Ortho-para transition in molecular hydrogen

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John Carl Raich

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For the hydrogen molecule in the lowest electronic state \('{\Sigma}_g^+'\) and the lowest vibrational excitation the energy levels are specified by the rotational quantum number \(J\). To the extent that hyperfine interactions may be neglected, the states are singlet (para) or triplet (ortho) in the proton spins according to whether \(J\) is even or odd.

The purpose of this paper is to give an estimate of the probability of a transition \(J \rightarrow J - 1\) with spontaneous emission of electric dipole radiation. It is to be assumed that orientationally degenerate states are equally likely to be populated so that the probability per unit time is found from

\[
W = \sum_{i,f} \frac{W_{if}}{(2I+1)(2J+1)} ,
\]

(1)

where \(I\) is the initial nuclear spin and \(W_{if}\) is the transition probability per unit time from an initial state \(i\) to a final state \(f\). This probability per unit time is given by (1, p. 178; 2, p. 1041)

\[
W_{if} = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \mu^* \cdot \mu ,
\]

(2)
\[ \mu = \int u_f^\dagger \sum_{\alpha} e_{\alpha} \beta_{\alpha} u_i. \] (3)

Here \( \hbar \omega \) is the energy of the emitted photon, \( u_i \) and \( u_f \) are the time-independent wave functions of the initial and final states of the system, and the sum on \( \alpha \) ranges over the two protons with charge \( e \) and the two electrons with charge \(-e\). The asterisk denotes the complex conjugate, the dagger the Hermitian conjugate, and the integration extends over the space coordinates of all four of the particles. The transition is forbidden; if the initial and final states were pure singlet or triplet in the proton spins the matrix element would be zero. However the hyperfine interaction produces a small mixing of nuclear spins and gives rise to a nonvanishing transition probability.

Wigner as quoted by Bonhoeffer and Harteck (3) established that the probability per unit time is less than \((300 \text{ year})^{-1}\), using the fine structure of atomic helium to estimate the matrix element of the interaction Hamiltonian.

Zwicky (4) and Osterbrock (5) have considered the possibility of finding an appreciable amount of orthohydrogen in interstellar space. They found that, if the ortho-para transition probability were as high as \((300 \text{ year})^{-1}\), appreci-
iable amounts of the orthohydrogen would be expected. The present research was undertaken at Osterbrock's suggestion to make an actual estimate of the transition probability. The reason why this estimate is so far from Wigner's bound is that he used the nuclear spin electron orbit term in the interaction Hamiltonian to establish the bound. It was found here that this term gives zero in the molecular problem as long as the transition is purely rotational. Field and Somerville* independently made this same argument and reached the conclusion that the actual probability would be $10^6$ to $10^{10}$ times smaller than $(300 \text{ year})^{-1}$. It was found that the term which gives the main contribution is the nuclear spin-orbit interaction, discussed and observed by Ramsey (6).

---

CALCULATION OF THE PROBABILITY

The Hamiltonian

The nonrelativistic Hamiltonian for two electrons and two protons is

\[ H = H_0 + H', \]  \hspace{1cm} (4)

where

\[ H_0 = \sum_{\alpha=1}^{4} \frac{p_{\alpha}^2}{2m_{\alpha}} + \sum_{\alpha, \beta \ (\alpha \neq \beta)} \frac{e_{\alpha}e_{\beta}}{\kappa_{\alpha\beta}}, \]  \hspace{1cm} (5)

\[ H' = \sum_{\alpha} \frac{i e_{\alpha} \hbar}{m_{\alpha} c} \sum_{\beta (\neq \alpha)} \gamma_{\beta} \frac{I_{\alpha} \times \frac{p_{\alpha}}{\kappa_{\alpha\beta}}}{\kappa_{\alpha\beta}} \cdot \nabla_{\alpha} \]

\[ - \sum_{\alpha} \frac{g_{\alpha}-1}{g_{\alpha}} \frac{i \gamma_{\alpha} \hbar^2}{m_{\alpha} c} (I_{\alpha} \times \nabla_{\alpha}) \cdot \sum_{\beta (\neq \alpha)} \frac{e_{\beta} \gamma_{\alpha\beta}}{\kappa_{\alpha\beta}^3} \]

\[ - \sum_{\alpha, \beta \ (\alpha \neq \beta)} \gamma_{\alpha} \gamma_{\beta} \hbar^2 \sum_{s} \frac{g_{\alpha} g_{\beta}}{g_{\alpha} g_{\beta} - 1} \frac{I_{\alpha} \cdot \frac{r_{\alpha\beta}}{\kappa_{\alpha\beta}}}{\kappa_{\alpha\beta}^5} \]

\[ - \sum_{\alpha, \beta \ (\alpha \neq \beta)} \frac{8 \pi}{3} \gamma_{\alpha} \gamma_{\beta} \hbar^2 \frac{I_{\alpha} \cdot I_{\beta}}{\kappa_{\alpha\beta}^3} \delta(\kappa_{\alpha\beta}). \]  \hspace{1cm} (6)
Here the sums on $\alpha$ and $\sigma$ range over all four of the particles. The mass $m_\alpha$ is $m$ for electrons, $M$ for protons; the charge $e_\alpha$ is $-e$ for electrons, $e$ for protons; $\gamma_\alpha$ is an abbreviation for $g_\alpha e_\alpha / 2m_\alpha c$, where $g_\alpha$ is 2 for electrons and 5.6 for protons; $I_\alpha$ is the spin of the particle so that $I_\alpha$ is $\frac{1}{2} \sigma_\alpha$, where $\sigma_\alpha$ is the Pauli matrices; $\omega_\alpha$ is $\gamma_\alpha - \sigma_\beta$. Discussions of this Hamiltonian have been made by Bethe and Salpeter (7, p. 267) and by Slater (8, p. 189). The second term in Equation 5 includes Ramsey's (6) nuclear spin-orbit coupling. This term is derived in Appendix A.

Perturbation Calculation

One may consider $H'$, which includes the hyperfine effects, as a perturbation on $H_0$. Let the eigenstates of $H_0$ be $u_{0k}$, corresponding to eigenvalues $E_0$. Then

$$u_k = u_{0k} + \sum_{m(\neq k)} \frac{H'_m u_{0m}}{E_{0k} - E_{0m}}$$

(7)

are the eigenfunctions of the perturbed Hamiltonian $H$. The values $E_0$ are close to the experimental energies of the system as given by, for example, Herzberg (9, p. 340). The states $u_{0k}$ are $\sum g^+$ electronically; they correspond to the ground vibrational state; they are specified by the rotational
quantum numbers \( J_k, m_k \); and they are singlet in the nuclear spins when \( J \) is even, triplet when \( J \) is odd.

The dipole matrix element of Equation 3 can be expressed in terms of the unperturbed functions by using Equation 7 in the usual way. In the problem considered here, if \( u_{0i} \) is para \( u_{of} \) is ortho and vice versa. Consequently the direct term involving \( u_{of} \) and \( u_{0i} \) is zero and, in the first approximation,

\[
\mu = \int u_{of}^\dagger \left( \sum_\alpha e_{\alpha \alpha} \right) \sum_{m(\phi_i)} \frac{H_{mi}}{E_{0i} - E_{om}} u_{om} + \int \sum_{m(\phi_f)} \frac{u_{om}^\dagger H'_{fm}}{E_{of} - E_{om}} \left( \sum_\alpha \theta_{\alpha \alpha} \right) u_{0i}.
\]  

The only states \( m \) which contribute here are those which fulfill the selection rules for the dipole operator \( \sum e_{\alpha \alpha} \) with the states \( u_{0i} \) or \( u_{of} \). Since \( u_{0i} \) and \( u_{of} \) are \( ' \Sigma_+ \) electronically, \( u_{om} \) must also be singlet in the electron spins but must not be \( ' \Sigma_+ \). An inspection of the actual spectrum (9, p. 230) shows that the only levels \( m \) that apply are 12 ev or more higher than the states involved in the transition. It is a sensible approximation therefore to suppose that there is a range of energies near a single fixed level \( E_{0k} \) that gives the main contributions to both integrals of Equation 8. One
assumes that \( E_{om} - E_{ok} \) is small compared to either \( E_{oi} - E_{om} \) or \( E_{of} - E_{om} \) and expands

\[
\frac{1}{E_{oi} - E_{om}} = -\frac{1}{\mathcal{E}} \left[ 1 + \frac{\hbar \omega}{\mathcal{E}} + \frac{E_{ok} - E_{om}}{\mathcal{E}} + \ldots \right],
\]

\[
\frac{1}{E_{of} - E_{om}} = -\frac{1}{\mathcal{E}} \left[ 1 + \frac{E_{ok} - E_{om}}{\mathcal{E}} + \ldots \right],
\]

where

\[
\mathcal{E} = E_{ok} - E_{of},
\]

\[
\hbar \omega = E_{oi} - E_{of}.
\]

Here \( E_{ok} \) is determined by the fact that the terms linear in \( E_{ok} - E_{om} \) in this expansion of \( \mu \) must vanish. From the actual spectrum one may conclude that \( \mathcal{E} \) is approximately 12 eV. It is clear that this assumption about the nature of the intermediate states limits the accuracy of the final numerical value for the transition probability.

The result of these considerations is

\[
\mu = -\frac{1}{\mathcal{E}} \left( 1 + \frac{\hbar \omega}{\mathcal{E}} \right) \int u_{of}^\dagger \sum_{\alpha} \sum_{m(\neq i)} e_\alpha \omega_\alpha \sum_{m(\neq i)} H'_{mi} u_{om} \\
- \frac{1}{\mathcal{E}} \int \sum_{m(\neq f)} u_{om}^\dagger H'_{fm} \sum_{\alpha} e_\alpha \xi_{\alpha} u_{oi}. \tag{9}
\]
the sums on \( m \) may be permitted to range over all states since when \( m \) is \( i \) or \( f \) there is no contribution to the matrix element \( \mu \) anyway.

Let \( x \) or \( y \) denote all the space coordinates on which the wave function depends. Then, writing the matrix elements of \( H' \) out explicitly, one obtains

\[
\mu = -\frac{i}{\hbar} \left( 1 + \frac{\hbar \omega}{\varepsilon} \right) \int dx \int dy \ u_{of}^\dagger(x) \left( \sum_\alpha e_\alpha k_\alpha \right) \\
\sum_m u_{om}(x) u_{om}(y) H'(y) u_{o\alpha}(y) \\
- \frac{1}{\hbar} \int dx \int dy \ u_{of}^\dagger(y) H'(y) \\
\sum_m u_{om}(y) u_{om}^\dagger(x) \left( \sum_\alpha e_\alpha k_\alpha \right) u_{o\alpha}(x).
\]  

(10)

Here the completeness relation of the form

\[
\sum_m u_{om}(x) u_{om}^\dagger(y) = \delta(x-y)
\]  

(11)

applies so that the matrix element becomes simply
\[ \mathcal{H} = -\frac{1}{\mathcal{E}} \int u_{of}^\dagger \left[ \sum_{\alpha} e_{\alpha} \mathcal{H}_{\alpha} \right]_{+} u_{oi} \]

\[ -\frac{\hbar \omega}{\mathcal{E}^2} \int u_{of}^\dagger \sum_{\alpha} e_{\alpha} \mathcal{H}'_{\alpha} u_{oi} . \]  

(12)

where \( \mathcal{H}' \) is given by Equation 6 and \( [ , ]_{+} \) denotes the anti-commutator.

Some of the terms in \( \mathcal{H}' \) do not contribute to an ortho = para transition. Consider the terms proportional to \( \mathcal{I}_{\alpha} \cdot \mathcal{I}_{\beta} \):

if \( \alpha \) and \( \beta \) are both electrons the nuclear spin parts of the wave functions \( u_{oi} \) and \( u_{of} \) are orthogonal, if \( \alpha \) and \( \beta \) are both protons the operator \( \mathcal{I}_{\alpha} \cdot \mathcal{I}_{\beta} \) is scalar in nuclear spin space and gives zero between spin zero and spin one, if \( \alpha \) and \( \beta \) are proton and electron and electron operator gives zero between two electron singlet states. One can also see that the \( \mathcal{I}_{\alpha} \cdot \mathcal{I}_{\alpha} \mathcal{I}_{\beta} \cdot \mathcal{I}_{\beta} \) term does not contribute. From the same reasoning as above only \( \alpha \) and \( \beta \) both protons need be considered. Also the term may be rewritten as

\[ \mathcal{I}_{\alpha} \cdot \mathcal{K}_{\alpha\beta} \mathcal{I}_{\beta} \cdot \mathcal{K}_{\alpha\beta} = \mathcal{K}_{\alpha\beta i} \mathcal{K}_{\alpha\beta j} \left[ \frac{1}{2} (\mathcal{I}_{\alpha i} \mathcal{I}_{\beta j} + \mathcal{I}_{\alpha j} \mathcal{I}_{\beta i} \right] \]
Neither of the terms in the square brackets can contribute in a $1 \neq 0$ matrix element since the first has the transformation properties of spin two and the second of spin zero.

In view of these considerations only the first two terms in Equation 6 contribute and the matrix element to be evaluated is

$$
\varepsilon_{\mu
u} = -\int u_{\alpha}^\dagger \left[ \sum \varepsilon_{\gamma \delta} \sum \left( H_1' + H_2' \right) \right] u_{\beta i} 
- \frac{\hbar \omega}{\varepsilon} \int u_{\alpha}^\dagger \sum \varepsilon_{\gamma \delta} \left( H_1' + H_2' \right) u_{\beta i}, \tag{13}
$$

where

$$
H_1' = \sum_{\alpha} \frac{i e_{\alpha \hbar}}{m_{\alpha} c} \sum_{\beta (\neq \alpha)} \varepsilon_{\gamma \delta} \frac{\hbar \beta \times \kappa_{\alpha \beta}}{\kappa_{\alpha \beta}} \cdot \nabla_{\alpha},
$$

$$
H_2' = -\sum_{\alpha} \frac{g_{\alpha} - 1}{g_{\alpha}} \frac{i e_{\alpha \hbar}}{m_{\alpha} c} \left( \frac{\vec{I}_\alpha \times \nabla_{\alpha}}{\kappa_{\alpha \beta}^3} \right) \sum_{\beta (\neq \alpha)} \varepsilon_{\beta \gamma \delta} \kappa_{\alpha \beta}.
$$
Consider first the term in $\sum g \times \alpha \beta$. Here it is seen that $\beta$ must be a proton in order to give a contribution between the singlet and triplet nuclear functions. The functions $u_\alpha$ are antisymmetric with respect to interchange of electrons and of protons. This means that in the sum on $\alpha$ the two electron terms contribute equally and the two proton terms contribute equally. Accordingly one lets $\alpha$ be electron one and proton one only and puts in a factor of two. Similar considerations apply in the $I_\alpha \times \nabla_\alpha$ term. One inserts a factor of two and lets $\alpha$ be proton one only. The terms when $\beta$ is proton two and when $\beta$ is an electron are separated. The second integral in Equation 13 is smaller by a factor of $10^3$ than the first integral, so one is mainly interested in the contribution from the case when $\alpha$ is an electron and $\beta$ a proton in $H_1$. That is, only terms proportional to $1/m$ are retained in the second integral. The result of these considerations is this formula for the matrix element:

$$
\left( \frac{2\hbar^2 e}{M c} \right)^{-1} \begin{vmatrix} \sum \tiny \text{terms} \end{vmatrix}\begin{pmatrix} \frac{I P^2 \times \nabla_{P^2}}{\kappa_{p1} \hbar P^2} \cdot \nabla_{P^1} \\
\end{pmatrix} u_{\alpha \beta}
$$
The wave function for the initial state is

$$u_{oi} = f(x) \sum_{p} e^{i \frac{p \cdot x}{\hbar}} \left( \frac{\frac{1}{2} p_1 \times \hbar \epsilon_{pl}}{\hbar \epsilon_{pl}^3} + \frac{\frac{1}{2} p_2 \times \hbar \epsilon_{pl}}{\hbar \epsilon_{pl}^3} \right) \cdot \nabla_1 u_{oi}$$

$$+ \frac{3p-1}{3} \int u_{of}^{\dagger} \sum_{p} e^{i \frac{p \cdot x}{\hbar}} \left( \frac{\frac{1}{2} p_1 \times \hbar \epsilon_{pl}}{\hbar \epsilon_{pl}^3} \right) \cdot \nabla_1 u_{oi}$$

$$- \frac{2}{3} \frac{(3p-1)}{3} \int u_{of}^{\dagger} \sum_{p} e^{i \frac{p \cdot x}{\hbar}} \left( \frac{\frac{1}{2} p_1 \times \hbar \epsilon_{pl}}{\hbar \epsilon_{pl}^3} \right) \cdot \nabla_1 u_{oi}$$

$$+ \frac{M}{m} \frac{\hbar \omega}{\hbar} \int u_{of}^{\dagger} \sum_{p} e^{i \frac{p \cdot x}{\hbar}} \left( \frac{\frac{1}{2} p_2 \times \hbar \epsilon_{pl}}{\hbar \epsilon_{pl}^3} \right) \cdot \nabla_1 u_{oi}.$$ (14)

The wave function for the initial state is

$$u_{oi} = f(x) Y_{j, m_{j}}(\hat{x}) \Psi(x_1, x_2, x) \chi_{j} \chi_{0},$$ (15)

where the coordinates are defined by

$$\chi = \frac{1}{2} ( \hbar \epsilon_{pl} + \hbar \epsilon_{p2} ),$$ (16)

$$x = \hbar \epsilon_{pl} - \hbar \epsilon_{p2},$$ (17)

$$x_1 = \hbar \epsilon_{el} - \frac{1}{2} ( \hbar \epsilon_{pl} + \hbar \epsilon_{p2} ).$$ (18)
Here \( f(x) \) is the vibrational part, \( Y (\hat{x}) \) the rotational part, \( \Psi(x_1, x_2, x) \) the electronic part, and \( \chi_1 \) and \( \chi_0 \) are the nuclear and singlet electron spin parts. Recoil considerations are disregarded here, they are discussed in Appendix B. A similar formula applies for the final state with the same functions \( f \), \( \Psi \), \( \chi_0 \). The electron wave function is to be determined by solving the Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(x_1, x_2, x) \right] \Psi = E_e \Psi.
\]

Here \( V \) is the sum of the Coulomb energies for the \( \Sigma_g^+ \) state. The symbols \( \nabla \), \( \nabla_1 \), \( \nabla_2 \) are used for the gradients on the \( x, x_1, x_2 \) coordinates.

Since Equation 20 for \( \Psi \) is real, the function \( \Psi(x_1, x_2, x) \) may be chosen real. Consequently one sees that the second term in Equation 14 does not contribute. The point is that the term is proportional to

\[
\int \Psi^\dagger \left[ \chi_1 + \chi_2 - \frac{1}{2} \left( \frac{I_{e1p_1} \times \kappa_{e1p1}}{\kappa_{e1p1}^3} + \frac{I_{e2p2} \times \kappa_{e2p2}}{\kappa_{e2p2}^3} \right) \cdot \nabla_1 \right] \Psi
\]

and is evidently real. However by inserting appropriate factors of \( i \) the same quantity can be written as
\[ i \int \psi^\dagger \left[ 0_1, 0_2 \right]_+ \psi, \]

where \( 0_1 \) and \( 0_2 \) are Hermitian operators, and so it is pure imaginary. The conclusion is that the quantity is zero.

In these coordinates the first and third terms on the right in Equation 14 become

\[
e^{\i \int u_{0f}^\dagger \left[ x_1 + x_2, \frac{\mathcal{L}_{p1} X^2}{\chi^3} \cdot \left( \nabla - \frac{1}{2} \nabla_1 - \frac{1}{2} \nabla_2 \right) \right]_+ u_{0f},
\]

\[- \frac{e(\mathcal{Gp})}{\mathcal{Gp}} \i \int u_{0f}^\dagger \left[ x_1 + x_2, \frac{\mathcal{L}_{p1} X}{\chi^3} \cdot \left( \nabla - \frac{1}{2} \nabla_1 - \frac{1}{2} \nabla_2 \right) \right]_+ u_{0f}.\]

It is seen that the terms in \( \nabla_1 \) and \( \nabla_2 \) are zero from the same argument as in the previous paragraph. As for the terms in \( \nabla \), in the electronic integration the function \( \psi \) has even parity whereas the integrand is odd so these terms vanish also.

The result of these considerations is that only the last two terms in Equation 14 survive. Using the property

\[
\int \psi^\dagger \left[ x_1 + x_2, \left( \frac{\mathcal{L}_{p1} X}{\kappa_{el p1}^3} + \frac{\mathcal{L}_{p2} X}{\kappa_{el p2}^3} \right) \cdot \nabla_1 \right]_+ \psi = 0
\]

the last term of Equation 14 may be written as

\[
\frac{1}{2} e \frac{\hbar \omega}{m} \int u_{0f}^\dagger \left( \frac{\mathcal{L}_{p1} X}{\kappa_{el p1}^3} + \frac{\mathcal{L}_{p2} X}{\kappa_{el p2}^3} \right) u_{0f}.\]
One expands the anticommutator and writes separately the terms where the gradient acts to get

\[
\left( \frac{g_p - 1}{g_p} \frac{4 \alpha_p h^2 e^2}{iM} \right)^{-1} E M
\]

\[
= \int Y^*_f M f^* Y^*_i M_i f P \Gamma_{pl f i} x \int \psi^\dagger \frac{k_{el pl}}{k_{el pl}^3} \psi
\]

\[
+ 2 \left[ \int Y^*_f M f^* P \Gamma_{pl f i} x \nabla (Y^*_i M_i f) \right] \alpha \int \psi^\dagger (x_1 + x_2) \frac{k_{el pl} \alpha}{k_{el pl}^3} \psi
\]

\[
+ 2 \int Y^*_f M f^* Y^*_i M_i f \int \psi^\dagger (x_1 + x_2) \left( \frac{k_{el pl} \times P \Gamma_{pl f i}}{k_{el pl}^3} \right) \cdot \nabla_{pl} \psi
\]

\[
- \frac{1}{4} m \frac{\hbar \omega}{m} \frac{g_p}{g_p - 1} \int Y^*_f f^* Y^*_i M_i f \int P \Gamma_{pl f i} x \int \psi^\dagger \frac{k_{el pl}}{k_{el pl}^3} \psi
\]

\[
- \frac{1}{4} m \frac{\hbar \omega}{m} \frac{g_p}{g_p - 1} \int Y^*_f f^* Y^*_i M_i f \int P^2 \Gamma_{pl f i} x \int \psi^\dagger \frac{k_{el pl}^2}{k_{el pl}^3} \psi, \tag{21}
\]

where \( P \Gamma_{pl f i} \) denotes the matrix element of \( P \Gamma_p \) between the final and initial spin states. In the second term the gradient acts on \( (Y^*_i M_i f) \) only. Here and below the subscript \( \alpha \) signifies the three cartesian components.
Electronic integrals

The next step is to evaluate the electronic integrals.

In making the present estimate it is adequate to use the simple Heitler-London functions as given by Pauling and Wilson (10, p. 340):

$$\psi(x_1, x_2, x_3) = \frac{Z'^3}{\pi \alpha_o^3 \sqrt{1 + 2\Delta^2}} \left[ e^{-\frac{Z'}{\alpha_o}(\kappa_{elp1} + \kappa_{e2p2})} + e^{-\frac{Z'}{\alpha_o}(\kappa_{elp2} + \kappa_{e2p1})} \right].$$

(22)

Here $Z' = 1.17$, $\Delta^2 = .48$, and $\alpha_o$ is the Bohr radius $\hbar^2/me^2$.

The various electronic integrals that occur in Equation 21 can be evaluated using spherical or prolate spheroidal coordinates to give explicit functions of $x$. There is a considerable amount of algebraic detail so an example of the evaluation of two-center integrals is given in Appendix C, and a table of integrals is provided in Appendix D. These two-center integrals are discussed by Slater (11, p. 263), and many of the integrals can be found in Ruedenberg's (12) tables.

In order to evaluate the electronic integrals the dimensionless variables
\[ y = \frac{Z'}{a_o} \frac{\rho}{\rho} \]  

(23)

are used. The molecular coordinates are defined as in Figure 1.

The electronic integral from the first and fourth terms of Equation 21 is then

\[
\int \psi^\dagger \frac{\kappa_{elpl}}{\kappa_{elpl}^3} \psi
= -\frac{\hbar}{\omega} \left(\frac{Z'}{\pi a_o}\right)^2 \frac{1}{2(1+\Delta^2)} \int dy_1 \int dy_2 \frac{\cos \Theta_{1A}}{y_{elpl}^{1/2}} \left[ e^{-2y_{elpl} - 2y_{elpl}^2}ight.
+ 2 e^{-y_{elpl} - y_{elpl}^2 - y_{elpl}^2 - y_{elpl}^2} + e^{-2y_{elpl} - 2y_{elpl}^2} \right]
\]

\[
= -\frac{\hbar}{\omega} \left(\frac{Z'}{\pi a_o}\right)^2 \frac{1}{2(1+\Delta^2)} \left[ 2 S_2 S_{15} + S_1 S_{14} \right],
\]

(24)

since only the component along the x axis contributes. Here the integrals S are given in Appendix D.

It is easily shown that

\[(I_{p1} + I_{p2})_{fi} = 0\]
Figure 1. Molecular coordinates
or

\[ (I_{p1})_{fi} = -(I_{p2})_{fi}, \]

and that

\[
\int \psi^\dagger \frac{\kappa_{\text{el}p1}}{\kappa_{\text{el}p1}^3} \psi = - \int \psi^\dagger \frac{\kappa_{\text{el}p2}}{\kappa_{\text{el}p2}^3} \psi,
\]

so that the fifth term in Equation 21 is seen to be equal to the fourth term.

The electronic integral of the second term in Equation 21 can be written in the form

\[
\partial_{\beta\alpha} = \int \psi^\dagger (x_1 + x_2)_{\beta} \frac{\kappa_{\text{el}p1,\alpha}}{\kappa_{\text{el}p1}^3} \psi. \tag{25}
\]

First of all the integrand is broken up into irreducible parts according to the scheme

\[
\partial_{\beta\alpha} = \int \psi^\dagger v_{\beta} w_{\alpha} \psi
\]

\[
= \int \psi^\dagger \left[ \frac{1}{2} (v_{\beta} w_{\alpha} + w_{\alpha} v_{\beta}) - \frac{1}{3} \delta_{\beta\alpha} \psi \cdot \psi \right] \psi
\]

\[
+ \frac{1}{2} \int \psi^\dagger (v_{\beta} w_{\alpha} - w_{\alpha} v_{\beta}) \psi + \frac{1}{3} \delta_{\beta\alpha} \int \psi^\dagger \psi \cdot \psi. \tag{26}
\]

At this point one can use the symmetry properties of the \( \Sigma_g^+ \) electronic state to simplify the problem (13, p. 261).
In diatomic molecules the electric field of the nuclei has axial symmetry about an axis through the two nuclei. Therefore the projection of the electronic angular momentum on this axis is conserved. The letter $\Sigma$ indicates that the absolute value of the projected electronic orbital angular momentum along the internuclear axis is zero.

The subscript g indicates that the state is invariant with respect to a simultaneous change of sign of the coordinates of all the electrons in the molecule, the coordinates of the nuclei remaining unchanged, where the point bisecting the internuclear axis is taken as the origin.

The superscript + means that the wave function is unchanged when the electrons are reflected in a plane containing the internuclear axis.

Let the z-axis for the electron integration be in the x direction. From the $\Sigma$ symmetry of the wave function about this axis it is seen that only the $M = 0$ components of the operators contribute. The + symmetry gives further information. The operator $R$ for reflection in the $yz$ plane is defined by

\[
\begin{align*}
R x_{1\alpha} &= \pm x_{1\alpha}, \\
R x_{2\alpha} &= \pm x_{2\alpha}, \\
R x_\alpha &= x_\alpha,
\end{align*}
\]

(27)
where the sign is + for \( \alpha = y \) or \( z \) and - for \( \alpha = x \). The operator has the properties

\[
R \psi = \psi,  \\
R v_\alpha = \pm v_\alpha,  \\
R w_\alpha = \pm w_\alpha.  
\]

When one applies the reflection operation to the \( M = 0 \) component of the three terms of Equation 26 one obtains

\[
R \left( 2v_x w_x - v_x w_x - v_y w_y \right) = (2v_x w_x - v_x w_x - v_y w_y),  \\
R \left( v_x w_y - v_y w_x \right) = -(v_x w_y - v_y w_x),  \\
R \left( \psi \cdot \omega \right) = \psi \cdot \omega,  
\]

and so one sees that the \( M = 0 \) component of the second term is Equation 26, \( \int \psi^\dagger (v_x w_x - v_y w_x) \psi \), is zero so this term never contributes. To evaluate the first term on the right in Equation 26 one observes that it is a symmetric second rank tensor with zero spur which depends only on the vector \( \mathbf{x} \) so it must be that
\[
\int \psi^\dagger \left[ \frac{1}{2} (\nu_\beta w_\alpha + \nu_\alpha w_\beta) - \frac{1}{3} \delta_{\alpha\beta} \nu \cdot w \right] \psi
\]

\[
= (\hat{x}_\alpha \hat{x}_\beta - \frac{1}{3} \delta_{\alpha\beta}) C,
\]

where \( \hat{x} \) is \((x/x)\) and \( C \) is a function of \( x \). To evaluate \( C \) one chooses axes with \( x \) in the \( z \) direction and evaluates the \( zz \) component:

\[
\frac{2}{3} C = \int \psi^\dagger (v_z w_z - \frac{1}{3} \nu \cdot w) \psi.
\]

(28)

Therefore one can write

\[
\partial_{\beta\alpha} = C (\hat{x}_\alpha \hat{x}_\beta - \frac{1}{3} \delta_{\alpha\beta}) + \frac{1}{3} \delta_{\alpha\beta} \int \psi^\dagger \nu \cdot w \psi.
\]

From Equation 27 it is seen that

\[
\partial_{\beta\alpha} = \frac{1}{2} \hat{x}_\alpha \hat{x}_\beta (3 \int \psi^\dagger v_z w_z \psi - \int \psi^\dagger \nu \cdot w \psi)
\]

\[
- \frac{1}{2} \delta_{\alpha\beta} \left( \int \psi^\dagger v_z w_z \psi - \int \psi^\dagger \nu \cdot w \psi \right).
\]

(29)

The first electronic integral of Equation 29 is, by Equation 22,
\[
\int \psi^* v_z w_z \psi \\
= \frac{Z'}{2\pi^2 a_o (1 + \Delta^2)} \int dx_1 \int dx_2 \left[ e^{-\frac{Z'}{a_o} (\kappa_{el1} + \kappa_{el2})} + e^{-\frac{Z'}{a_o} (\kappa_{el2} + \kappa_{el2})} \right] \left( x_{1z} + x_{2z} \right) \frac{\kappa_{el1} x_{1z}}{\kappa_{el1}^2}.
\] (30)

In terms of the dimensionless variables defined by Equation 23, Equation 30 becomes

\[
\int \psi^* v_z w_z \psi = \frac{Z'}{2\pi^2 a_o (1 + \Delta^2)} \int dy_1 \int dy_2 \left[ e^{-2y_{el1}} - 2y_{el2} \right] \\
\frac{y_{el1} \cos^2 \Theta_{1A} - y_{el2} \cos \Theta_{1A} \cos \Theta_{2B}}{y_{el1}^2} \\
+ 2e^{-y_{el1} - y_{el2} - y_{el2} - y_{el2}} + e^{-2y_{el1} - 2y_{el2}}
\]

\[
= \frac{Z'}{2\pi^2 a_o (1 + \Delta^2)} \left( s_1 s_{16} + 2s_2 s_{18} + s_1 s_{17} - 2s_{10} s_{15} - s_9 s_{14} \right). \] (31)
Similarly

\[ \int \psi^\dagger \nabla \cdot \mathbf{W} \psi = \int \psi^\dagger \frac{1}{\kappa \epsilon_1} \psi + \int \psi^\dagger \frac{\kappa \epsilon_2 \omega \kappa \epsilon_1 \omega}{\kappa \epsilon_1^3} \psi \]

\[ = \frac{Z'}{2\pi^2 \alpha_0 (1 + \Delta^2)} \left\{ \int dy_1 \int dy_2 \frac{1}{\epsilon_1} \left[ e^{-2 \epsilon_1 \omega - 2 \epsilon_2 \omega} + 2 e^{-2 \epsilon_1 \omega - 2 \epsilon_2 \omega} - 2 S_{10} S_{15} - S_9 S_{14} \right] \right\} \]

\[ = \frac{Z'}{2\pi^2 \alpha_0 (1 + \Delta^2)} \left( S_1 S_3 + 2 S_2 S_5 + S_1 S_4 - 2 S_6 S_{15} - S_9 S_{14} \right). \quad (32) \]

Combining Equations 31 and 32 one obtains

\[ \mathcal{D}_{\beta \alpha} = \frac{1}{2} \hat{x}_\beta \hat{x}_\alpha \frac{Z'}{2\pi^2 \alpha_0 (1 + \Delta^2)} \left\{ 3 [S_1 S_{16} + 2 S_2 S_{10} + S_1 S_{17}] \right\} \]

\[ - 2 \left[ 2 S_{10} S_{15} + S_9 S_{14} \right] - \left[ S_1 S_3 + 2 S_2 S_9 + S_1 S_4 \right] \left\} \right. \]
\[ + \frac{1}{2} \delta_{\beta \alpha} \frac{Z'}{2 \pi^2 a_0 (1 + \Delta^2)} \left\{ \left[ S_1 S_3 + 2 S_2 S_5 + S_1 S_4 \right] \right. \\
\left. - \left[ S_1 S_{16} + 2 S_2 S_{18} + S_1 S_{17} \right] \right\} \]  

Finally the electronic integral in the third term of Equation 21 can be written

\[ J_{\beta \alpha} = \int \psi^\dagger(x_{1\beta} + x_{2\beta}) \left( \frac{\beta_{\text{elpl}} \times \nabla_{\text{pl}}}{\kappa_{\text{elpl}}^3} \right) \psi. \]  

Elementary differentiation gives

\[ \nabla_{\text{pl}} \psi = \frac{(Z')^4}{\pi \sqrt{2 + 2 \Delta^2}} \left[ \hat{\kappa}_{\text{elpl}} e^{-\frac{Z'}{a_0} (\kappa_{\text{elpl}} + \kappa_{\text{e2pl}})} \right] \left( \hat{\kappa}_{\text{e2pl}} e^{-\frac{Z'}{a_0} (\kappa_{\text{elpl}} + \kappa_{\text{e2pl}})} \right), \]

so that

\[ J_{\beta \alpha} = \frac{(Z')^4}{\pi \sqrt{2 + 2 \Delta^2}} \int \psi^\dagger \psi W_{\beta \alpha} e^{-\frac{Z'}{a_0} (\kappa_{\text{elpl}} + \kappa_{\text{e2pl}})}, \]

where \( \psi = \psi_1 + \psi_2 \),

\[ W = \frac{\beta_{\text{elpl}} \times \beta_{\text{e2pl}}}{r_{\text{elpl}}^3 r_{\text{e2pl}}}. \]

Again, the integrand is broken up into irreducible parts.
according to a scheme similar to Equation 26, and the reflection operation \( R \) defined by Equation 27 is applied. Now the operator \( R \) has the properties

\[
R \psi = \psi
\]

\[
R e^{-\frac{Z}{a_0}(\kappa_{\text{el}} + \kappa_{\text{e}} \Omega_{\text{a}})} = e^{-\frac{Z}{a_0}(\kappa_{\text{el}} + \kappa_{\text{e}} \Omega_{\text{a}})},
\]

\[
R v_x = -v_x,
\]

\[
R v_y = v_y,
\]

\[
R v_z = v_z,
\]

\[
R w_x = w_x,
\]

\[
R w_y = -w_y,
\]

\[
R w_z = -w_z.
\]

Considering the \( M = 0 \) components, it is seen that

\[
R \left( 2v_z w_x - v_x w_x - v_y w_y \right) = - \left( 2v_z w_x - v_x w_x - v_y w_y \right),
\]

\[
R \left( v_x w_y - v_y w_x \right) = \left( v_x w_y - v_y w_x \right),
\]

\[
R \mathbf{v} \cdot \mathbf{w} = - \mathbf{v} \cdot \mathbf{w},
\]

so that only the term containing \((v_y w_x - v_x w_y)\) contributes to
\( J_{\beta \alpha} \). Using the property
\[
\varepsilon_{\alpha \beta \gamma} \varepsilon_{\gamma \mu \nu} = \delta_{\alpha \mu} \delta_{\beta \nu} - \delta_{\alpha \nu} \delta_{\beta \mu},
\]
it is seen that
\[
V_{\beta} W_{\alpha} - V_{\alpha} W_{\beta} = -\varepsilon_{\alpha \beta \gamma} (y \times w)_y.
\]
The result of these considerations is
\[
J_{\beta \alpha} = -\frac{(\frac{Z'}{a_o})^4}{2\pi \sqrt{2 + 2\Delta^2}} \varepsilon_{\alpha \beta \gamma} \hat{x}_y \int \psi_1^y (y \times w)_\gamma \hat{x} e^{-\frac{Z'}{a_o} (\kappa_{a_1} + \kappa_{a_2})}.
\] (36)

Using Equation 23, \( J_{\beta \alpha} \) can be written
\[
J_{\beta \alpha} = -\frac{(\frac{Z'}{a_o})^2}{4\pi^2 (1 + \Delta^2)} \varepsilon_{\alpha \beta \gamma} \hat{x}_y \int dy_1 \int dy_2 \left[ e^{-Y_{e1} - Y_{e2}} + e^{Y_{e1} - Y_{e2}} \right] \left( \frac{(Y_{e1} + Y_{e2}) \times (Y_{e1} \times Y_{e2})}{Y_{e1}^3 \, Y_{e2}^1} \right) \hat{x}.
\]

When the cross product is expanded one obtains
\[
J_{\beta \alpha} = -\frac{(\frac{Z'}{a_0})^2}{4\pi^2(1+\Delta^2)} \varepsilon_{\alpha \beta \gamma} \hat{x}_y \int dy_1 \int dy_2 \left[ e^{-\delta_{\text{elpl}-\text{elpl}}} \right] \\
+ e^{-\delta_{\text{plp2}-\text{plp1}}} \left[ y_{\text{elpl}} \cdot \hat{x} y_{\text{elpl}} \cdot y_{\text{plp1}} - y_{\text{elpl}} \cdot \hat{x} y_{\text{plp1}} \right] \\
+ y_{\text{elpl}} \cdot \hat{x} y_{\text{plp2}} \cdot y_{\text{plp1}} - y_{\text{elpl}} \cdot \hat{x} y_{\text{plp2}} \cdot y_{\text{plp1}} \right] e^{-\delta_{\text{elpl}-\text{elpl}}} \\
\frac{y_{\text{elpl}} y_{\text{plp1}}}{y_{\text{elpl}} y_{\text{plp1}}}
\]

\[
= -\frac{1}{4\pi^2(1+\Delta^2)} (\frac{Z'}{a_0})^2 \varepsilon_{\alpha \beta \gamma} \hat{x}_y \left( -S_7 S_{18} + S_5 S_7 \\
- S_{20} S_{15} - S_{15} S_{12} - S_{19} S_{14} - S_{14} S_{11} \right). \tag{37}
\]
Vibrational Matrix Elements

The next step is to evaluate the matrix elements of the electronic integrals, given by Equations 24, 33 and 37, between the vibrational functions $f(x)$ for the lowest vibrational state. An approximation for $f(x)$ is

$$f(x) = \frac{1}{x} \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2} \alpha (x-x_0)^2},$$

where $x_0$ is about 0.74 Å (10, p. 271). The value of $\alpha$ is related to the vibration frequency $\omega_e$ by $\alpha = M \omega_e/(2 \hbar)$, but the numerical results below are independent of it. Since only values of $x$ in the region where $f(x)$ is appreciable are pertinent, one can expand the electronic integrals about $x_0$:

$$\mathcal{J}(x) = \mathcal{J}(x_0) + (x-x_0) \left( \frac{d^2}{dx^2} \right)_{x=x_0} + \cdots,$$

where $\mathcal{J}(x)$ is any one of the electronic integrals, given by Equations 24, 33 or 37.

It is seen that two types of vibrational integrals occur. The first type is of the form

$$\int_0^\infty f^2(x) \mathcal{J}(x) x^2 \, dx.$$

Substituting the expansion 38 and keeping only the first term the approximate value this integral is $\mathcal{J}(x_0)$.

The second type of vibrational integral is...
\[
\int_0^\infty f(x) \varphi(x) (\nabla f(x)) x^2 \, dx.
\]

Here one may approximate \( \varphi(x) \) by the first two terms in Equation 38 to obtain

\[
\begin{align*}
\int_0^\infty f(x) \varphi(x) (\nabla f(x)) x^2 \, dx \\
&= - \hat{x} \alpha \left( \frac{d^2}{dx^2} \right)_{x=x_0} \int_0^\infty f^2(x)(x-x_0)^2 x^2 \, dx \\
&\quad - \hat{x} \alpha \frac{d}{dx} \int_0^\infty f^2(x) \frac{x-x_0}{x} x^2 \, dx \\
&\quad - \hat{x} \alpha \varphi(x_0) \int_0^\infty f^2(x) (x-x_0) x^2 \, dx \\
&\quad - \hat{x} \alpha \varphi(x_0) \int_0^\infty f^2(x) \frac{1}{x} x^2 \, dx.
\end{align*}
\]

Evaluation of these integrals gives to the same order of approximation

\[
\int_0^\infty f(x) \varphi(x) (\nabla f(x)) x^2 \, dx = - \hat{x} \left[ \frac{1}{2} \left( \frac{d^2}{dx^2} \right)_{x=x_0} + \frac{\varphi(x_0)}{x_0} \right].
\]

Using these results Equation 21 may be written
\[
\left( \frac{g_p - 1}{g_p} - \frac{4 \delta_p \hbar^2 e^2}{i M C} \right)^{-1} \varepsilon_M
\]

\[
= (1 - \frac{M \hbar \omega}{m \varepsilon \frac{g_p}{g_p-1}}) \int Y_{J_f M_f}^* Y_{J_i M_i} \mathbf{I}_{\text{pl} \mathbf{i}} \times (\int \psi^\dagger \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi)_{x=x_0}
+ 2 \left[ \int Y_{J_f M_f}^* \mathbf{I}_{\text{pl} \mathbf{i}} \times (\nabla Y_{J_i M_i}) \right]_\alpha \left( \int \psi^\dagger \left( x_1 + x_2 \right) \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi \right)_{x=x_0}
- 2 \left[ \int Y_{J_f M_f}^* \mathbf{I}_{\text{pl} \mathbf{i}} \times \hat{\mathbf{x}} Y_{J_i M_i} \right]_\alpha \left[ \frac{1}{2} \left( \frac{d}{dx} \int \psi^\dagger \left( x_1 + x_2 \right) \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi \right)_{x=x_0}
+ \frac{1}{x_0} \left( \int \psi^\dagger \left( x_1 + x_2 \right) \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi \right)_{x=x_0} \right]
+ 2 \int Y_{J_f M_f}^* Y_{J_i M_i} \left( \int \psi^\dagger \left( x_1 + x_2 \right) \left( \frac{\kappa_{\text{elpl}}^2 \mathbf{I}_{\text{pl} \mathbf{i}} \cdot \mathbf{v}_{\mathbf{pl}}}{\kappa_{\text{elpl}}^3} \right) \nabla \psi \right)_{x=x_0}. ~\tag{39}
\]

The results of evaluating the electronic integrals, given by Equations 24, 33, and 37, at \( x_0 \) are

\[
\left( \int \psi^\dagger \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi \right)_{x=x_0} = - \frac{0.202}{A_0^2} \hat{x},
\]

\[
\left( \int \psi^\dagger (x_1 + x_2) \frac{\kappa_{\text{elpl}}}{\kappa_{\text{elpl}}^3} \psi \right)_{x=x_0} = - \frac{0.091}{A_0} \hat{x}_\beta \hat{x}_\alpha + \frac{0.255}{A_0} \delta_{\beta \alpha},
\]

\[
\tag{41}
\]
\[
\left( \int \phi^\dagger(x_1 \beta + x_2 \beta) \left( \frac{k_{el pl} X \nabla_{pl}}{k_{el pl}^3} \right) \phi \right)_{x = x_0} = \frac{0.059}{Q_0^2} \epsilon_{\alpha \beta \gamma} \hat{x}_\delta, \tag{42}
\]

\[
\left( \frac{d}{dx} \int \phi^\dagger(x_1 \beta + x_2 \beta) \left( \frac{k_{el pl} \alpha}{k_{el pl}^3} \phi \right) \right)_{x = x_0} = \frac{1}{Q_0^2} \left( A \hat{x}_\beta \hat{x}_\alpha - 0.147 \delta_{\beta \alpha} \right). \tag{43}
\]

Here the number \(A\) need not be evaluated since that term does not contribute in Equation 39.

Now Equations 40 to 43 may be substituted into Equation 39. This leads to

\[
\left( \frac{g_p - 1}{g_p} \frac{4 \delta_p \hbar^2 e^2}{\hbar MC Q_0^2} \right)^{-1}
\]

\[
\left( \frac{g_p}{g_p - 1} \frac{4 \delta_p \hbar^2 e^2}{\hbar MC Q_0^2} \right)^{-1}
\]

\[
= -(0.302 - 0.101 \frac{M \hbar \omega}{m \epsilon} \frac{g_p}{g_p - 1}) I_{pl f i} X \int Y_{T_f M_f}^\alpha \hat{x} Y_{T_e M_e}
\]

\[
+ 0.364 I_{pl f i} X \int Y_{T_f M_f}^\alpha (x \nabla) Y_{T_e M_e}
\]

\[
- 0.130 I_{pl f i \alpha} \int \hat{x}_{x}^\alpha (x \nabla \hat{x}) Y_{T_e M_e}. \tag{44}
\]
Here and below it is understood that the gradient acts only on the spherical harmonic. Equation 44 may be simplified by writing

\[
\left( x \nabla \times \hat{x} \right)_\alpha \hat{x}_\beta = \frac{1}{2} \left[ \left( x \nabla \times \hat{x} \right)_\alpha \hat{x}_\beta + \left( x \nabla \times \hat{x} \right)_\beta \hat{x}_\alpha \right]
\]

\[
+ \frac{1}{2} \left[ \left( x \nabla \times \hat{x} \right)_\alpha \hat{x}_\beta - \left( x \nabla \times \hat{x} \right)_\beta \hat{x}_\alpha \right]
\]

\[
= \frac{1}{2} \left[ \left( x \nabla \times \hat{x} \right)_\alpha \hat{x}_\beta + \left( x \nabla \times \hat{x} \right)_\beta \hat{x}_\alpha \right] - \frac{1}{2} \epsilon_{\alpha \beta \gamma} \nabla \gamma ,
\]

and one obtains

\[
\left( \frac{g_p-1}{g_p} \frac{4 \epsilon_p \hbar^2 e^2}{i \hbar \alpha_0^2} \right)^{-1} E \mu
\]

\[
= -(0.302-0.10i) \left( \frac{m \hbar \omega}{E \frac{g_p}{g_p-1}} \right) \mathcal{I}_{p' \mu'} \times \int Y_{J_f M_f}^* \hat{x} Y_{J_i M_i}
\]

\[
+ 0.299 \mathcal{I}_{p' \mu'} \times \int Y_{J_f M_f}^* (x \nabla) Y_{J_i M_i}
\]

\[
- 0.065 \mathcal{I}_{p' \mu' \alpha} \int Y_{J_f M_f}^* \left[ \left( x \nabla \times \hat{x} \right)_\alpha \hat{x} + \left( x \nabla \times \hat{x} \right) \hat{x}_\alpha \right] Y_{J_i M_i} .
\]
Nuclear Matrix Elements

Let the spherical components of a vector be defined by

\[ v_{\pm 1} = \mp 2^{-1/2} (v_x \pm i v_y), \]
\[ v_0 = v_z, \]  \hspace{1cm} (46)

and of a symmetric second rank tensor with zero spur by

\[ T_{\pm 2} = \tfrac{1}{2} (T_{xx} \pm 2i T_{xy} - T_{yy}), \]
\[ T_{\pm 1} = \mp T_{zx} - i T_{zy}, \]
\[ T_0 = 6^{-1/2} (2T_{zz} - T_{xx} - T_{yy}). \]  \hspace{1cm} (47)

The rule for the decomposition of the cross product is obtained by noting that a vector \( u_{M_1} \) may be constructed from two vectors \( v_{M_2} \) and \( w_{M_3} \) the following way:

\[ u_{M_1} = \sum_{M_2 M_3} C_{M_2 M_3 M_1}^{M_1} v_{M_2} w_{M_3} \]
\[ = \sum_{M_2} C_{M_2, M_1-M_2}^{M_2, M_1} v_{M_2} w_{M_1-M_2}. \]

The notation for the Clebsch-Gordon coefficients is the same as in Rose (14, p. 33). Next one calculates the \( M_1 = 0 \) component to see how \( u_0 \) is related to the rectangular component contraction. The \( M_1 = 0 \) component is

\[ \sum_{M_2} C_{M_2, M_2}^{M_2, -M_2} v_{M_2} w_{-M_2} = \frac{i}{\sqrt{2}} (v_x w_y - v_y w_x). \]
The result is

\[(\mathbf{v} \times \mathbf{w})_M = -i\sqrt{2} \sum_{M_2} C^1_{M_2, M_1-M_2} v_{M_2} w_{M_1-M_2}. \] (48)

Similarly, from a vector \(v_{M_2}\) and a tensor \(T_{M_3}\) another vector \(w_{M_1}\) may be formed this way:

\[w_{M_1} = \sum_{M_2, M_3} C^{1,2,1}_{M_2, M_3, M_1} v_{M_2} T_{M_3}. \]

Again one calculates the \(M_1 = 0\) component in terms of the rectangular components:

\[\sum_{M_2} C^{1,2,1}_{M_2, -M_2} v_{M_2} T_{-M_2} = -\sqrt{\frac{3}{5}} (V_x T_{xz} + V_y T_{yz} + V_z T_{zz}), \]

and one obtains the relation

\[(\nu_{\alpha} T_{\alpha\beta})_M = -\sqrt{\frac{5}{3}} \sum_{M_2} C^{1,2,1}_{M_2, M_1-M_2} v_{M_2} T_{M_1-M_2}. \] (49)

In terms of spherical components Equation 45 becomes

\[
\left( \frac{g_p^{-1} 4 \chi_p \xi^2 e^2}{g_p \mu_0} \right)^{-1} \varepsilon \mu_{M_1} \\
= \frac{0.302 - 0.101}{m} \frac{\mu_0}{\xi} \left( \frac{g_p}{g_p - 1} \right) \sqrt{2} \sum_{M_2} C^{1,1,1}_{M_2, M_1-M_2} \eta_{P M_2} \int Y_{M_1}^* \chi_{M_1} Y_{M_1}^{M_1}. \]
- 0.299 \sqrt{2} \sum_{M_2} C_{M_2,M_1-M_2}^{1,1,1} I_{plfM_2} \int Y_{J_fM_f}^* (x \nabla)_{M_1-M_2} Y_{J_iM_i} \\
- 0.065 i \sqrt{\frac{5}{3}} \sum_{M_2} C_{M_2,M_1-M_2}^{1,2,1} I_{plfM_2} \\
\int Y_{J_fM_f}^* \left[ (x \nabla \times \hat{x})_{\alpha} \hat{x}_{\beta} + (x \nabla \times \hat{x})_{\beta} \hat{x}_{\alpha} \right]_{M_1-M_2} Y_{J_iM_i}, \quad (50)

where Equations 48 and 49 have been used.

The next step is the evaluation of the rotational integrals in Equation 50. From Rose (14, p. 62), Equations 4.34 and 4.35, one obtains easily

$$\int Y_{J_fM_f}^* \hat{x}_{l-M_2} Y_{J_iM_i} = -\left( \frac{J}{2J-1} \right)^{1/2} C_{M_i,M_1-M_2,M_f}^{J,J-1}, \quad (51)$$

where $J_1$ has been replaced by $J$, and $J_f$ by $J-1$, and Equation 3.32 in Rose (14, p. 47) has been used to evaluate $C_{0,0,0,0}^{J,1,J-1}$. Similarly the relation

$$\int Y_{J_fM_f}^* (x \nabla)_{M_1-M_2} Y_{J_iM_i} = -\left( \frac{J}{2J-1} \right)^{1/2} (J+1) C_{M_i,M_1-M_2,M_f}^{J,J-1} \quad (52)$$

is obtained from Edmonds (15, p. 80), Equation 5.7.2.
The angular integral in the last term of Equation 50 can be written as

\[
\int Y_{J_f}^{*} \left[ (x \nabla \times \hat{x})_\alpha \hat{x}_\beta + (x \nabla \times \hat{x})_\beta \hat{x}_\alpha \right]_{M_1 - M_2} Y_{J_i} M_i
\]

\[= T \left\{ M_i, M_1 - M_2, M_f \right\}. \]

The reduced matrix element \( T \) is most easily evaluated for the case when \( M_i = -J_i = -J \), and \( M_f = -J_f = -(J-1) \). For that case, using Equations 47, one obtains

\[
\int Y_{J-1,-(J-1)}^{*} \left[ (x \nabla \times \hat{x})_\alpha \hat{x}_\beta + (x \nabla \times \hat{x})_\beta \hat{x}_\alpha \right] Y_{J,-J}
\]

\[= - \frac{[(2J-1)! (2J+1)!]^{1/2}}{4\pi 2^{2J-1} J!(J-1)!} \int_0^{2\pi} \int_0^\pi d\phi d\theta (\sin \theta)^J e^{i(J-1)\phi}
\]

\[\left[ xy \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) - i \varepsilon^2 \left( \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) - (y \varepsilon - i x \varepsilon) \frac{\partial}{\partial z}
\]

\[- x^2 \frac{\partial}{\partial y} + iy^2 \frac{\partial}{\partial x} \right] (\sin \theta)^J e^{-iJ\phi}, \]

where the relation (15, p. 21)
\[ Y_{l,-l}(\theta, \phi) = \frac{1}{2^l l!} \left[ \frac{(2l+1)!}{4\pi} \right]^{\frac{1}{2}} (\sin \theta)^l e^{-i l \phi} \]

has been used. When the indicated differentiation is carried out and the angular integration is performed the result is

\[ T = i \left[ \frac{2(J-1)J(J+1)}{2J-1} \right]^{\frac{1}{2}}, \]

where the Clebsch-Gordon coefficient \( \zeta^J_{J, l, -l} \) has been evaluated from the explicit formulas for the Clebsch-Gordon coefficients as given by Condon and Shortley (16, p. 76).

Therefore one obtains

\[ \int Y_{J_1 M_1}^* \left[ (\hat{x} \cdot \hat{x})_\alpha \hat{x}_\beta + (\hat{x} \cdot \hat{x})_\beta \hat{x}_\alpha \right]_{M_1 - M_2} Y_{J_2 M_2} \]

\[ = i \left[ \frac{2(J-1)J(J+1)}{2J-1} \right]^{\frac{1}{2}} \zeta^J_{J_1, J_2, M_1 - M_2, M_2}. \quad (53) \]

The matrix elements of the nuclear spin are easily worked out also. They are found to be

\[ I_{\pi_1 \pi_2 M_2} = \frac{1}{2} (\mp 1)^{m_\pi} \delta_{m_\pi, -M_2} \]

where the sign is - for ortho → para, + for para → ortho.

Here \( m_\pi \) is the projection quantum number of the initial nuclear spin for an ortho → para transition, and \((-m_\pi)\) is
the projection quantum number of the final nuclear spin for
a para-ortho transition.

When these results are collected one finds this formula for the dipole matrix element:

\[
\left[ \frac{g_p^{-1} \langle \mp \rangle^{m_i} g_p \hbar^2 e^2}{M c a_o^2} \left( \frac{8J}{2^J-1} \right)^{1/2} \right]^{-1} E \mu_{M_f}
\]

\[
= \left[ 0.299 (J+1) - 0.302 + 0.101 \frac{M}{m} \frac{\hbar \omega}{E} \frac{g_p}{g_p - 1} \right]
\]

\[
C_{M_i, M_{i1} + m_i, M_f} \ C_{-m_i, M_{i1} + m_i} \]

\[
+ 0.065 \left[ \frac{5}{3} (J^2-1) \right]^{1/2} C_{M_i, M_{i1} + m_i, M_f} \ C_{-m_i, M_{i1} + m_i}. \tag{54}
\]
The transition probability per unit time is found by combining Equations 1, 2 and 54. The dot product in terms of spherical components is

\[ \mathbf{M}^* \cdot \mathbf{M} = \sum_{M_1} \mathbf{M}_{M_1}^* \mathbf{M}_{M_1}, \]

so that

\[ W = \sum_{M_i, M_f, m_z, M_1} \frac{4}{3} \frac{\omega^3}{\hbar c^3} \frac{1}{(2I+1)(2J+1)} \mathbf{M}_{M_i}^* \mathbf{M}_{M_1}. \]  

(55)

Using the unitary property of the Clebsch-Gordon coefficients (14, p. 34)

\[ \sum_{m_1} C_{m_1, m-m_1} C_{m_1, m-m_1} = \delta_{m \dot{m}}, \]

and the relation (14, p. 38)

\[ C_{m_1 m_2 m_3} = (-1)^{j_1-m_1} \left[ \frac{2j_3+1}{2j_2+1} \right]^{\frac{1}{2}} C_{j_1 j_2 j_3}, \]

it is seen that the sums over the Clebsch-Gordon coefficients that occur in Equation 55 are evaluated by

\[ \sum_{M_i, m_1} C_{M_i, m_1} C_{-m_1, M_1} C_{-m_1, M_1} C_{M_i, m_1} C_{M_i, m_1} = \frac{3(2J-1)}{2j_2+1} \delta_{j_1 j_2}, \]

(56)
and the probability reduces to the form

\[ W = \frac{8}{3} \frac{(g_p-1)^2}{(2I+1)(2J+1)} \left( \frac{m}{M} \right)^4 \left( \frac{e^2}{\hbar c} \right)^7 \left( \frac{\hbar \omega}{\epsilon} \right)^2 \hbar J \left\{ \frac{0.299 (J+1)}{-0.302 + 0.101 \frac{\hbar \omega}{\epsilon} \frac{g_p}{g_p-1}} + 0.004 (J^2-1) \right\} . \] (57)

Here one may set \( g_p = 5.58 \), \( M/m = 1836 \), \( (e^2/\hbar c) = 1/137 \), \( \epsilon = 12 \text{ ev} \). Also the transition energy \( J \to J-1 \) is, as given by Herzberg (9, p. 531), is

\[ \hbar \omega = 1.5(10)^{-2} \text{J eV}. \]

The final result for the probability per unit time is

\[ W = \frac{J^6}{(2I+1)(2J+1)} \frac{1}{5(10)^{11} \text{ yr}} . \] (58)

Because of the uncertainty in the choice of the value of the result is considered to be of about 20% accuracy.
LITERATURE CITED


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Derivation of the Spin-Orbit Interaction Term

Consider a Dirac particle in a central electrostatic potential \( e\Phi(r) \). To determine the effect of this potential in the non-relativistic approximation one calculates the non-relativistic limit of the Dirac theory (2, p. 944). When the Pauli (17) anomalous moment is included, the Hamiltonian is

\[
\mathcal{H} = \beta m + \mathcal{J} + \mathcal{P},
\]

where

\[
\mathcal{J} = \mathbf{\alpha} \cdot \mathbf{P} + \frac{i}{4} \frac{e \mu}{m} \mathbf{\alpha} \cdot \mathbf{E} \quad \text{and} \quad \mathcal{P} = e \Phi.
\]

Here

\[
\mathbf{\alpha} = \begin{pmatrix} 0 & \delta \\ \delta & 0 \end{pmatrix}, \quad \mathbf{\beta} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
\]

and units where \( \hbar = c = 1 \) are used.

It is seen that \( \mathcal{P} \) is an even operator because it has no matrix elements linking small and large components of the Dirac equation

\[
(\beta m + \mathcal{J} + \mathcal{P})(\Psi_L) = \mathcal{W}(\Psi_L),
\]

where \( \Psi_S \) and \( \Psi_L \) are known as the small and large components of the Dirac wave function. It is clear from Equation 60 that

\[
\Psi_S \ll \Psi_L
\]
in the non-relativistic limit $\omega \ll \omega$. $\mathcal{O}$ is an odd operator because its non-vanishing matrix elements link small and large components. It is equivalent to say that $\mathcal{P}$ is an operator that commutes with $\mathcal{B}$ and $\mathcal{J}$ an operator that anticommutes with $\mathcal{B}$

$$\mathcal{P} = \beta \mathcal{P} \beta, \quad \mathcal{J} = -\beta \mathcal{J} \beta.$$  

In general, there exists no representation in which the Hamiltonian is exactly even and the small and large components can be decoupled in all orders of $v/c$, but by applying successive unitary transformations one may obtain representations in which the respective Hamiltonians have an odd part of higher and higher order in $v/c$. The unitary transformation is given by (18)

$$U = e^{\frac{\beta \mathcal{J}}{2m}}.$$  

The Hamiltonian $H_1$ which governs the evolution of states in the new representation is given by

$$H_1 = U H U^\dagger - i U \frac{\partial H}{\partial \xi}.$$  

By making use of the fact that $\mathcal{B} \mathcal{J}$ anticommutes with $(\mathcal{B} m + \mathcal{J})$ and that

$$U^\dagger = e^{-\frac{\beta \mathcal{J}}{2m}},$$

one obtains
\[ U(\beta m + \alpha) U^\dagger = U^\varepsilon (\beta m + \alpha) \]
\[ = \beta m \left\{ \cos \left( \frac{\alpha}{m} \right) + \left( \frac{\alpha}{m} \right) \sin \left( \frac{\alpha}{m} \right) \right\} \]
\[ + m \left\{ \left( \frac{\alpha}{m} \right) \cos \left( \frac{\alpha}{m} \right) - \sin \left( \frac{\alpha}{m} \right) \right\} . \]

The terms \( U^\varepsilon U^\dagger \) and \( iU \frac{\partial U^\dagger}{\partial t} \) may be expanded into a power series in \( \alpha/m \) by using the following operator identity, valid for any two operators A and B:
\[ e^A B e^{-A} = B + [A,B] + \frac{1}{2!} [A,[A,B]] + \cdots \]
\[ \cdots \frac{1}{n!} [A,[A,\ldots [A,[A,B]]\ldots]] + \cdots . \]

For the case when \( \alpha \) is time-independent one finds to first order
\[ H_i = \beta m + \hat{p}_i + \hat{\alpha}_i , \]
where
\[ \hat{p}_i = \hat{p} + \beta \frac{\alpha^2}{2m} - \frac{1}{6} m \left[ \frac{\alpha}{m}, \frac{\alpha}{m}, \hat{p} \right] - \frac{1}{3} \beta m \left( \frac{\alpha}{m} \right)^4 + \cdots , \]
\[ \hat{\alpha}_i = m \left( \frac{1}{2} \beta \left[ \frac{\alpha}{m}, \frac{\hat{p}}{m} \right] - \frac{1}{6} \left( \frac{\alpha}{m} \right)^3 \right) + \cdots . \]

The terms given in these expansions of the even and odd parts of \( H_i \) allow the determination of \( \hat{p}_i \) to within \( \left( \frac{\alpha}{m} \right)^6 \) or \( \left( \frac{\hat{p}}{m} \right) \left( \frac{\alpha}{m} \right)^4 \), whichever is the larger and the determination of \( \hat{\alpha}_i \) to within \( \left( \frac{\alpha}{m} \right)^5 \) or \( \left( \frac{\hat{p}}{m} \right) \left( \frac{\alpha}{m} \right)^3 \), whichever is the larger.
The odd part of $H_1$ is therefore smaller than that of $H$ by a factor of the order of the larger of $\left(\frac{\mathbf{p}}{m}\right)$ or $\left(\frac{\mathbf{a}}{m}\right)^2$. In the non-relativistic limit $\left(\frac{\mathbf{p}}{m}\right)$ and $\left(\frac{\mathbf{a}}{m}\right)$ are of the order of $\left(\frac{\mathbf{v}}{c}\right)^2$ and $\frac{\mathbf{v}}{c}$ respectively, $\mathcal{A}_1$ is therefore of the order of $\left(\frac{\mathbf{v}}{c}\right)^3$.

Now one performs on $H_1$ the operation which was performed on $H$. The new unitary transformation is

$$U_1 = e^{\frac{\mathcal{A}_1}{2m}},$$

and the new Hamiltonian is denoted by $H_2$. Its odd part $\mathcal{A}_2$ is smaller than that of $H_1$ by a factor of the order of $\left(\frac{\mathbf{p}^1}{m}\right)$ or $\left(\frac{\mathbf{a}^1}{m}\right)$, whichever is the larger. In the non-relativistic limit $\left(\frac{\mathbf{p}^1}{m}\right)$ is of the order of $\left(\frac{\mathbf{v}}{c}\right)^2$, $\left(\frac{\mathbf{a}^1}{m}\right)^2$ is of the order of $\left(\frac{\mathbf{v}}{c}\right)^6$, and $\mathcal{A}_2$ is therefore of the order of $\left(\frac{\mathbf{v}}{c}\right)^5$. If one neglects terms of this order, $H_2$ is an even operator given by:

$$H_2 \cong \beta m + \mathbf{P} + \mathcal{O}(\mathbf{v}^5)$$

$$\cong \beta m + \mathbf{P} + \beta \frac{\mathbf{a}^2}{2m} - \frac{1}{8} m \left[ \frac{\mathbf{a}}{m}, \left[ \frac{\mathbf{a}}{m}, \frac{\mathbf{p}}{m} \right] \right]$$

$$- \frac{1}{8} \beta m \left(\frac{\mathbf{a}}{m}\right)^4 + \mathcal{O}(\mathbf{v}^5)$$

(61)
\[ H_2 \approx \beta m + e\Phi + \frac{\beta}{2m} (\hat{S} \cdot \hat{P} + \frac{i e u \beta}{m}\hat{S} \cdot \hat{E})^2 \]

\[-\frac{1}{8m^2} [\hat{S} \cdot \hat{P} + \frac{i e u \beta}{m}\hat{S} \cdot \hat{E}, [\hat{S} \cdot \hat{P} + \frac{i e u \beta}{m}\hat{S} \cdot \hat{E}, e\Phi]] \]

\[-\frac{\beta}{8m^3} (\hat{S} \cdot \hat{P} + \frac{i e u \beta}{m}\hat{S} \cdot \hat{E})^4 + \mathcal{O}(\nu^5) \quad (62)\]

\[= \beta m + e\Phi + \frac{\beta}{2m} (\hat{S} \cdot \hat{P})^2 - (q-1)\frac{e}{4m^2} \hat{S} \cdot (\hat{E} \times \hat{P}) \]

\[= (q-1)\frac{e}{8m^2} \nabla \cdot \hat{E} - \frac{\beta}{8m^3} \left\{ (\hat{S} \cdot \hat{P})^2 + \frac{i e u \beta}{m} \nabla \cdot \hat{E} \right\} + \frac{1}{4} \frac{i e u \beta}{m} \hat{E} \cdot \hat{P} \] \[+ \frac{1}{4} \frac{i e u \beta}{m} \hat{E} \cdot \hat{P} \}^2 + \mathcal{O}(\nu^5). \quad (63)\]

One may now pass over to the two-component theory. To within \((\nu/c)^5\), the positive energy solutions are represented by the wave functions \(\Psi'_L\), obtained from \(\Psi_L\) by the unitary transformations, which obey the equation

\[ i \frac{\partial \Psi'_L}{\partial t} = \left( m + H_{NR} \right) \Psi'_L, \]

where \((m + H_{NR})\) is the projection of the projection of the approximate expression for \(H_2\) onto the space of the large components. The only spin-dependent term of \(H_{NR}\) is
This is the spin-orbit coupling term.

This result may be extended to the case of a many-particle system. It is easily seen that the spin-orbit term for the hydrogen molecule is

\[ H_{so}' = -\sum_{\alpha} \left( g_{\alpha} - 1 \right) \frac{e_{\alpha}}{4m_{\alpha}^2} \leq \alpha \cdot \left( \mathbf{E}_{\alpha} \times \mathbf{P}_{\alpha} \right) \],

where the sum ranges over the two protons and the two electrons. Here

\[ \leq \alpha = 2 \mathbf{I}_{\alpha} \],

\[ \phi(\mathbf{r}^\alpha) = \sum_{\beta(\neq \alpha)} \frac{e_{\beta}}{\hbar_{\alpha\beta}} \],

\[ \mathbf{E}(\mathbf{r}^\alpha) = -\nabla_{\alpha} \phi(\mathbf{r}^\alpha) = \sum_{\beta(\neq \alpha)} \frac{e_{\beta} \hbar_{\alpha\beta}}{\hbar_{\alpha\beta}^3} \],

so that Equation 65 becomes

\[ H_{so}' = -\sum_{\alpha} \left( g_{\alpha} - 1 \right) \frac{e_{\alpha}}{g_{\alpha}} \frac{i\hbar_{\alpha}}{m_{\alpha}^2} (\mathbf{I}_{\alpha} \times \nabla_{\alpha}) \cdot \sum_{\beta(\neq \alpha)} \frac{e_{\beta} \hbar_{\alpha\beta}}{\hbar_{\alpha\beta}^3} \] (66)

which is identical to the second term of \( H' \) given by Equation 6 if the units \( \hbar = c = 1 \) are used.
APPENDIX B

Effect of Recoil

In this Appendix the derivation of Equation 2 will be outlined with special considerations given to the contributions of recoil effects to the ortho-para transition probability.

The probability per unit time of an ortho-para transition $J_i \rightarrow J_f$, accompanied by the emission of a photon of momentum $p = h \mathbf{k}$, within a solid angle $d\Omega$, is given by (2, p. 991)

$$\omega d\Omega = \frac{2\pi}{h} \rho \left| \langle f, k\lambda | \mathcal{H}_{\text{int}} | i \rangle \right|^2,$$

where $| i \rangle$ denotes the initial state of the molecule and $| f, k\lambda \rangle$ the final state of the molecule and the emitted photon. $\rho$ is the density of final states determined by

$$\rho = \frac{\mathcal{N}}{8\pi^3} k^2 dk,$$

where $\mathcal{N}$ is the normalization volume. Here the interaction Hamiltonian is written

$$\mathcal{H}_{\text{int}} = -\left( m_\alpha c \sum_{\alpha} e_\alpha \left( \frac{\hbar}{i} \nabla \alpha \right) \right) + \mathcal{A}_{\text{rad}}(\mathcal{N} \alpha)$$
\[
- \int \cdots \int \mathcal{W}_{\Pi} \cdots d\mathcal{W}_{\Pi 2} \Psi^\dagger \sum_\alpha \frac{g_{\alpha \alpha} e_\alpha}{2m_\alpha c} \hbar i \mathcal{W}_{\Pi} \Psi \cdot \mathbf{B}_{\text{rad}}(r_\alpha),
\]
(68)

where \( \Psi \) is the wave function operator for the molecule. The vector potential \( \mathbf{A}_{\text{rad}}(r_\alpha) \) of the radiation field is given by

\[
\mathbf{A}_{\text{rad}}(r_\alpha) = \sum_{k\lambda} \sqrt{\frac{2\pi c \hbar}{k \Omega}} \hat{\mathbf{e}}_{k\lambda} b_{k\lambda} e^{i(k \cdot r_\alpha - \omega t)} + \text{h.c.},
\]
(69)

where \( b \) is a photon destruction operator, \( \hat{\mathbf{e}}_\lambda \) is the polarization vector, \( \lambda = 1,2 \) represents the two polarization directions perpendicular to \( k \). Here

\[
\nabla \cdot \mathbf{A}(r_\alpha) = 0
\]

and

\[
\mathbf{B}(r_\alpha) = \nabla \times \mathbf{A}(r_\alpha)
\]

\[
= i \sum_{k\lambda} \sqrt{\frac{2\pi c \hbar}{k \Omega}} \hat{\mathbf{e}}_{k\lambda} \times \hat{\mathbf{e}}_{k\lambda} b_{k\lambda} e^{i(k \cdot r_\alpha - \omega t)} + \text{R.c.}
\]
(70)

If one can assume that the wave function operator \( \Psi \) may be expanded in terms of the molecular destruction operators \( a_m \)

\[
\Psi = \sum_m a_m u_m,
\]

the matrix element of Equation 67 may be written
\begin{align*}
\langle f, k\lambda | \mathcal{H}_{\text{int}} | i \rangle &= -\langle f | \sqrt{\frac{2\pi c}{k\Omega}} \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha} c} \frac{t_N}{i} \nabla_{\alpha} \cdot \hat{\xi}_{k\lambda} e^{-ik\cdot\xi_{k\lambda}} | i \rangle \\
&\quad + \langle f | \sqrt{\frac{2\pi c}{k\Omega}} \sum_{\alpha} \frac{e^2}{m_{\alpha} c^2} \sum_{\beta(\neq \alpha)} t_{N\beta} \frac{I_{\beta\alpha}}{K_{\beta\alpha}} \cdot \hat{\xi}_{k\lambda} e^{-ik\cdot\xi_{k\lambda}} | i \rangle \\
&\quad - i \langle f | \sqrt{\frac{2\pi c}{k\Omega}} \sum_{\alpha} \frac{g_{\alpha} e_{\alpha}}{2m_{\alpha} c} t_N \hat{\xi}_{k\lambda} e^{-ik\cdot\xi_{k\lambda}} | i \rangle, \quad (71)
\end{align*}

where Equations 69 and 70 have been used.

In order to simplify the problem one introduces the center-of-mass coordinates defined by

\begin{align*}
\mathbf{r}_0 &= \sum_{\alpha} \frac{m_{\alpha} \mathbf{r}_\alpha}{m_t}, \quad m_t = \sum_{\alpha} m_{\alpha}, \\
\mathbf{r}_\alpha' &= \mathbf{r}_\alpha - \mathbf{r}_0, \quad \sum_{\alpha} m_{\alpha} \mathbf{r}_\alpha' = 0, \\
\mathbf{p}_0 &= \sum_{\alpha} \mathbf{p}_\alpha, \quad \mathbf{p}_\alpha = \frac{t_N}{i} \nabla_{\alpha}, \\
\mathbf{p}_\alpha' &= \mathbf{p}_\alpha - \frac{m_{\alpha}}{m_t} \mathbf{p}_0.
\end{align*}
In terms of these coordinates Equation 71 becomes

\[ \langle f, k\lambda | \mathcal{H}_{\text{int}} | i \rangle \]

\[ \propto - \langle f \mid \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}c} \left( p_{\alpha}' + \frac{m_{\alpha}}{m_{t}} p_{0}' \right) \cdot \xi_{k\lambda} e^{i k \cdot (\xi_{\alpha}' + \xi_{\alpha}')} | i \rangle \]

\[ + \langle f \mid \sum_{\alpha} \frac{e_{\alpha}^2}{m_{\alpha}c^2} \sum_{\beta (\neq \alpha)} \frac{I_{\beta} \times I_{\alpha}}{h_{\alpha}} \cdot \xi_{k\lambda} e^{i k \cdot (\xi_{\alpha}' + \xi_{\alpha}')} | i \rangle \]

\[ - \langle f \mid \sum_{\alpha} \frac{g_{\alpha}e_{\alpha}}{2m_{\alpha}c} i \hbar I_{\alpha} \cdot k \cdot \xi_{k\lambda} e^{i k \cdot (\xi_{\alpha}' + \xi_{\alpha}')} | i \rangle. \]

(72)

It is seen that the second member of the first term vanishes because \( \sum_{\alpha} e_{\alpha} = 0. \)

The hyperfine interaction produces a small mixing of the nuclear spins, however if one can assume that the initial and final state wave functions for the hydrogen molecule may be written in the form

\[ u_{i} = e^{i K_{i} \cdot \xi_{i}} \phi_{i} (\xi_{p1}', \xi_{p2}', \xi_{e1}', \xi_{e2}'), \]

\[ u_{f} = e^{i K_{f} \cdot \xi_{f}} \phi_{f} (\xi_{p1}', \xi_{p2}', \xi_{e1}', \xi_{e2}'), \]

where \( \hbar K_{i} \) and \( \hbar K_{f} \) are the initial and final momenta of the molecule, respectively, the center-of-mass and relative parts
of the problem can be separated. Here the exponential terms describe the center-of-mass motion of the molecule and the \( \Phi \) terms the relative motion in a manner similar to Equation 15.

Using these wave functions Equation 72 becomes

\[
\langle f, k \lambda | \mathcal{H}_{\text{int}} | i \rangle
\]

\[
= ( \int e^{-i \mathbf{k} \cdot \mathbf{\Delta}} ) \left[ \left( \sum_{\alpha} \frac{e^\alpha}{m_c} \mathbf{p}_\alpha \cdot \hat{\mathbf{E}}_{k \lambda} e^{i \mathbf{k} \cdot \mathbf{\alpha}} | \Phi_i \rangle \right) + \left( \int e^{-i \mathbf{k} \cdot \mathbf{\Delta}} \right) \left( \sum_{\alpha} \frac{e^2}{2m_c^2} \sum_{\beta \neq \alpha} \mathbf{h}_\beta \cdot \frac{\mathbf{I}_\beta \times \mathbf{\alpha}_\beta}{\mathbf{\alpha}_\beta^3} \cdot \hat{\mathbf{E}}_{k \lambda} e^{i \mathbf{k} \cdot \mathbf{\alpha}} | \Phi_i \rangle \right) \right.
\]

\[
\left. - \left( \int e^{-i \mathbf{k} \cdot \mathbf{\Delta}} \right) \left( \sum_{\alpha} \frac{i g_{\alpha \lambda} e^\alpha}{2m_c} \mathbf{h}_\alpha \cdot \mathbf{k} \times \hat{\mathbf{E}}_{k \lambda} e^{i \mathbf{k} \cdot \mathbf{\alpha}} | \Phi_i \rangle \right) \right].
\] (73)

The two selection rules for dipole emission are: \( J_i, 1, J_f \) must form a triangle and initial and final states must have opposite parity. If one assumes that these conditions are
satisfied one obtains

\[ \langle f, k, \lambda | H_{\text{int}} | i \rangle \]

\[ \alpha = \langle \Phi_f | \sum_{\alpha} \frac{e_\alpha}{m_\alpha c^2} \mathbf{p}_\alpha \cdot \mathbf{F}_{k, \lambda} | \Phi_i \rangle \delta(k - k_f - k) \]

\[ + \langle \Phi_f | \sum_{\alpha} \frac{e_\alpha^2}{2m_\alpha c^2} \sum_{\beta(\neq \alpha)} \gamma_{\beta} \frac{\mathbf{I}_\beta \cdot \mathbf{F}_{k, \lambda}^{\prime}}{r_{\alpha, \beta}^3} \cdot \mathbf{a}_{k, \lambda} | \Phi_i \rangle \delta(k - k_f - k) \]

\[ + \langle \Phi_f | \sum_{\alpha} \frac{g_{3, \alpha} e_\alpha}{2m_\alpha c} \hbar (\mathbf{a}_{k, \lambda} \cdot \mathbf{k} \times \mathbf{I}_\alpha)(k \cdot \mathbf{n}_\alpha') | \Phi_i \rangle \delta(k - k_f - k), \quad (74) \]

where only the first non-vanishing terms of the dipole expansion

\[ e^{-i \mathbf{k} \cdot \mathbf{n}_\alpha} = 1 - i \mathbf{k} \cdot \mathbf{n}_\alpha - \frac{1}{2} (\mathbf{k} \cdot \mathbf{n}_\alpha)^2 - \cdots \]

have been retained, since the second-order terms are smaller by a factor of about 10^5. As discussed above the contribution to the transition probability from the first term of the dipole expansion is smaller by a factor of m/M than expected by numerical considerations, so the contribution of the second term of the dipole expansion would be smaller by a factor of at least 10^2 than the contribution of the first term and is therefore neglected.

The contribution of the third term of Equation 74 is negligible to that of the first two. Therefore, to first
order of approximation, the only effect of recoil is the condition $K_i - K_f = k$. Thus recoil may be neglected in the calculation of the ortho-para transition probability.

It is easily shown that

$$[H, x_{\alpha j}] = \frac{\hbar}{i m_{\alpha}} \left( \frac{\hbar}{c} x_{\alpha} - \frac{e_{\alpha}}{c} \sum_{\beta(\neq \alpha)} \frac{1}{\hbar \alpha \beta} \frac{x_{\alpha beta}}{\hbar \alpha \beta} \right)_{j}, \tag{75}$$

where $H$ is given by Equation 4. Using Equation 75 it is seen that the matrix element 71 simplifies to

$$\langle f, k \lambda | \mathcal{H}_{\text{int}} | i \rangle = \langle u_f | \sqrt{\frac{2 \pi e c \hbar}{k \Omega}} \sum_{\alpha} \frac{i}{c \hbar} \hat{\xi}_{k \lambda} \cdot [H, x_{\alpha}] | u_i \rangle. \tag{76}$$

Here and below it is understood that recoil effects are to be neglected.

Using the definition of $\mu$, as given by Equation 3, one obtains

$$\langle f, k \lambda | \mathcal{H}_{\text{int}} | i \rangle = (E_i - E_f) \frac{i}{c \hbar} \sqrt{\frac{2 \pi e c \hbar}{k \Omega}} \mu \cdot \hat{\xi}_{k \lambda}$$

and Equation 67 becomes

$$\omega \frac{d \hat{P}}{d \omega} = \frac{\omega^3}{2 \pi \hbar c^3} | \mu \cdot \hat{\xi}_{k \lambda} |^2.$$
where $\hbar \omega = \varepsilon_i - \varepsilon_f$. Summing over polarizations and integrating over angles one finds the total probability per unit time of an electric dipole transition to be (2, p. 1044).

$$W_{if} = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \mu^* \cdot \mu.$$
Evaluation of Two-Center Integrals

In this Appendix the evaluation of two-center integrals which occur in the Heitler-London treatment of the hydrogen molecule will be illustrated.

A typical example of the electronic integral which occurs is the integral

\[ S_{14} = \int dy_1 \frac{\cos \Theta_{1A}}{y_{elp}^2} \varepsilon^2 y_{elp}^2, \]

which appears in Equation 24. This integral may be expressed in terms of the prolate spheroidal coordinates \( \xi, \eta \), and \( \phi \) by means of the following relations (19) (see Figure 2)

\[ y_A = \frac{y}{2}(\xi + \eta), \]
\[ y_B = \frac{y}{2}(\xi - \eta), \]
\[ \cos \Theta_A = \frac{1 + \xi \eta}{\xi + \eta}, \]
\[ \cos \Theta_B = \frac{1 - \xi \eta}{\xi - \eta}. \]
Figure 2. Electronic coordinates
where
\[ 1 < \xi < \infty \]
\[-1 < \eta < 1 \]
\[ 0 < \phi < 2\pi \, . \]

In terms of these variables the volume element takes the form
\[
dy = \left(\frac{y}{2}\right)^3 d\xi d\eta d\phi \left(\xi^2 - \eta^2\right).\]

In terms of the new coordinates \( S_{14} \) becomes
\[
S_{14} = \Pi y \int_{1}^{\infty} d\xi \int_{-1}^{1} d\eta e^{-y(\xi-\eta)} \frac{(\xi-\eta)(1+\xi\eta)}{(\xi+\eta)^2} .
\]

Now the trick is to make use of the fact that
\[
\frac{1}{(\xi+\eta)^2} = -\frac{d}{d\xi} \left(\frac{1}{\xi+\eta}\right) = -\frac{d}{d\eta} \left(\frac{1}{\xi+\eta}\right)
\]
and partially integrate with respect to \( \xi \) first and then with respect to \( \eta \) and finally add the two expressions.

Performing the partial integration with respect to \( \xi \) one obtains
\[
\frac{S_{14}}{\Pi y} = e^{-y} \int_{-1}^{1} d\eta e^{y\eta} (1-\eta) - y \int_{1}^{\infty} d\xi \int_{-1}^{1} d\eta e^{-y(\xi-\eta)} \frac{(\xi-\eta)(1+\xi\eta)}{\xi+\eta} + \int_{1}^{\infty} d\xi \int_{-1}^{1} d\eta e^{-y(\xi-\eta)} \frac{1+\xi\eta}{\xi+\eta} .
\]
The result of the partial integration with respect to \( \eta \) is

\[
\frac{S_{14}}{\pi y} = -e^y \int_{-1}^{1} d\eta e^{y \eta} (1-\eta) - e^y \int_{1}^{\infty} d\xi e^{-y \xi} (\xi-1) \\
- e^y \int_{-1}^{1} d\xi e^{-y \xi} (\xi+1) + \int_{1}^{\infty} d\xi \int_{-1}^{1} d\eta e^{-y (\xi-\eta)} \frac{(\xi-\eta)(1+\xi \eta)}{\xi+\eta}.
\]

Adding Equations 78 and 79 one obtains

\[
\frac{2S_{14}}{\pi y} = e^y \int_{-1}^{1} d\eta e^{y \eta} (1-\eta) - e^y \int_{1}^{\infty} d\xi e^{-y \xi} (\xi-1) \\
- e^y \int_{-1}^{1} d\xi e^{-y \xi} (\xi+1) + \int_{1}^{\infty} d\xi \int_{-1}^{1} d\eta e^{-y (\xi-\eta)} (\xi-\eta).
\]

The integrations on \( \xi \) and \( \eta \) are now separable and the integrals are easily evaluated. The result is

\[
S_{14} = \frac{\pi}{y^2} \left[ 1 - e^{-2y} (1 + 2y + 2y^2) \right].
\]

The same result is obtained from Ruedenberg's (13) tables.
Appendix D

Table of Electronic Integrals

In this Appendix the one-electron two-center integrals which occur in the calculation of the ortho ≠ para transition probability are tabulated.

The notation used in this Appendix is: A stands for π, B for p₂, and N can be either π or p₂. The integrals are written so that the table applies for both electrons, for example y_A can indicate either y_e₁p₁ or y_e₂p₁ (see Figure 2). The numbers in brackets are the numerical values for the various electronic integrals evaluated at the equilibrium nuclear separation X₀ = 0.74Å. Here C is the Euler-Mascheroni constant 0.577215... .
\[ S_1 = \int dy \ e^{-2y_N} = \pi \]

\[ S_2 = \int dy \ e^{-y_A - y_B} = \pi e^{-y} (1 + y + \frac{1}{3} y^2) \quad (2.16) \]

\[ S_3 = \int dy \ \frac{e^{-2y_N}}{y_N} = \pi \]

\[ S_4 = \int dy \ \frac{e^{-2y_B}}{y_B} = \frac{\pi}{y} \left[ 1 - e^{2y} (1 + y) \right] \quad (1.73) \]

\[ S_5 = \int dy \ \frac{e^{-y_A - y_B}}{y_A} = \pi e^{-y} (1 + y) \quad (1.618) \]

\[ S_6 = \int dy \ \cos \Theta_N e^{-2y_N} = 0 \]

\[ S_7 = \int dy \ \cos \Theta_A e^{-y_A - y_B} = \frac{\pi}{3} e^{-y} y (1 + y) \quad (0.880) \]

\[ S_8 = \int dy \ y_N \cos \Theta_N e^{-2y_N} = 0 \]
\[ S_9 = \int dy \, y_B \cos \theta_B \, e^{-2y_A} = \pi y \] (5.12)

\[ S_{10} = \int dy \, y_B \cos \theta_B \, e^{-y_A-y_B} = \frac{\pi}{2} \, e^{-y} \, y \left( 1 + y + \frac{1}{3} \, y^2 \right) \] (1.764)

\[ S_{11} = \int dy \, y_B \cos \theta_A \cos \theta_B \, e^{-2y_A} = -\frac{\pi}{2} \]

\[ S_{12} = \int dy \, y_B \cos \theta_A \cos \theta_B \, e^{-y_A-y_B} = \frac{\pi}{6} \, e^{-y} \left( y^3 - 3y - 3 \right) \] (-0.365)

\[ S_{13} = \int dy \, \frac{\cos \theta_N}{y_N^2} \, e^{-2y_N} = 0 \]

\[ S_{14} = \int dy \, \frac{\cos \theta_A}{y_A^2} \, e^{-2y_B} = \frac{\pi}{y^2} \left[ 1 - e^{-y} \left( 1 + 2y + 2y^2 \right) \right] \] (0.748)
\[ S_{15} = \int dy \frac{\cos \theta_A}{y_A^2} e^{-y_A - y_B} \]
\[ = \frac{6\pi}{y^2} \left[ - e^{-y} y (2+y) + e^{-y} (1 + \ln 2y)(1+y+\frac{1}{3}y^2) \right. \]
\[ \left. - e^{-y} \text{Ei}(-2y)(1-y+\frac{1}{3}y^2) \right] \]
\[ (0.457) \]

\[ S_{16} = \int dy \frac{\cos^2 \theta_N}{y_N} e^{-2y_N} = \frac{\pi}{3} \]

\[ S_{17} = \int dy \frac{\cos^2 \theta_A}{y_A} e^{-2y_B} \]
\[ = \frac{\pi}{y^3} \left[ (y^2 - 2) + e^{2y} (1+y)(2+2y+y^2) \right] \]
\[ (1.058) \]

\[ S_{18} = \int dy \frac{\cos^2 \theta_A}{y_A} e^{-y_A - y_B} \]
\[ = \frac{\pi}{y^3} \left[ e^{-y} (120 + 60y + 15y^2 + y^3) y \right. \]
\[ + e^{-y} (60 - 60y + 24y^2 - 4y^3) \text{Ei}(-2y) \]
\[ - e^{-y} (60 + 60y + 24y^2 + 4y^3)(1 + \ln 2y) \right] \]
\[ (0.678) \]
\[
S_{19} = \int dy \frac{y_A \cdot y_B}{y_A} e^{-2y_A} = \frac{3\pi}{2}
\]

\[
S_{20} = \int dy \frac{y_A \cdot y_B}{y_A} e^{-y_A-y_B}
\]

\[
= \frac{\pi}{6} e^y (9 + 9y + 2y^2 - y^3)
\] (2.53)