathcal{R})\frac{\partial\Psi(\mathbf{x},\mathbf{X},J,\Omega)}{\partial \mathbf{X}'_k}\right\}. \tag{B-15}$$

To evaluate the second term in (B-15) one expresses $\frac{1}{i}\frac{\partial}{\partial \mathbf{X}'_k}$ in terms of the rotated coordinates by means of the chain rule. Before doing so, however, we observe that $\Psi(\mathbf{x},\mathbf{X})$ depends on spin as well as space variables. Since $\mathcal{H}_\alpha$ is included in $\mathcal{H}$ these must be rotated, too. The Pauli matrices can be used to rotate the spin axes,[33] but they can also be rotated simultaneously with the space rotation as follows. We define a formal vector $\underset{\sim}{u}_i$ with body-fixed coordinates $\mathcal{U}_i$, such that the spin operator of electron i is

$$\underset{\sim}{S}_i = \underset{\sim}{u}_i \times \mathbf{p}_{u_i}, \tag{B-16}$$

in analogy with $\underset{\sim}{\ell}_i = \underset{\sim}{r}_i \times \underset{\sim}{p}_i$. Then, if $\underset{\sim}{U}_i$ is a true vector, $\underset{\sim}{S}_i$ will transform like an angular momentum. And Ψ becomes

$$\Psi(\mathbb{x},\mathbb{X},J,\Omega) = \Psi(\mathbb{x},\mathbb{u},\mathbb{X};J,\Omega) . \tag{B-17}$$

$\mathbb{u}$ will be explicitly listed in Ψ only when its being acted on. Now by the chain rule,

$$\frac{1}{i}\frac{\partial\Psi(\mathbb{x},\mathbb{X},\mathbb{u};J,\Omega)}{\partial X_k'} = \frac{1}{i}\left\{\sum_{\ell=1}^{3}\frac{\partial\mathbb{X}_\ell}{\partial\mathbb{X}_k'}\frac{\partial}{\partial\mathbb{X}_\ell} + \right.$$

$$\left.\sum_{i=1}^{N}\sum_{\ell=1}^{3}\left[\frac{\partial(x_i)_\ell}{\partial\mathbb{X}_k'}\frac{\partial}{\partial(x_i)_\ell} + \frac{\partial(u_i)_\ell}{\partial\mathbb{X}_k'}\frac{\partial}{\partial(u_i)_\ell}\right]\right\}\Psi(\mathbb{x},\mathbb{u},\mathbb{X}). \tag{B-18}$$

Using (B-3) one finds that

$$\frac{1}{i}\frac{\partial\Psi(\mathbb{x},\mathbb{u},\mathbb{X};J,\Omega)}{\partial\mathbb{X}_k'} = \frac{1}{i}\left\{\sum_{\ell=1}^{3}\mathbb{R}_{\ell k}\frac{\partial}{\partial\mathbb{X}_\ell} + \sum_{\ell,j,m=1}^{3}\left(\frac{\partial\mathbb{R}_{\ell j}}{\partial\mathbb{X}_k'}\right)\mathbb{R}_{mj}\mathbb{X}_m\frac{\partial}{\partial\mathbb{X}_\ell} + \right.$$

$$\left.\sum_{i=1}^{N}\sum_{\ell,j,m=1}^{3}\left(\frac{\partial\mathbb{R}_{\ell j}}{\partial\mathbb{X}_k'}\right)\mathbb{R}_{mj}\left[(X_i)_m\frac{\partial}{\partial(X_i)_\ell} + (u_i)_m\frac{\partial}{\partial(u_i)_\ell}\right]\right\}\Psi. \tag{B-19}$$

Thus the quantities needed to complete the transformation of Eq. (B-15) are

$$\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial\mathbb{X}_k'} \quad \text{and} \quad \frac{\partial\mathbb{R}_{\ell j}}{\partial\mathbb{X}_k'} .$$

c. Derivatives of the rotation matrices.

Because $\mathbb{R} = \mathbb{R}(\alpha,\beta,\gamma)$ is well-known explicitly in terms of the Euler angles,[46,57] it could be differentiated explicitly. However, HWC have shown that by treating the matrices $\mathbb{D}^J$ and $\mathbb{R}$ similarly, one can obtain the derivatives of $\mathbb{D}^J$ from those of $\mathbb{R}$. They have shown that differentiation of the matrices is equivalent to changing the rotation $\mathcal{R}$ by an infinitesimal rotation $\mathcal{S}$. The derivatives are

$$\frac{\partial \mathbb{R}_{\ell j}}{\partial \chi'_k} = \lim_{\delta\chi'_k \to 0} \left[(\mathbb{S}\mathbb{R})_{\ell j} - \mathbb{R}_{\ell j} \right] / \delta\chi'_k \tag{B-20}$$

and

$$\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \chi'_k} = \lim_{\delta\chi'_k \to 0} \left[D^J_{\Omega M}(\mathcal{S}\mathcal{R}) - D^J_{\Omega M}(\mathcal{R}) \right] / \delta\chi'_k \,. \tag{B-21}$$

Here $\mathbb{S}$ is the matrix representation of $\mathcal{S}$. HWC represent it as the product of an infinitesmal rotation about each of the three axes. To determine $\mathbb{S}$, they only need derivatives evaluated at special points,

$$\left[\frac{\partial \mathbb{R}_{ij}(\alpha,\beta,\gamma)}{\partial\alpha}\right]_{(0,0,0)}, \quad \left[\frac{\partial \mathbb{R}_{ij}(\alpha,\beta,\gamma)}{\partial\beta}\right]_{(0,0,0)}, \text{ and } \left[\frac{\partial \mathbb{R}_{ij}(\alpha,\beta,\gamma)}{\partial\beta}\right]_{(-\frac{\pi}{2},0,\frac{\pi}{2})} . \tag{B-22}$$

These quantities are readily determined from the explicit form of $\mathbb{R}$. Using them, one finds that

$$\frac{\partial \mathbb{R}_{\ell j}}{\partial \mathcal{X}'_k} = \sum_{m=1}^{3} \epsilon^k_{\ell m} \mathbb{R}_{mj} \qquad \text{(B-23)}$$

where ϵ^k is an antisymmetric matrix. Similarly, HWC show that since $\mathbb{D}^J$ is a homomorphic representation of the group,

$$\mathbb{D}^J(\mathcal{S}\mathcal{R}) = \mathbb{D}^J(\mathcal{S})\,\mathbb{D}^J(\mathcal{R}), \qquad \text{(B-24)}$$

and all that is needed to determine $\mathbb{D}^J(\mathcal{S})$ are the quantities

$$\left[\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \alpha}\right]_{(0,0,0)}, \quad \left[\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \beta}\right]_{(0,0,0)}, \quad \text{and} \quad \left[\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \beta}\right]_{(-\frac{\pi}{2},0,\frac{\pi}{2})}. \qquad \text{(B-25)}$$

HWC determine these quantities by differentiation of the explicit expressions for $\mathbb{D}^J$. However, they can more easily be obtained from Eq. (B-10) as follows. It is well known that $\mathcal{R}$ can be written in terms of the Euler angles and angular momenta. If all the rotations are performed about the space-fixed axes, Rose[56] shows that

$$\mathcal{R} = e^{i\gamma J_{z'}}\, e^{i\beta J_{y'}}\, e^{i\alpha J_{z'}}. \qquad \text{(B-26)}$$

Then, Eq. (B-10) is just[99]

$$D^J_{\Omega M}(\mathcal{R}) = e^{i\Omega\gamma} \langle \mathcal{X}', \ast'; J\Omega |\, e^{i\beta J_{y'}} \,| \mathcal{X}', \ast'; JM \rangle\, e^{iM\alpha}, \qquad \text{(B-27)}$$

and the quantities of (B-25) are obtained by direct differentiation and use of the raising and lowering operators. With (B-30) and the $\boldsymbol{\epsilon}^k$ matrix of Eq. (B-23), Eq. (B-21) becomes

$$\frac{\partial D^J_{\Omega M}(\mathcal{R})}{\partial \mathbf{X}'_k} = i\,\Omega\,\epsilon^k_{12}\,D^J_{\Omega M}(\mathcal{R}) + \tfrac{1}{2}\lambda_-(J,\Omega)(\epsilon^k_{31} + i\,\epsilon^k_{23})\,D^J_{\Omega-1,M}(\mathcal{R})$$

$$-\tfrac{1}{2}\lambda_+(J,\Omega)(\epsilon^k_{31} - i\,\epsilon^k_{23})\,D^J_{\Omega+1,M}(\mathcal{R})\,. \tag{B-28}$$

The differences between this result and that of the latest in the HWC series are due just to (B-12) and the fact that $\boldsymbol{\epsilon}^k$ is antisymmetric. Using this antisymmetry, the orthogonality of $\mathbb{R}$, and Eq. (B-16), Eq. (B-19) becomes

$$\frac{1}{i}\frac{\partial \Psi(\mathbf{X},\mathbf{u},\mathcal{X},J,\Omega)}{\partial \mathbf{X}'_k} = \left[\frac{1}{i}\sum_{\ell=1}^{3}\mathbb{R}_{\ell k}\frac{\partial}{\partial \mathbf{X}_\ell} + \frac{1}{i}\sum_{\ell\neq m}\sum_{m}\epsilon^k_{\ell m}\mathbf{X}_m\frac{\partial}{\partial \mathbf{X}_\ell} - \sum_{\substack{\ell,m,n \\ \text{cyclic}}}\epsilon^k_{\ell m}\,\mathcal{J}_n\right]\Psi, \tag{B-29}$$

where $\mathcal{J}_n$, n = 1,2,3 are the components in the body-fixed system of $\mathcal{J} = \underset{\sim}{\mathcal{L}} + \underset{\sim}{S}$, the total electronic angular momentum.

d. The standard configuration

Thus far, except for the restriction that it be independent of the electronic coordinates, $\mathcal{R}$ has been left general. To evaluate the elements of $\boldsymbol{\epsilon}^k$ explicitly, $\mathcal{R}$ must be fixed by the choice of body-fixed axes. We choose $\mathcal{R}$ such that the new

z axis lies in the direction of $\underset{\sim}{R}$ and such that the new y axis lies in the old xy plane (See Figure 2). With these restrictions Eq. (B-3) becomes

$$\sum_j \mathbb{R}_{ij} X_j' = \delta_{i3} R, \tag{B-30}$$

and Eq. (B-6) for $\hat{e}_2$ leads to the conclusion that

$$\mathbb{R}_{23} = 0. \tag{B-31}$$

Eq. (B-30 and 31) are all that is needed to determine ϵ^k . However, it is of interest to present $\mathbb{R}$ explicitly. For this choice of $\mathbb{R}$, the Euler angles become $\alpha = \varphi$, $\beta = \theta$, and $\gamma = 0$, where θ and φ are the spherical polar angles of $\underset{\sim}{R}$. The matrix $\mathbb{R}$ becomes simply[46,57]

$$\mathbb{R}(\varphi,\theta,0) = \begin{pmatrix} \cos\theta\cos\varphi & \cos\theta\sin\varphi & -\sin\theta \\ -\sin\varphi & \cos\varphi & 0 \\ \sin\theta\cos\varphi & \sin\theta\sin\varphi & \cos\theta \end{pmatrix}. \tag{B-32}$$

To obtain ϵ^k , let us differentiate (B-30 and 31) with respect to X_k' . One has ϵ^k_{ii} , and the others elements are easily found to be

$$\epsilon^k_{31} = -\epsilon^k_{13} = \mathbb{R}_{1k}/R \,,$$

$$\epsilon^k_{23} = -\epsilon^k_{32} = -\mathbb{R}_{2k}/R \,, \quad \text{and} \qquad \text{(B-33)}$$

$$\epsilon^k_{12} = -\epsilon^k_{21} = -\mathbb{R}_{2k}\mathbb{R}_{33}/\mathbb{R}_{13}R \,.$$

e. Derivatives of $\Psi(\mathbf{x}',\mathbf{X}')$

Combining (B-28, 29, and 33), using the properties of $\mathbb{R}$ and rearranging the sums slightly, Eq. (B-20) becomes

$$\frac{1}{i}\frac{\partial\Psi}{\partial X'_k}(\mathbf{x}',\mathbf{X}';J,M) = \sum_{\Omega}\sum_{j=1}^{3} D^J_{\Omega M}(\mathcal{R})\,\mathbb{R}_{jk}\,\Lambda_j\,\Psi(\mathbf{x},R;J,\Omega)\,, \qquad \text{(B-34)}$$

where from (B-30) we have used the fact that

$$\mathbf{X} = \begin{pmatrix}0\\0\\R\end{pmatrix} \qquad \text{(B-35)}$$

to write R instead of $\mathbf{X}$ in Ψ . The Λ_j are defined by

$$\Lambda_1 = \frac{1}{R}\left[\frac{\lambda_+(J,\Omega)\sigma_+ - \lambda_-(J,\Omega)\sigma_-}{2i} - j_y \right], \tag{B-36}$$

$$\Lambda_2 = \frac{1}{R}\left[\frac{\mathbb{R}_{33}}{\mathbb{R}_{13}}(j_z - \Omega) + j_x - \frac{\lambda_+(J,\Omega)\sigma_+ + \lambda_-(J,\Omega)\sigma_-}{2} \right], \tag{B-37}$$

$$\Lambda_3 = \frac{1}{i}\frac{\partial}{\partial R}. \tag{B-38}$$

Here $\sigma_\pm$ are not ordinary raising and lowering operators, but are defined simply to raise or lower the index Ω of any arbitrary function, f: $\sigma_\pm f(\Omega) = f(\Omega \pm 1)$. The reason for treating Ψ as arbitrary will become apparent below. If the properties of Ψ are invoked, one sees that Eq. (B-36 and 37) are equivalent to

$$\Lambda_1 \Psi(x,R;J,\Omega) = \frac{1}{R}(J_y - j_y)\Psi(x,R,J,\Omega), \text{ and} \tag{B-39}$$

$$\Lambda_2 \Psi(x,R,J,\Omega) = -\frac{1}{R}(J_x - j_y)\Psi(x,R,J,\Omega). \tag{B-40}$$

where the J_i are to be evaluated in terms of the raising and lowering operators relative to body-fixed axes. Eq. (B-45) has used the fact that the only angular momentum along the internuclear axis is electronic angular momentum,

$$J_z = j_z. \tag{B-41}$$

Eq. (B-34) now provides the first derivative. The second derivative is

$$-\frac{\partial^2 \Psi(\mathcal{X}',\mathcal{X}',J,M)}{\partial \mathcal{X}_k'^2} = \frac{1}{i}\sum_{\Omega,j}\left(\frac{\partial \mathbb{R}_{jk}}{\partial \mathcal{X}_k'}\right) D^J_{\Omega M}(\mathbb{R})\,\Lambda_j\,\Psi(\mathcal{X},R;J,\Omega) +$$

$$\sum_j \mathbb{R}_{jk}\left[\frac{1}{i}\frac{\partial}{\partial \mathcal{X}_k'}\sum_\Omega D^J_{\Omega M}(\mathbb{R})\,\Lambda_j\,\Psi(\mathcal{X}\ R;J,\Omega)\right].$$

As HWC observed, the second term here is just given by Eq. (B-34) if one lets $\Lambda_j\Psi$ play the role of the arbitrary function of body-fixed coordinates played by Ψ before. And using Eq. (B-28), one obtains

$$-\frac{\partial^2 \Psi(\mathcal{X}',\mathcal{X}';J,M)}{\partial \mathcal{X}_k'^2} = \sum_\Omega \sum_{j,\ell}^{3} D^J_{\Omega M}(\mathbb{R})\,\mathbb{R}_{\ell k}\left[\frac{\epsilon^k_{j\ell}}{i} + \mathbb{R}_{jk}\Lambda_\ell\right]\Lambda_j\,\Psi(\mathcal{X},R;J,\Omega). \qquad \text{(B-42)}$$

The Λ_j in $\Lambda_\ell\Lambda_j$ can be represented by Eq. (B-38 to 40), but the second one, Λ_ℓ, must be represented by Eq.(B-36 to 38).

Summing over k and using the properties of ϵ^k and $\mathbb{R}$, we obtain

$$\frac{1}{2\mu}\not{p}_R^{\,2}\,\Psi(\mathcal{X}',\mathcal{X}';J,M) = \frac{1}{2\mu}\sum_\Omega D^J_{\Omega M}(\mathbb{R})\left[\frac{2}{iR}\Lambda_3 - \frac{\mathbb{R}_{33}\Lambda_1}{iR\,\mathbb{R}_{13}} + \sum_j^3 \Lambda_j^2\right]\Psi(\mathcal{X},R;J,\Omega). \qquad \text{(B-43)}$$

Substituting in Eq. (B-36 to 40) as appropriate and using the commutation relations among the components of $\mathfrak{j}$, one finds that the terms containing the components of $\mathbb{R}$ drop out, leaving

$$\frac{1}{2\mu}\mathcal{P}_R^2\,\Psi(\mathcal{X}',\mathcal{X}';J,M) = \frac{1}{2\mu}\sum_{\Omega} D^J_{\Omega M}(\mathcal{R})\Big(-\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} +$$

$$\frac{1}{R^2}\Big\{\mathfrak{j}_x - \frac{1}{2}\left[\lambda_+(J,\Omega)\sigma_+ + \lambda_-(J,\Omega)\sigma_-\right]\Big\}^2 + \qquad \text{(B-44)}$$

$$\frac{1}{R^2}\Big\{\frac{1}{2i}\left[\lambda_+(J,\Omega)\sigma_+ - \lambda_-(J,\Omega)\sigma_-\right] - \mathfrak{j}_y\Big\}^2\Big)\,\Psi(\mathcal{X},R;J,\Omega).$$

When these expressions are worked out and the $\sigma_\pm$ allowed to raise and lower all Ω's that follow them, the result obtained is the same as if this equation were written as

$$\frac{1}{2\mu}\mathcal{P}_R^2\,\Psi(\mathcal{X}',\mathcal{X}';J,M) = \frac{1}{2\mu}\sum_{\Omega} D^J_{\Omega M}(\mathcal{R})\left[\frac{-1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{R^2}(\underset{\sim}{J} - \mathfrak{j})^2\right]\Psi(\mathcal{X},R;J,\Omega),$$

(B-45)

and the components of $\underset{\sim}{J}$ allowed to act via the raising and lowering operators.

The cross derivatives $\underset{\sim}{P}\cdot\mathcal{P}_R$ are also needed. The P_k' don't affect $\mathbb{D}^J(\mathcal{R})$ and simply transform according to Eq. (B-3). From (B-34) one has

$$\frac{1}{\mu}\underset{\sim}{p}\cdot\underset{\sim}{P}_R\,\Psi(\underset{\sim}{x}',\underset{\sim}{X}';J,M)=\frac{1}{\mu}\sum_{\Omega}\sum_{j}D^{J}_{\Omega M}(\mathcal{R})\,p_j\,\Lambda_j\,\Psi(\underset{\sim}{x},R;J,\Omega)\,,$$

$$=\frac{1}{\mu}\sum_{\Omega}D^{J}_{\Omega M}(\mathcal{R})\left\{\frac{1}{R}\left[p_x(J_y-j_y)-p_y(J_x-j_x)\right]+\right.$$

$$\left.p_z\frac{1}{i}\frac{\partial}{\partial R}\right\}\Psi(\underset{\sim}{x},R,J,\Omega)\,, \qquad \text{(B-46)}$$

f. Transformation of the Hamiltonian

The Schrödinger equation can now be written out, with all the operators transformed, as

$$\sum_{\Omega}D^{J}_{\Omega M}(\mathcal{R})\left\{-\frac{1}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}+\frac{\underset{\sim}{L}^2}{2\mu R^2}+\frac{1}{\mu}\left[\frac{1}{R}(p_xL_y-p_yL_x)+p_z\frac{1}{i}\frac{\partial}{\partial R}\right]\right.$$

$$\left.+\mathcal{H}_e-E_i\right\}\Psi(\underset{\sim}{x},R;J,\Omega)=0\;. \qquad \text{(B-47)}$$

Here Eq. (2-11), $\underset{\sim}{L}=\underset{\sim}{J}-\underset{\sim}{j}$, must be used when the components of $\underset{\sim}{L}$ act on Ψ. Thus, the only dependence on θ and Φ is in the $D^{J}_{\Omega M}(\mathcal{R})$.

To complete the removal of the rotation at this point, HWC use the orthogonality of their $D^{J}_{\Omega M}$. However, $\gamma=0$ in Eq. (B-27), and our $D^{J}_{\Omega M}$ are not orthogonal in different Ω values. Instead, the orthogonality relations become[100]

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \, D^{J'*}_{\Omega M}(\mathcal{R}) \, D^{J}_{\Omega M}(\mathcal{R}) = \frac{4\pi}{2J+1} \delta_{JJ'} \, \delta_{MM'} . \tag{B-48}$$

Although the $D^J_{\Omega M}$ cannot be used to complete the removal of the rotation, it can be accomplished as follows. If all the operators in Eq. (B-47) are written in terms of irreducible tensors, they all are zero components of the form T^0_L and commute with J_z (see Appendix D). Likewise, they commute with any function of J_z, say $f(J_z)$. Applying $f(J_z)$ to Eq. (B-47), one obtains

$$f(J_z) \sum_{\Omega} D^J_{\Omega M}(\mathcal{R}) \{ \} \Psi(x,R;J,\Omega) = \sum_{\Omega} f(\Omega) D^J_{\Omega M} \{ \} \Psi(x,R;J,\Omega) . \tag{B-49}$$

Let $f(\Omega) = e^{i\omega\Omega}$ where ω is a dummy parameter. Multiply by $f^*(\Omega')$ and integrate ω from 0 to 2π , and it is clear that

$$\begin{aligned} \Big\{ -\frac{1}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\underset{\sim}{L}^2}{2\mu R^2} + \frac{1}{\mu}\Big[\frac{1}{R}(P_x L_y - P_y L_x) + P_z \frac{1}{i} \frac{\partial}{\partial R}\Big] \\ + \mathcal{H}_e - E_i \Big\} \Psi(x,R,J,\Omega') = 0 . \end{aligned} \tag{B-50}$$

Except for the $P_z \frac{1}{i} \frac{\partial}{\partial R}$ term, this is the result of Section IIB. Let us now consider this term. The rest of the terms in (B-50) are Hermitian; hence, this one should also be Hermitian. But the integration over R now involves the Jacobian R^2 . By partial integration[66] one easily finds that

$$\left(\frac{1}{i}\frac{\partial}{\partial R}\right)^{\dagger} = \frac{1}{i}\frac{\partial}{\partial R} + \frac{2}{iR} . \qquad \text{(B-51)}$$

so that $\frac{1}{i}\frac{\partial}{\partial R}$ is not independently Hermitian. However, for all functions Ψ transforming as the irreducible representations of the rotation group, one can show (Appendix D) that

$$\frac{2}{i}\langle \Psi, \frac{P_z}{R}\Psi\rangle = 0 ,$$

so that $\frac{P_z}{i}\frac{\partial}{\partial R}$ is still Hermitian with respect to all the functions of interest. However, it is convenient to use a form in which the differential R operator is independently Hermitian. We thus take the Hermitian part of $P_z\frac{1}{i}\frac{\partial}{\partial R}$,

$$\frac{1}{2}\left[P_z\frac{1}{i}\frac{\partial}{\partial R} + \left(P_z\frac{1}{i}\frac{\partial}{\partial R}\right)^{\dagger}\right] = P_z\left(\frac{1}{i}\frac{\partial}{\partial R} + \frac{1}{iR}\right) . \qquad \text{(B-52)}$$

But this is the same as

$$p_R = \frac{1}{i}\frac{1}{R}\frac{\partial}{\partial R}R = \frac{1}{i}\frac{\partial}{\partial R} + \frac{1}{iR} , \qquad \text{(B-53)}$$

where p_R is the radial momentum used in Section II. The added term makes no contribution to expectation values and we are thus free to use (B-52) in place of $P_z\frac{1}{i}\frac{\partial}{\partial R}$ in Eq. (B-50).

2. The Inversion Operation

In this subsection, we want to determine $\mathcal{I}'\Psi(\mathbf{x}',\ast')$ for use in Section IIB. Applying $\mathcal{I}$ directly to Eq. (2-37), one has

$$(-1)^{p}\Psi(\mathbf{x}',\ast',J,M)=\mathcal{I}'\Psi(\mathbf{x}',\ast',J,M)=\sum_{\Omega}\mathcal{I}'\left\{D^{J}_{\Omega M}[\mathcal{R}(\theta,\varphi)]\,\Psi(\mathbf{x},\ast;J,\Omega)\right\}. \tag{B-54}$$

We now use the fact that $\mathbf{x}=\mathbb{R}\mathbf{x}'$, etc., and treat the quantity in $\{\ \}$ as though it were just a function of the space-fixed coordinates. $\mathcal{I}'\ast'=-\ast'$, and if R, θ, and φ are the spherical polar coordinates of $\underset{\sim}{R}$, it is easily shown that the spherical polar coordinates of $-\underset{\sim}{R}$ are R, $\pi-\theta$, and $\varphi\pm\pi$. Since $\mathcal{I}'$ acts simultaneously on all that follows it, Eq. (B-54) becomes

$$(-1)^{p}\Psi(\mathbf{x}',\ast';J,M)=\sum_{\Omega}D^{J}_{\Omega M}[\mathbb{R}(\pi-\theta,\varphi\pm\pi)]\,\mathcal{I}'\Psi(\mathbf{x},\ast,J,\Omega), \tag{B-55}$$

where

$$\begin{aligned}\mathcal{I}'\Psi(\mathbf{x},\ast;J,\Omega)&=\Psi[\mathbb{R}(\pi-\theta,\varphi\pm\pi)\mathcal{I}'\mathbf{x}',\mathbb{R}(\pi-\theta,\varphi\pm\pi)\mathcal{I}'\ast';J,\Omega],\\&=\Psi[-\mathbb{R}(\pi-\theta,\varphi\pm\pi)\mathbf{x}',-\mathbb{R}(\pi-\theta,\varphi\pm\pi)\ast';J,\Omega].\end{aligned} \tag{B-56}$$

From the explicit form of $\mathbb{R}$ given at (B-32) we can put $\mathbb{R}(\pi-\theta, \varphi\pm\pi) = \mathbb{T}\,\mathbb{R}(\theta,\varphi)$, where $\mathcal{T}$ is a rotation, and its matrix $\mathbb{T}$ is just

$$\mathbb{T} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} . \tag{B-57}$$

Using this in (B-56), we see that since

$$\mathbf{X} = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix},$$

$$\mathcal{I}'\,\Psi(\mathbf{x},\mathbf{X},J,\Omega) = \Psi\left[\begin{pmatrix} -x \\ y \\ z \end{pmatrix}, \mathbf{X}, J, \Omega\right] , \tag{B-58}$$

so that when acting directly on a function of the body-fixed coordinates, $\mathcal{I}'$ is just

$$\mathcal{I}' = \sigma_{yz} , \tag{B-59}$$

a reflection in the body-fixed yz plane. For greater clarity we replace $\mathcal{I}'$ by σ_{yz} hereafter when it operates on $\Psi(\mathbf{x},\mathbf{X})$. Thus, Eq. (B-55) becomes

$$(-1)^{p}\,\Psi(\mathbf{x},\mathbf{X}',J,M) = \sum_{\Omega} D^{J}_{\Omega M}(\mathcal{T}\mathbb{R})\;\sigma_{yz}\,\Psi(\mathbf{x},\mathbf{X},J,\Omega) . \tag{B-60}$$

In the most recent paper of the HWC series, Kouri and Curtiss[46] have used the explicit formulas for $D^J_{\Omega M}$ and shown that

$$D^J_{\Omega M}[\mathcal{J}\mathcal{R}] = (-1)^J D^J_{-\Omega,M}(\mathcal{R}). \tag{B-61}$$

Using Eq. (2-37) for the left hand side of Eq. (B-60) and changing the dummy index of summation on the left hand side, we obtain

$$\sum_{\Omega} D^J_{-\Omega,M}(\mathcal{R})\left[(-1)^p\,\Psi(\mathbf{x},\mathbf{X},J,-\Omega) - (-1)^J\sigma_{yz}\,\Psi(\mathbf{x},\mathbf{X},J,\Omega)\right] = 0 \tag{B-62}$$

Thus, if the body-fixed wave functions satisfy

$$\sigma_{yz}\,\Psi(\mathbf{x},\mathbf{X},J,\Omega) = (-1)^{p-J}\,\Psi(\mathbf{x},\mathbf{X},J,-\Omega), \tag{B-63}$$

then the space-fixed wavefunction $\Psi(\mathbf{x}',\mathbf{X}')$ will have definite parity under inversion.

3. Double-valued Representations of the Rotation Group

In this subsection we discuss the effect on the results of the previous two subsections if the total number, N, of electrons in the system is odd. Each electron has spin ½ , and if N is odd, then the total angular momentum of the system, J , will be a half integer. Wigner[101] has discussed this case in detail. He shows that if N is odd, the $\mathbb{D}^J$ form a double valued representation of the rotation group. And instead of using the $\mathbb{D}^J$ used in the preceding subsections, we should have used $(\pm)^N \mathbb{D}^J$ everywhere. The $\pm$ signs can take either value and cannot be fixed by any choice of convention. Furthermore, instead of Eq. (B-24), which was used for $\mathcal{I}$ and then later for $\mathfrak{J}$ at Eq. (B-60), there is the additional uncertainty

$$(\pm)^N \mathbb{D}^J(\mathcal{I}\mathbb{R}) = \mathbb{D}^J(\mathcal{I})\,\mathbb{D}^J(\mathbb{R}) . \tag{B-64}$$

For most of the symmetry operations this presents no problem, since they did not affect the rotation. However, for half integral J, Eq. (B-63) should read

$$\sigma_{yz}\,\Psi(\mathcal{X},\mathcal{Y},J,\mathcal{R}) = (\pm)^N(-1)^{p-J}\,\Psi(\mathcal{X},\mathcal{Y},J,-\mathcal{R}). \tag{B-65}$$

This equation presents two problems. One is that $(-1)^{-J} = (i)^{-2J}$ is imaginary for half integral J. The second is that while (B-65) causes $\Psi(\mathcal{X}',\mathcal{Y}')$ to have definite parity under $\mathcal{I}'$, the $\pm$ makes it impossible to say <u>which</u> parity $\Psi(\mathcal{X}',\mathcal{Y}')$ has.

To handle the imaginary factor, we follow Messiah[102], who puts $\sigma_{yz}(J) = (i)^{2J}\sigma_{yz}$. Then,

$$\sigma_{yz}(J)\,\Psi(\mathcal{X},\mathcal{Y},J,\mathcal{R}) = (\pm)^N(-1)^p\,\Psi(\mathcal{X},\mathcal{Y},J,-\mathcal{R}). \tag{B-66}$$

and $\sigma_{yz}(J)$ is used in place of σ_{yz} if J is a half-integer. The simplest way to handle the $(\pm)^N$ seems to be the following[103]. We use the symmetry operations only to find selection rules for transitions between states. And the matrix elements always involve two wavefunctions, so that any symmetry operation always produces two of the $(\pm)^N$ which cancel each other out. In such applications, which parity a wavefunction has doesn't matter. What matters is whether its parity is the same as or different from the parity of the other wavefunction in the matrix element. Hence, one obtains the same selection rules whether or not he includes the $(\pm)^N$, and for convenience the factor is simply ignored in the text.

To complete the conventions necessary to specify the behavior under all the symmetry operations, we choose to construct all angular momentum eigenfunctions out of the usual spherical harmonics[95-97] and spin functions. The spherical harmonics have the form

$$Y_\ell^m(\theta_i, \varphi_i) = \Theta_{\ell m}(\theta_i) \frac{e^{im\varphi_i}}{\sqrt{2\pi}} , \qquad \text{(B-67)}$$

where Θ is a real function. Also, they obey

$$\left(Y_\ell^m\right)^* = (-1)^m Y_\ell^{-m} . \qquad \text{(B-68)}$$

Because σ_{yz}, Eq. (B-58), reflects through the yz plane, one has $\sigma_{yz} f(r_i, \theta_i, \varphi_i) = f(r_i, \theta_i, \pi - \varphi_i)$. Hence,

$$\sigma_{4z} Y_\ell^m = (-1)^m (Y_\ell^m)^* = Y_\ell^{-m}. \qquad \text{(B-69)}$$

The spin functions $\alpha = |j,m\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle$ and $\beta = |\tfrac{1}{2},-\tfrac{1}{2}\rangle$ are chosen to behave similarly,

$$\sigma_{4z} |\tfrac{1}{2},\pm\tfrac{1}{2}\rangle = |\tfrac{1}{2},\mp\tfrac{1}{2}\rangle. \qquad \text{(B-70)}$$

Under inversion of their coordinates, the behavior of the spherical harmonics is well known[104],

$$\mathcal{I}\, Y_\ell^m(\theta_i,\varphi_i) = Y_\ell^m(\pi-\theta_i,\varphi_i\pm\pi) = (-1)^\ell Y_\ell^m(\theta_i,\varphi_i). \qquad \text{(B-71)}$$

But, in choosing the spin functions, as Heine[105] pointed out, we are free to take the usual convention,

$$\mathcal{I}\, |\tfrac{1}{2},\pm\tfrac{1}{2}\rangle = |\tfrac{1}{2},\pm\tfrac{1}{2}\rangle \qquad \text{(B-72)}$$

4. The Removal of Rotation in the CMN Coordinates

In Appendix A, we obtained the relative Hamiltonian in the center of mass of the nuclei (CMN) system. From Eq. (A-36) it can easily be written as

$$\mathcal{H} = \frac{1}{2\mu}\mathcal{P}_R^2 + \mathcal{H}_e(CMN), \qquad \text{(B-73)}$$

where

$$\mathcal{H}_e(CMN) = \frac{1}{2}\sum_{i=1}^{N} p_{in}^2 + \frac{1}{2(m_a+m_b)} \underset{\sim}{P}_n^2 + \alpha^2 H_\alpha . \qquad \text{(B-74)}$$

$\mathcal{H}_e(CMN)$ does not contain any nuclear momentum operators and is invariant under rotation. Let us rotate the axes as before. Then, p_R^2 transforms as before and the Schrödinger equation in body-fixed coordinates is just

$$\left[\frac{1}{2\mu} p_R^2 + \frac{\underset{\sim}{L}^2}{2\mu R^2} + \mathcal{H}_e(CMN) - E_i \right] \Psi(x_n, R, J, \Omega) = 0 \qquad \text{(B-75)}$$

where $\underset{\sim}{L}^2 = (\underset{\sim}{J} - \underset{\sim}{j})^2$ just as before. The angular momentum properties are the same as in the separated atom system and need not be repeated. The electron exchange is simple in this system and invariant under the rotation. Hence, it remains given by Eq. (A-39). It is convenient again to use $\bar{\mathcal{I}}_e$ instead of $\bar{\mathcal{P}}_{ab}$. In these coordinates, $\bar{\mathcal{I}}_e = \mathcal{I}\bar{\mathcal{P}}_{ab}$ is invariant under the rotation as before and given simply by

$$\mathcal{I}_e \Psi(x_n, X; J, \Omega) = \Psi(-x_n, X, J, \Omega) = (-1)^{p_e} \Psi(x_n, X, J, \Omega).$$

(B-76)

Once again, we use the $D^{J}_{\Omega M}$ to get a tractable way to treat $\mathscr{I}'$ and get the condition that

$$\sigma_{yz}\,\Psi(X_n, X; J, \Omega) = \Psi\left[\begin{pmatrix} -x \\ y \\ z \end{pmatrix}_n, X; J, \Omega\right] = (-1)^{p-J}\,\Psi(X_n, X, J, -\Omega). \tag{B-77}$$

Thus, the formulas in the CMN system are even simpler than those in the separated atom system.

The Hamiltonian in the ρ system transforms similarly, with ρ chosen to lie along the new z axis in place of $\underset{\sim}{R}$. The formulas, if needed, can be written by inspection, and we do not list them here.

Appendix C. Perturbation Formalisms

This appendix contains the development of the perturbation equations and energies for two special cases. In the first, the perturbation is an operator which is only defined when it acts on the zeroth order solution. In the second, the Hamiltonian is an infinite power series in the perturbation parameter λ .

1. A Differential Operator as a Perturbation

In Section IV the formulas of ordinary perturbation theory[65,68] are used for a perturbation which is an operator and only defined when acting on the zeroth order wavefunction. We now prove that that use was valid.

Consider an arbitrary wave equation,

$$\mathcal{H}\psi_i = E_i\psi_i , \tag{C-1}$$

for which the only thing known initially is a complete set of orthonormal approximate solutions, $\psi_j^{(0)}$, such that

$$\mathcal{H}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)} + \lambda\mathcal{H}^{(1)}\psi_j^{(0)} + \lambda^2\mathcal{H}^{(2)}\psi_j^{(0)}. \tag{C-2}$$

The last two terms simply contain everything left over when $\mathcal{H}$ acts on $\psi_j^{(0)}$. The terms are taken to be ordered by the parameter λ . The perturbations $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$ are operators and only $\mathcal{H}^{(1)}\psi_j^{(0)}$ and $\mathcal{H}^{(2)}\psi_j^{(0)}$ are defined. It is assumed that $E_j^{(0)}$ is non-degenerate and that

$$\psi_i = \sum_{n=0}^{\infty} \lambda^n \psi_i^{(n)}, \quad \text{and} \quad E_i = \sum_{n=0}^{\infty} \lambda^n E_i^{(n)}. \tag{C-3}$$

Since the set of $\psi_i^{(0)}$ was assumed complete, the higher order wave functions can be expanded in terms of them,

$$\psi_i^{(n)} = \sum_j C_{ij}^{(n)} \psi_j^{(0)}. \tag{C-4}$$

Eq. (C-4) keeps all the quantities well defined when (C-3) is substituted into (C-1) to obtain

$$\sum_{n=0}^{\infty} \lambda^n \sum_j \Big(C_{ij}^{(n)} E_j^{(0)} \psi_j^{(0)} + C_{ij}^{(n-1)} \mathcal{H}^{(1)} \psi_j^{(0)} + C_{ij}^{(n-2)} \mathcal{H}^{(2)} \psi_j^{(0)} - \sum_{m=0}^{n} E_i^{(m)} C_{ij}^{(n-m)} \psi_j^{(0)} \Big) = 0. \tag{C-5}$$

Setting the coefficient of each power of λ equal to zero and rearranging slightly, we obtain the n-th order perturbation equation,

$$\sum_j \Big[C_{ij}^{(n)} (E_j^{(0)} - E_i^{(0)}) \psi_j^{(0)} + C_{ij}^{(n-1)} \mathcal{H}^{(1)} \psi_j^{(0)} + C_{ij}^{(n-2)} \mathcal{H}^{(2)} \psi_j^{(0)} - \sum_{m=1}^{n} E_i^{(m)} C_{ij}^{n-m} \psi_j^{(0)} \Big] = 0. \tag{C-6}$$

Upon multiplication by $\psi_k^{(0)*}$ and integration, this becomes

$$c_{ik}^{(n)}\left(E_k^{(0)}-E_i^{(0)}\right)+\sum_j\left(c_{ij}^{(n-1)}\langle\psi_k^{(0)}|\mathcal{H}^{(1)}\psi_j^{(0)}\rangle+c_{ij}^{(n-2)}\langle\psi_k^{(0)}|\mathcal{H}^{(2)}\psi_j^{(0)}\rangle\right)$$

$$-\sum_{m=1}^{n}E_i^{(m)}c_{ik}^{(n-m)}=0\,, \qquad \text{(C-7)}$$

If n = 0 , one obtains

$$c_{ik}^{(0)}\left(E_k^{(0)}-E_i^{(0)}\right)=0\,, \quad \text{or} \qquad \text{(C-8)}$$

$$c_{ik}^{(0)}=\delta_{ik}\,, \qquad \text{(C-9)}$$

consistent with the choice of zeroth-order solution.

If n = 1 and k = i , then

$$E_i^{(1)}=\langle\psi_i^{(0)}|\mathcal{H}^{(1)}\psi_i^{(0)}\rangle\,. \qquad \text{(C-10)}$$

If n = 1, but k ≠ i , then

$$c_{ik}^{(1)}=-\frac{\langle\psi_k^{(0)}|\mathcal{H}^{(1)}\psi_i^{(0)}\rangle}{E_k^{(0)}-E_i^{(0)}}\,, \qquad \text{(C-11)}$$

which gives the usual spectral expansion formula for $\psi_i^{(1)}$ from Eq. (C-4). One is free to use the normality relations in the usual fashion[68] to set

$$C_{ii}^{(1)} = 0 . \tag{C-12}$$

If n=2 and k=i , Eq. (C-7) becomes

$$E_i^{(2)} = \langle \psi_i^{(0)} | \mathcal{H}^{(2)} \psi_i^{(0)} \rangle - \sum_j{}' \frac{\langle \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}} . \tag{C-13}$$

Since the Hamiltonian $\mathcal{H}$ must be Hermitian,

$$\langle \psi_i^{(0)} | \mathcal{H} \psi_j^{(0)} \rangle = \langle \mathcal{H} \psi_i^{(0)} | \psi_j^{(0)} \rangle . \tag{C-14}$$

Using Eq. (C-2) and equating powers of λ in (C-14), one sees that

$$\langle \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_j^{(0)} \rangle = \langle \mathcal{H}^{(1)} \psi_i^{(0)} | \psi_j^{(0)} \rangle . \tag{C-15}$$

This allows $E_i^{(2)}$ to be written in the more symmetric fashion,

$$E_i^{(2)} = \langle \psi_i^{(0)} | \mathcal{H}^{(2)} \psi_i^{(0)} \rangle - \sum_j{}' \frac{\langle \mathcal{H}^{(1)} \psi_i^{(0)} | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}} . \tag{C-16}$$

If the $E_j^{(0)} - E_i^{(0)}$ are replaced by a mean value, Δ_i , the sum can be performed to give the Unsöld approximation,

$$E_i^{(2)} = \langle \psi_i^{(0)} | \mathcal{H}^{(2)} \psi_i^{(0)} \rangle - \frac{1}{\Delta_i} \left\{ \langle \mathcal{H}^{(1)} \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle - \langle \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle^2 \right\} \tag{C-17}$$

To obtain an estimate for Δ_i, let us consider the first order wavefunction,

$$\psi_i^{(1)} = -\sum_j{}' \frac{|\psi_j^{(0)}\rangle \langle \psi_j^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}}, \tag{C-18}$$

and as an approximation to $\psi_i^{(1)}$, let us again perform the Unsöld approximation,

$$\tilde{\psi}_i^{(1)} = -\frac{1}{\Delta_i} (\mathcal{H}^{(1)} - E_i^{(1)}) \psi_i^{(0)}. \tag{C-19}$$

If ψ_i is a state to which the Rayleigh-Ritz variation principle applies, substitution of the unnormalized trial function $\psi_i^{(0)} + \lambda \tilde{\psi}_i^{(1)}$ into the variation principle and expansion in powers of λ gives the Hylleraas[67,68] principle for this case,

$$E_i^{(2)} \leq \tilde{E}_i^{(2)} = \langle \psi_i^{(0)} | \mathcal{H}^{(2)} \psi_i^{(0)} \rangle + \langle \tilde{\psi}_i^{(1)} | \mathcal{H} - E_i^{(0)} | \tilde{\psi}_i^{(1)} \rangle$$

$$+ 2\,\mathrm{Re} \langle \tilde{\psi}^{(1)} | \mathcal{H}^{(1)} | \tilde{\psi}^{(0)} \rangle. \tag{C-20}$$

Actually, only $\mathcal{H}^{(0)}$ is needed in the second integral instead of $\mathcal{H}$, but $\mathcal{H}^{(0)}$ is not known here.

Now let us assume that $E_i^{(1)} = 0$ and substitute Eq. (C-19) into (C-20). The result is

$$\tilde{E}_i^{(2)} = \langle \psi^{(0)} | \mathcal{H}^{(2)} \psi_i^{(0)} \rangle + \frac{1}{\Delta_i^2} \langle \mathcal{H}^{(1)} \psi_i^{(0)} | \mathcal{H} - E_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle$$

$$- \frac{2}{\Delta_i} \langle \mathcal{H}^{(1)} \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle . \qquad \text{(C-21)}$$

Let us now minimize this with respect to Δ by setting

$$\frac{\partial \tilde{E}_i^{(2)}}{\partial \Delta_i} = 0 . \qquad \text{(C-22)}$$

$\mathcal{H}^{(2)}$ is allowed to depend only on the final value of Δ_i, not on this variable value. The result is just

$$\tilde{\Delta}_i = \frac{\langle \mathcal{H}^{(1)} \psi_i^{(0)} | \mathcal{H} - E_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle}{\langle \mathcal{H}^{(1)} \psi_i^{(0)} | \mathcal{H}^{(1)} \psi_i^{(0)} \rangle} . \qquad \text{(C-23)}$$

Use of this $\tilde{\Delta}_i$ in Eq. (C-21) gives the same result as its use in (C-17), providing an upper bound to $E_i^{(2)}$ equivalent to the Dirichlet principle[67].

This completes the derivation of the formulas needed in Section IV.

2. Infinite Series Expansion of the Hamiltonian

The results of this appendix are not new. They are derived here (for use in Section V) because the formulas obtained from a Hamiltonian of the form of an infinite power series in the perturbation parameter λ,

$$\mathcal{H} = \sum_{n=0}^{\infty} \lambda^n \mathcal{H}^{(n)}, \tag{C-24}$$

are not so familiar as the usual $\mathcal{H} = \mathcal{H}^{(0)} + \lambda \mathcal{H}^{(1)}$ form.

We desire a perturbation solution of the Schrödinger equation,

$$\mathcal{H}\psi = E\psi. \tag{C-25}$$

Let us assume that

$$E = \sum_{n=0}^{\infty} \lambda^n E^{(n)} \quad \text{, and} \tag{C-26}$$

$$\psi = \sum_{n=0}^{\infty} \lambda^n |n\rangle, \tag{C-27}$$

where $|n\rangle = \psi^{(n)}$ is the n-th order wavefunction.

The wavefunctions are subjected to the usual normalization[68] conditions,

$$\langle\psi|\psi\rangle = \langle 0|0\rangle = 1. \tag{C-28}$$

Substitution of Eq. (C-27) into this and requiring that it hold for all allowed λ leads to

$$\sum_{k=0}^{n} \langle k | n-k \rangle = \delta_{n0} . \tag{C-29}$$

To obtain this result we used the Cauchy product of sums definition,

$$\sum_{n=0}^{\infty} a_n \sum_{k=0}^{\infty} b_k = \sum_{n=0}^{\infty} \sum_{k=0}^{n} a_k b_{n-k} = \sum_{n=0}^{\infty} c_n . \tag{C-30}$$

Next, let us substitute the sums into Eq. (C-25) and equate powers of λ . This leads to the nth order perturbation equation,

$$\sum_{k=0}^{n} D^{(k)} | n-k \rangle = 0 , \tag{C-31}$$

where

$$D^{(k)} = \mathcal{H}^{(k)} - E^{(k)} . \tag{C-32}$$

Using Eq. (C-29), (C-31), and the fact that $D^{(k)}$ is Hermitian, one can show by a series of algebraic manipulations that the (2n)-th and (2n+1)-st order energies can be obtained from the n-th order wavefunction. The formulas for them are

$$E^{(2n)} = \langle 0 | \mathcal{H}^{(2n)} | 0 \rangle + \sum_{m=n+1}^{2n-1} \langle 0 | D^{(m)} | 2n-m \rangle + \sum_{k=1}^{n} \sum_{m=n+1-k}^{2n-k} \langle k | D^{(m)} | 2n-m-k \rangle , \tag{C-33}$$

and

$$E^{(2n+1)} = \langle 0|H^{(2n+1)}|0\rangle + \sum_{m=n+1}^{2n} \langle 0|D^{(m)}|2n+1-m\rangle + \sum_{k=1}^{n} \sum_{m=n+1-k}^{2n+1-k} \langle k|D^{(m)}|2n+1-m-k\rangle . \tag{C-34}$$

The procedure for obtaining these results is essentially that explained by Hirschfelder, Byers Brown, and Epstein.[106]

Before considering special cases, let us obtain the expression for the expectation value of any Hermitian operator A which can be expanded in λ ,

$$A = \sum_{n=0}^{\infty} \lambda^n A^{(n)}. \tag{C-35}$$

Using this, (C-27), and (C-30) one obtains

$$\langle \psi|A|\psi\rangle = \sum_{n=0}^{\infty} \lambda^n a^{(n)}, \tag{C-36}$$

where

$$a^{(n)} = \sum_{m=0}^{n} \sum_{k=0}^{m} \langle m-k|A^{(k)}|n-m\rangle . \tag{C-37}$$

Before ending this appendix, we give the formulas which will be needed in Section V and VI. For neutral atoms two of the terms in the multipole expansion are zero,

$$\mathcal{H}^{(1)} = \mathcal{H}^{(2)} = 0, \tag{C-38}$$

which leads immediately to

$$E^{(1)} = D^{(1)} = 0 \text{ , and} \tag{C-39}$$

$$E^{(2)} = D^{(2)} = 0 . \tag{C-40}$$

The first three perturbation equations become

$$D^{(0)} |k\rangle = 0 \quad , \quad k = 0, 1, 2. \tag{C-41}$$

Since $|0\rangle$ is assumed to be the proper zeroth order wavefunction, the only allowed solutions for the first and second order wavefunctions are

$$\begin{aligned} |1\rangle &= C^{(1)} |0\rangle \\ |2\rangle &= C^{(2)} |0\rangle \end{aligned} \tag{C-42}$$

From the normalization conditions (C-29), one finds restrictions on the constants,

$$\mathrm{Re}\ C^{(1)} = 0 \text{, and} \tag{C-43}$$

$$2\,\mathrm{Re}\,C^{(2)} + |C^{(1)}|^2 = 0, \tag{C-44}$$

and the imaginary parts of $C^{(1)}$ and $C^{(2)}$ cannot affect the energy or the expectation values of any Hermitian operator. Hence, one is free to choose

$$\mathcal{I}m\, C^{(1)} = \mathcal{I}m\, C^{(2)} = 0. \tag{C-45}$$

Then, Eq. (C-42) becomes

$$|1\rangle = |2\rangle = 0, \tag{C-46}$$

which merely says that a zero perturbation does not perturb the wavefunction or the energy.

With these results, the perturbation equations up through the sixth order are

$$\begin{aligned}
&D^{(0)}|0\rangle = 0, \\
&D^{(0)}|3\rangle + D^{(3)}|0\rangle = 0, \\
&D^{(0)}|4\rangle + D^{(4)}|0\rangle = 0, \\
&D^{(0)}|5\rangle + D^{(5)}|0\rangle = 0, \quad \text{and} \\
&D^{(0)}|6\rangle + D^{(3)}|3\rangle + D^{(6)}|0\rangle = 0.
\end{aligned} \tag{C-47}$$

Thus, $|n\rangle$, for n=3,4,5, are all obtained by solving "first-order" perturbation equations. The normalization conditions (C-29) also are simplified,

$$\begin{aligned} &\langle 0|0\rangle = 1, \\ &\mathrm{Re}\langle 0|3\rangle = 0, \\ &\mathrm{Re}\langle 0|4\rangle = 0, \\ &\mathrm{Re}\langle 0|5\rangle = 0, \text{ and} \\ &2\mathrm{Re}\langle 0|6\rangle + \langle 3|3\rangle = 0. \end{aligned} \tag{C-48}$$

The first few perturbation energies become

$$\begin{aligned} &E^{(1)} = E^{(2)} = 0, \\ &E^{(3)} = \langle 0|\mathcal{H}^{(3)}|0\rangle, \\ &E^{(4)} = \langle 0|\mathcal{H}^{(4)}|0\rangle, \\ &E^{(5)} = \langle 0|\mathcal{H}^{(5)}|0\rangle, \text{ and} \\ &E^{(6)} = \langle 0|\mathcal{H}^{(6)}|0\rangle + \langle 0|\mathcal{H}^{(3)}|3\rangle. \end{aligned} \tag{C-49}$$

And finally, the first few terms in the series (C-36) for the expectation value of a Hermitian operator become

$$\begin{aligned}
a^{(k)} &= \langle 0|A^{(k)}|0\rangle, \quad k=0,1,2, \\
a^{(3)} &= \langle 0|A^{(3)}|0\rangle + 2\mathrm{Re}\langle 3|A^{(0)}|0\rangle, \\
a^{(4)} &= \langle 0|A^{(4)}|0\rangle + 2\mathrm{Re}\langle 4|A^{(0)}|0\rangle + 2\mathrm{Re}\langle 3|A^{(1)}|0\rangle, \\
a^{(5)} &= \langle 0|A^{(5)}|0\rangle + 2\mathrm{Re}\langle 5|A^{(0)}|0\rangle + 2\mathrm{Re}\langle 4|A^{(1)}|0\rangle + \\
&\qquad 2\mathrm{Re}\langle 3|A^{(2)}|0\rangle, \text{ and} \qquad \text{(C-50)} \\
a^{(6)} &= \langle 0|A^{(6)}|0\rangle + 2\mathrm{Re}\langle 6|A^{(0)}|0\rangle + 2\mathrm{Re}\langle 5|A^{(1)}|0\rangle \\
&\qquad + 2\mathrm{Re}\langle 4|A^{(2)}|0\rangle + 2\mathrm{Re}\langle 3|A^{(3)}|0\rangle + \langle 3|A^{(0)}|3\rangle .
\end{aligned}$$

This completes the derivation of the formulas needed in Section V.

Appendix D. Matrix Elements

In the body of the paper a number of assertions were made about the values of certain matrix elements. In this appendix the properties of irreducible tensors used in the text are reviewed, and some particular matrix elements encountered in the text are discussed.

1. Irreducible Tensors[107]

The quantity T_L^M is the M component of an L-th rank irreducible spherical tensor if it satisfies the commutation relations,

$$[J_\pm, T_L^M] = [(L \pm M+1)(L \mp M)]^{1/2} T_L^{M\pm 1}, \quad \text{and}$$

$$[J_z, T_L^M] = M T_L^M. \tag{D-1}$$

Here the J_i are components of the total angular momentum of the system, and T_L^M depends on the coordinates of any or all of the particles in the system.

The components of a vector are easily written in terms of first rank tensors. If $\underset{\sim}{P}$ is any vector, then

$$P_1^1 = -\frac{1}{\sqrt{2}}(P_x + i P_y) ,$$

$$P_1^0 = P_z , \text{ and} \qquad \text{(D-2)}$$

$$P_1^{-1} = \frac{1}{\sqrt{2}}(P_x - i P_y)$$

are the associated irreducible tensor components. Thus, the raising and lowering operators themselves are irreducible tensors (except for a normalization factor),

$$J_+ = -\sqrt{2}\, J_1^1 , \quad \text{and}$$

$$J_- = \sqrt{2}\, J_1^{-1} . \qquad \text{(D-3)}$$

The spherical harmonics, Y_ℓ^m , also are irreducible tensors to within a normalization factor.

The Clebsch-Gordan Theorem. To write a tensor which depends on all the coordinates in terms of products of tensors, each involving the coordinates of only one atom, one uses the Clebsch-Gordan theorem,

$$T_L^M = \sum_{M_1, M_2} C(L_1, L_2, L; M_1, M_2, M)\, T_{L_1}^{M_1} T_{L_2}^{M_2} , \qquad \text{(D-4)}$$

where $-L_1 \leq M_1 \leq L_1$ and $-L_2 \leq M_2 \leq L_2$. The Clebsch-Gordan coefficients $C(\;)$ are well known. To form irreducible tensors from products of irreducible tensors as was done at Eq. (6-37), one uses the inverse of this theorem,

$$T_{L_1}^{M_1} T_{L_2}^{M_2} = \sum_{L} C(L_1, L_2, L; M_1, M_2, M_1+M_2)\, T_{L}^{M_1+M_2}, \qquad \text{(D-5)}$$

where the sum on L runs over $|L_1 - L_2| \leq L \leq L_1 + L_2$.

The Wigner-Eckart Theorem. The great value of irreducible tensor operators lies in the ease with which their matrix elements and selection rules are obtained using the Wigner-Eckart theorem. If $|j\ m\rangle$ is an eigenfunction of the total angular momentum (or of the angular momentum associated with the variables on which T_L^M depends), then

$$\langle j'm' | T_L^M | j m\rangle = C(j\, L\, j'; m\, M\, m')\, \langle j' \| T_L \| j\rangle . \qquad \text{(D-6)}$$

The reduced matrix element $\langle \| \ \| \rangle$ is independent of m, M and m'. It is obtained by evaluating the integral on the left for any one value of m, m' and M. Then the matrix elements for all other values are obtained directly from (D-6). The Clebsch-Gordan coefficient directly gives the rotational selection rules. It vanishes unless

$$m + M = m' \qquad \text{(D-7)}$$

and unless j, L and j' satisfy the triangle inequalities,

$$|j-L| \le j' \le j+L\,, \qquad \text{(D-8)}$$

2. Some Matrix Elements

At Eq. (4-16) we obtained the matrix element

$$\langle \Psi(\mathbf{x};R,j) |\, P_z + \frac{1}{i}\frac{\partial}{\partial R} \,| \Psi(\mathbf{x};R,j) \rangle_{\mathbf{x}}\,, \qquad \text{(D-9)}$$

where the Ψ are electronic wavefunctions, and the integration is over the electronic variables. To treat it, let us observe that the electronic wavefunction can always be constructed such that its only imaginary part is due to a phase e^{if} , where f depends only on the azimuthal angles, φ , of the electrons relative to the body-fixed axes. Neither P_z nor $\frac{\partial}{\partial R}$ affects the azimuthal angles of the electrons, and the phase is thus independent of them. Hence, the results in (D-9) will be the same as if the Ψ were real functions[108].

Now consider the first part of (D-9). Because P_z is Hermitian, one has

$$\langle \psi_j | P_z \psi_j \rangle_x = \langle P_z \psi_j | \psi_j \rangle_x$$

$$= \langle \psi_j | P_z \psi_j \rangle_x^* .$$

Now either integrating out the φ's first, so that the functions left are real or else treating the ψ as real, one can take the complex conjugation inside. P_z is an imaginary Hermitian operator, and the result is

$$\langle \psi_j | P_z \psi_j \rangle_x = - \langle \psi_j | P_z \psi_j \rangle_x = 0 . \qquad \text{(D-10)}$$

To evaluate the second part of (D-9) let us use the fact that R is independent of the electronic integration,

$$0 = \frac{\partial}{\partial R} 1 = \frac{\partial}{\partial R} \langle \psi_j | \psi_j \rangle_x ,$$

$$= \left\langle \frac{\partial \psi_j}{\partial R} \middle| \psi_j \right\rangle_x + \left\langle \psi_j \middle| \frac{\partial \psi_j}{\partial R} \right\rangle_x ,$$

$$= 2 \left\langle \psi_j \middle| \frac{\partial \psi_j}{\partial R} \right\rangle_x . \qquad \text{(D-11)}$$

This last result is again due to the fact that only the real part of ψ_j depends on R . This concludes the demonstration that (D-9) is identically zero.

In connection with Eq. (5-44), let us consider

$$0 = \frac{\partial^2}{\partial R^2}\langle\psi_j|\psi_j\rangle_x ,$$

$$= \left\langle\frac{\partial^2\psi_j}{\partial R^2}\middle|\psi_j\right\rangle_x + \left\langle\psi_j\middle|\frac{\partial^2\psi_j}{\partial R^2}\right\rangle_x + 2\left\langle\frac{\partial\psi_j}{\partial R}\middle|\frac{\partial\psi_j}{\partial R}\right\rangle ,$$

$$= 2\left\langle\psi_j\middle|\frac{\partial^2\psi_j}{\partial R^2}\right\rangle_x + 2\left\langle\frac{\partial\psi_j}{\partial R}\middle|\frac{\partial\psi_j}{\partial R}\right\rangle_x . \qquad \text{(D-12)}$$

The last step again was possible because only the real part of ψ_j was operated on.

Finally, we want to prove Eq. (4-40),

$$h_{0,-1} = (-1)^{p-J} h_{01} . \qquad \text{(4-40)}$$

From Eq. (4-29) this is

$$h_{0,\pm1} = \langle\psi(0)\,|\,\mathcal{H}_{0,\pm1}\,|\psi(\pm1)\rangle_x , \qquad \text{(4-29)}$$

where

$$\mathcal{H}_{0,\pm1} = \frac{\lambda_\pm(J,0)}{\mu R}\left(\frac{-1}{2R}\mathcal{J}_\mp + \frac{1}{\sqrt{2}\,i}P_1^{\mp1}\right). \qquad \text{(3-3)}$$

Now $\psi(0)$ is an eigenfunction of reflection,

$$\psi(0) = (-1)^{p-J}\sigma_{yz}\psi(0) . \qquad \text{(4-34)}$$

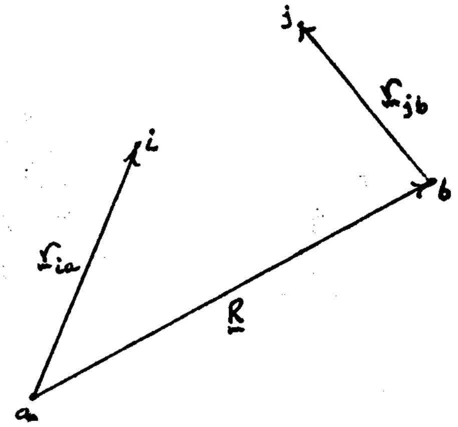
Using this and the fact that σ_{yz} is Hermitian, one has

$$h_{0,-1} = (-1)^{p-J}\langle \psi(0)|\sigma_{yz}\mathcal{H}_{0,-1}\psi(-1)\rangle_{*} . \qquad \text{(D-13)}$$

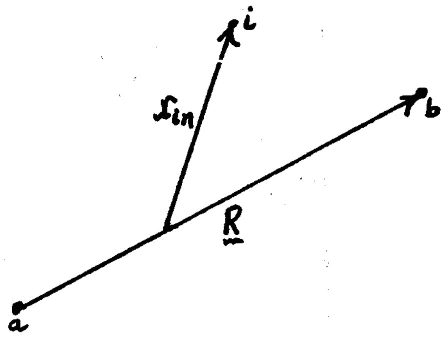
The components of $\underset{\sim}{P}$ behave like the coordinates (2-44) under σ_{yz} but the components of J behave oppositely, like angular momenta. Using Eq. (D-2) and the definitions of the raising and lowering operators one immediately finds that

$$\sigma_{yz}\mathcal{H}_{0,-1} = \mathcal{H}_{01}\sigma_{yz} , \qquad \text{(D-14)}$$

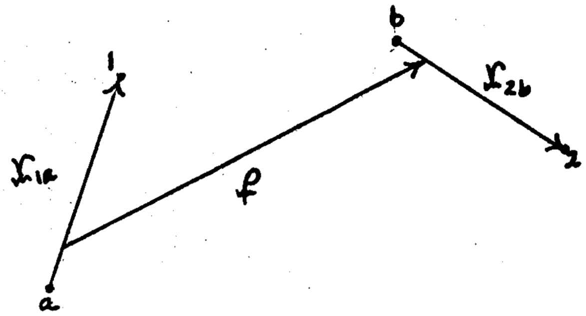
and using Eq. (4-33) and (2-24), Eq. (D-13) becomes Eq. (4-40), the desired result.



a. The Separated Atom Relative Coordinates



b. The Center of Mass of the Nuclei (CMN) System



c. The "ρ" System for Two One-Electron Atoms

Figure 1. Relative Coordinates. The directional axes (not shown) are space-fixed.

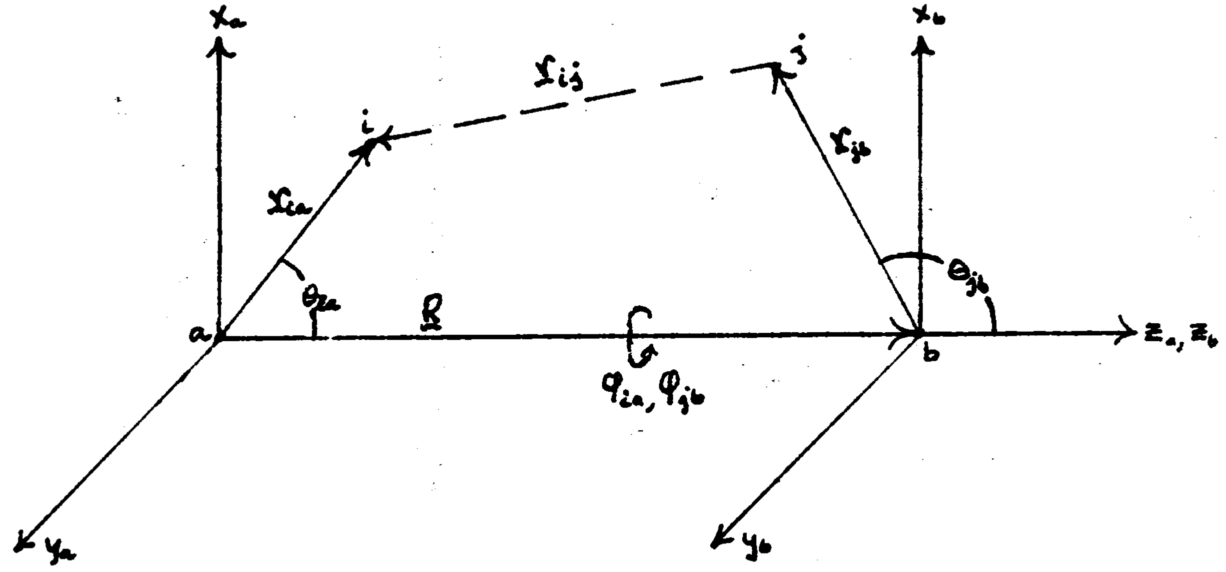


Figure 2. The Body-fixed Separated Atom Coordinates. The angle φ_{ia} is measured from x_a toward y_a, and φ_{jb} is measured from x_b toward y_b. The two sets of atomic axes are parallel, and both systems are right-handed.

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51. We write $\mathcal{H}$ in terms of the Hermitian $\mathbf{p}$'s instead of ∇'s to facilitate later handling of some matrix elements. See Appendix D.

52. J. P. Vinti, Phys. Rev. 58, 882 (1940). See also Ref. 39, p. 166.

53. There are other operators which commute with $\mathcal{H}$, but they all appear to either be redundant or fail to commute with all the members of the set. An example is time inversion which does not commute with $J_{z'}$. It could be used instead of $J_{z'}$ but not together with it.

54. Since $\mathcal{H}$ does not contain nuclear spin and there are only two nuclei, the nuclear spin functions can often be handled like those of the two electron atom.

55. M. E. Rose, Elementary Theory of Angular Momentum (John Wiley and Sons, Inc., New York, 1957) p.25.

56. Ref. 55, p. 51, his Eq. (4.7). Due to the difference in conventions our $\mathcal{R}$ is his $\mathcal{R}^{-1}$.

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57. Ref. 55, p. 65.

58. This is a necessity not a luxury. Some of the variables on which $\underset{\sim}{J}$ depends are being separated off in the process of rotation, and the operators are only defined in terms of Eq. (2-34 to 36). A trivial example of this occurs in the radial Schrödinger equation for the hydrogen atom. After rotation is separated, the $\ell(\ell+1)$ could certainly be written formally as $\underset{\sim}{\mathcal{L}}^2$, but that $\underset{\sim}{\mathcal{L}}^2$ could not be written in terms of the single variable r, on which the radial wave function depends.

59. See for example, A. Messiah, <u>Quantum Mechanics</u> (John Wiley and Sons, Inc., New York, 1961) p. 346.

60. Ref. 28, p. 218f.

61. See, for example, L. Collatz, <u>Numerische Behandlung von Differentialgleichungen</u> (Springer-Verlag, Berlin, 1951), or W. Lester, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI- (to be published).

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63. Ref. 28, p. 420.

64. A trivial illustration is given by the r_{12} dependence of the Unsöld approximation to the first order helium wavefunction.

$$\tilde{\psi}^{(1)} = -\frac{1}{\Delta E}\left(\frac{1}{r_{12}} - E^{(1)}\right)\psi^{(0)}$$

This wavefunction is infinite at $r_{12}=0$, while the true first order wavefunction is bounded everywhere.

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80. T. Y. Chang, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI- (to be published).

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87. See Ref. 3, p. 33, for example.

88. This value is given by J. O. Hirschfelder and P. O. Löwdin, Mol. Phys. **2**, 229 (1959); **9**, 491 (1965). See also Y. M. Chan and A. Dalgarno, Mol. Phys. **9**, 349 (1965); and L. Pauling and J. Y. Beach, Phys. Rev. **47**, 686 (1935).

89. See~~, for example, H.~~ Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (D. Van Nostrand Co. Inc., Princeton, N.J., 1956) 2nd ed., p. 411.

90. If one wishes to use confocal elliptic coordinates for the ~~electrons, he~~ should center the electronic coordinates on the geometrical center of the nuclei. For heteronuclear systems this adds a cross derivative term which could be treated in the same fashion as the ~~term in the~~ separated atom system. For $\mathcal{H}$ expressed in these coordinates, see Ref. 16.

91. At extremely small R , $\mathbf{R}$ is not well-defined and electronic coordinates relative to space-fixed axes should be used. See Refs. 5 and 35.

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96. Ref. 92, p. 154.

97. Ref. 55, p. 240.

98. Ref. 23, p. 906.

99. This choice of conventions makes $\mathbb{D}^J$ automatically a homomorphic representation. The combination of conventions we use for $\mathcal{R}$, $\mathbb{R}$ and $\mathbb{D}^J$ leads to

$$D^J_{\Omega M}(\alpha,\beta,\gamma;\,here) = (-1)^{\Omega-M} D^J_{\Omega M}(\alpha,\beta,\gamma;\,HWe) = D^J_{\Omega M}(-\gamma,-\beta,-\alpha;\,Rose)$$

$$= D^J_{\Omega M}(\gamma,\beta,\alpha;\,Wigner),$$

REFERENCES AND FOOTNOTES (cont'd)

as the connecting relations between our representations and those of some well-known works.

100. A minor point should be noted. If $\langle \Psi(\mathcal{X},R) | \Psi(\mathcal{X},R) \rangle = 1$, then $\langle \Psi(\mathcal{X}',\mathcal{X}') | \Psi(\mathcal{X}',\mathcal{X}') \rangle = 4\pi/(2J+1)$ when these $\mathbb{D}^J$ matrices are used.

101. Ref. 92, Chapters 15 and 21.

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