RELATIVISTIC INTERMOLECULAR FORCES

by

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ABSTRACT

The generalized Breit-Pauli Hamiltonian is used to give a systematic treatment of magnetic and other relativistic intermolecular energies through \(O(\alpha^2)\) (where \(\alpha\) is the fine structure constant) for intermolecular separations, \(R\), sufficiently large that the charge distributions of the two molecules do not overlap and yet not large enough to involve retardation effects.

In part I the theory is discussed in general and many interesting types of interaction energies are obtained. These energies depend upon the spin and orbital angular momentum states of the interacting molecules.

In part II the interaction of two neutral non-degenerate atoms (with zero spin and orbital angular momentum quantum numbers) is considered as an example of the general theory. It is shown that the interaction energy has a term varying as \(\alpha^2/R^4\) which is of longer range than the usual London dispersion energy and which may be significant in low energy atomic scattering problems.

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1.1 Introduction

Magnetic coupling terms are included in the relativistic corrections to the Schrödinger equation. The magnitude of the energy corrections due to these coupling terms is small in atoms of low atomic number where Russell-Saunders coupling is applicable and becomes larger in j-j coupled atoms. The relativistic energy of a molecule is comparable to the sum of the relativistic energies of its component atoms. Even though the relativistic corrections to the energy are often small, the magnetic coupling terms are nevertheless important. They are responsible for "forbidden transitions" which are frequently significant in atomic and molecular spectroscopy and may also play an important role in atomic and molecular collision processes.

In this paper we give a systematic treatment of relativistic intermolecular energies, accurate through $O(\alpha^2)$ (where $\alpha \sim \frac{e}{\hbar c}$ is the fine structure constant). Many interesting new types of interaction energies are obtained. For example, in part II, we consider in detail the interaction of two ground state rare gas atoms separated by a large interatomic distance $R$. It is shown that the interaction energy has a term varying as $1/R^4$ which is of longer range than the usual London dispersion energy. The $1/R^4$ term, which is often small since it is of $O(\alpha^2)$, is due to the dispersion type coupling of the orbital-currents and the electrostatic-dipoles of the two atoms.
The existence of relativistic intermolecular energies has been known for a long time, but they do not seem to have been studied systematically before. Indeed, three of the orbital-magnetic interaction terms were recently obtained by Mavroyannis and Stephen (see Sec. 1.4). One of these energies, \( \Theta(\alpha^2/R^6) \), is non zero only for the interaction of optically active molecules and may be of biological significance.

The development presented here is based on the generalized Breit-Pauli approximation to the exact molecular relativistic Hamiltonian,

\[
\hat{H} = \hat{H}_e + \alpha^2 \hat{H}_{\text{rel}} \tag{1.2-2}
\]

where

\[
\hat{H}_{\text{rel}} = \hat{H}_{\text{LL}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{SL}} + \hat{H}_{\text{P}} + \hat{H}_{\text{D}} \tag{1.2-5}
\]

Here \( \hat{H}_e \) is the usual non-relativistic electronic Hamiltonian (we assume the Born-Oppenheimer approximation) and the term linear in \( \alpha^2 \) gives the effects of orbit-orbit, spin-spin, and spin-orbit coupling and other relativistic effects. If \( \psi \) and \( E_e \) are the electronic non-relativistic wave function and energy of the system then the relativistic correction to \( E_e \), correct through \( \Theta(\alpha^2) \), is

\[
\Delta E^{(1)} = \alpha^2 \langle \psi | \hat{H}_{\text{rel}} | \psi \rangle \tag{1.2-4}
\]

3. The equations given in the Introduction are numbered according to where they occur in the main text.
In Sec. 1.3 we discuss briefly some of the results of the usual non-relativistic treatment of long range molecular interaction energies. By long range we mean an intermolecular separation, $R$, sufficiently large that the charge distributions of the two molecules do not overlap and yet not large enough to involve retardation effects (see Sec. 1.3). For these values of $R$ the non-relativistic interaction energy of the molecules $a$ and $b$, $E_{ab}$, and the wave function, $\psi$, can be written in the form

$$E_{ab} = \sum_{s=1}^{\infty} \frac{C_s}{R^s} \quad (1.3-1)$$

$$\psi = \sum_{s=0}^{\infty} \frac{\psi_s}{R^s} \quad (1.3-2)$$

In Sec. 1.4 $H_{\text{rel}}$ is expanded in powers of $1/R$. Then using Eq. (1.2-2) and (1.2-4) we obtain

$$E^{(1)} = E^{(0)} + E^{(1)} = E^{(0)} + \sum_{s=1}^{\infty} \frac{\mathcal{W}_s}{R^s} \quad (1.4-5)$$

Here $E^{(0)}_o$ gives the relativistic energy of the isolated molecules $a$ and $b$ and $E^{(0)}_{ab}$ is the relativistic interaction energy (all accurate through $\Theta(\alpha^4)$). The interaction energy (including non-relativistic and relativistic effects) is then given by

$$E_{ab} = \sum_{s=1}^{\infty} \left( \frac{c_s + \alpha^2 \mathcal{W}_s}{R^s} / R^s \right) \quad (1.4-6)$$
In Appendix 1.A the general coefficient for the $1/R$-expansion of $H_{rel}$ is expressed as a sum of terms involving products of irreducible tensor operators of the molecules $a$ and $b$. In Appendix 1.B these coefficients are given explicitly through $O(1/R^3)$ both in irreducible tensorial form and in terms of Cartesian coordinates.

In this work we use the following notation: The two molecules $a$ and $b$ contain together $V$ nuclei and $\mathcal{M}$ electrons. In general we use Greek indices for nuclei and Roman indices for electrons. The operators for the spin and linear momentum of the $j$-th electron are denoted by $S_j$ and $\mathbf{p}_j = \hbar \mathbf{\nabla}_j$, respectively. All results are in atomic units; energy $\sim e^2/a_0$, length $\sim a_0$, where $a_0$ is the Bohr radius. Further, the vector going from electron $k$ to electron $j$, say, is $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$.

In particular for the computation of long range energies we denote the $n_a$ electrons in molecule $a$ by the subscripts $j$ and $k$; the $V_a$ nuclei in molecule $a$ by $\alpha$ and $\beta$; the $n_b$ electrons in $b$ by $\upsilon$ and $\tau$; the $V_b$ nuclei in $b$ by $\gamma$ and $\delta$.

The intermolecular separation, $R$, is defined as the distance between the "center" of molecule $a$ and the "center" of molecule $b$ (the precise location of these "centers" is arbitrary). For infinite $R$ the states of the isolated molecules $a$ and $b$ are characterized by the collection of quantum numbers $A$ and $B$ respectively. The geometry of the problem is given in Fig. 1.1-1 with the $z$-axis pointed from $a$ to $b$.

4. Note that $\alpha$ is also used to denote the fine structure constant. No confusion will result in the context in which this symbol is used here.
Fig. 1.1-1: Coordinate system used for the computation of molecular interaction energies. Point \( a \) is the origin of a right-hand coordinate system in molecule \( a \), and \( i \) is the location of a charge (nuclear or electronic) in this molecule. Point \( b \) is the origin of a right-hand coordinate system in molecule \( b \), and \( q \) is the location of a charge in this molecule.
1.2 The Breit-Pauli Approximation

In the usual calculation of molecular electronic energies (with nuclei held fixed) the Hamiltonian for the system is assumed to be

\[ \hat{H}_e = -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \sum_\beta \frac{Z_\beta}{r_{j\beta}} + \sum_\beta \sum_\beta' \frac{1}{r_{\beta\beta'}} + \sum_\beta \sum_\beta' \frac{Z_{\alpha\beta} Z_{\beta'}}{r_{\alpha\beta}} \] (1.2-1)

However, in addition to the non-relativistic Hamiltonian, \( \hat{H}_e \), the complete Hamiltonian contains additional terms which allow for relativistic effects (which include magnetic interactions). In order to treat these relativistic effects exactly one has to employ quantum electrodynamics. However, corrections to the non-relativistic energy, through \( O(\alpha^2) \), can be obtained by using the generalized Breit-Pauli approximation. The generalized Breit-Pauli Hamiltonian has the form

\[ \hat{H} = \hat{H}_e + \alpha^2 \hat{H}_{\text{rel}} \] (1.2-2)

If \( \psi \) and \( E_e \) are the electronic non-relativistic wave function


and energy for the system,

\[ H_e \psi = E_e \psi \]  \hspace{1cm} (1.2-3)

then the relativistic correction to \( E_e \), correct through \( \mathcal{O}(\alpha^2) \), is

\[ \mathcal{E}'' = \alpha^2 \langle \psi | H_{\text{rel}} | \psi \rangle \]  \hspace{1cm} (1.2-4)

For most practical purposes, this accuracy is sufficient. Our paper is specifically concerned with the determination of molecular interaction energies with accuracy through \( \mathcal{O}(\alpha^2) \).

The Breit-Pauli Hamiltonian, \( \mathcal{H}_B \), accurate through \( \mathcal{O}(\alpha^2) \), is derived for a two electron atom by Bethe and Salpeter. The

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7. If higher order perturbation theory is used one can obtain some, but not all, of the correction terms of order \( \alpha^2, \alpha^4, \ldots \). Of course, one cannot obtain corrections of odd order in \( \alpha \) with this approximation. Furthermore, the Breit-Pauli equation is not completely self-consistent and divergences are encountered if it is treated in higher order perturbation theory; see ref. 11, p. 179.


10. The starting point for this Hamiltonian is the Breit Hamiltonian: G. Breit, Phys. Rev. 34, 553 (1929); 36, 383 (1930); 39, 616 (1932).

generalization to a molecular system is given by Hirschfelder, Curtiss and Bird.\textsuperscript{6,12,13}

\[ H_{\text{rel}} = H_{\text{LL}} + H_{\text{SS}} + H_{\text{SL}} + H_\rho + H'_D, \]  
(1.2-5)

\[ H_{\text{LL}} = -\frac{1}{2} \sum_{R \neq J} \frac{1}{r_{RJ}^3} \left[ \frac{r_{RJ}^2}{r_{RJ}} \cdot p_j \cdot p_R + \frac{1}{r_{RJ}^3} \left( \sum_{j} \frac{r_{Rj}^2}{r_{Rj}} \cdot p_j \cdot p_R \right) \right] \]  
(1.2-6)

\[ H_{\text{SS}} = \sum_{R \neq J} \left\{ -\frac{8 \pi (S_{Rj} \cdot S_{Rk}) \delta(\xi_{Rj})}{3} + \frac{1}{r_{RJ}^3} \left[ S_{Rj}^2 \cdot S_R^2 - 3 (S_{Rj} \cdot S_{Rk}) (S_{Rj} \cdot S_{Rk}) \right] \right\} \]  
(1.2-7)

\[ H_{\text{SL}} = \frac{1}{2} \sum_{\rho \neq j} \frac{Z_{\rho j}}{r_{\rho j}^3} \left( \sum_{\rho} Z_{\rho j} \delta(\xi_{\rho j}) - \sum_{R \neq j} \delta(\xi_{Rj}) \right) - \frac{1}{2} \sum_{R \neq j} \frac{1}{r_{Rj}^3} \left[ \sum_{\rho} Z_{\rho j} \delta(\xi_{\rho j}) - 2 (\xi_{Rj} \cdot \xi_{\rho j}) \right] \]  
(1.2-8)

\[ H_\rho = -\frac{1}{8} \sum_{j} p_j^4 \]  
(1.2-9)

\[ H'_D = \sum_{j} \left[ \sum_{\rho} Z_{\rho j} \delta(\xi_{\rho j}) + \sum_{R \neq j} \delta(\xi_{Rj}) \right] + \frac{1}{4} \sum_{j} \left[ \sum_{\rho} Z_{\rho j} \frac{1}{r_{\rho j}^3} \left( \sum_{R \neq j} \frac{1}{r_{Rj}^3} \right) \right] \]  
(1.2-10)


13. The form of $H'_D$ is different from the corresponding equation of ref. 6. However, in the context of Eq. (1.2-4) these operators are equivalent, see ref. 11, p. 182.
In the generalized Breit-Pauli Hamiltonian we have omitted terms which take into account the effects of nuclear spin; they are of order $\alpha^2/M$, where $M$ is a nuclear mass. Also we have assumed that no external electric or magnetic fields are present. The additional terms arising from the effects of external fields are discussed in Appendix 1D.


created by their motion. It contains terms which couple the orbital magnetic moments of the electrons.

$H_{SS}$ gives the interaction between the spin magnetic moments of the electrons. The Fermi contact term, involving the delta function, gives the behaviour when $r_{jk} = 0$. The second term, corresponding to the usual (magnetic-dipole)-(magnetic-dipole) interaction, is only applicable when $r_{jk} \neq 0$. 9,11

$H_{SL}$ represents the spin-orbit magnetic coupling between electrons. The first term gives the interaction between the spin of an electron and the magnetic moment associated with its motion. The remainder of $H_{SL}$ gives the spin-other orbit coupling between the spin of one electron and the orbital magnetic moment of another.

$H_p$ is the relativistic correction due to the variation of mass with velocity.

$H'_b$ is a term characteristic of the Dirac theory, which has no simple interpretation. It is important to note that in the context of Eq. (1.2-4) $H'_b$ can be replaced by the more useful Hamiltonian $H_b^{18}$

$$H_b = \frac{\hbar}{2} \left[ \sum_{\beta} \sum_j Z_{\beta} \delta r_{\beta j} - 2 \sum_{k \neq j} \delta (r_{jk}) \right] , \quad (1.2-11)$$

provided that $\psi$ obeys the boundary conditions associated with stationary states.

18. This is easily shown using the method of ref. 11, p. 182-3.
Strictly speaking, the use of the generalized Breit-Pauli Hamiltonian is limited\(^{11}\) to systems having nuclei with \(Z \ll 137\). However, this does not seem to be a practical limitation for many problems of chemical interest since the valence electrons are shielded by the inner shell electrons and are not appreciably affected by the bare nuclear charge.

Bethe and Salpeter\(^{19}\) emphasize that: "The Breit equation gives the leading term for the relativistic corrections to the interaction between two electrons; if the Breit operator is treated by first order perturbation theory." This term is of order \(\alpha^2\). The Breit equation cannot, without modification, be used consistently to evaluate higher order corrections. This applies equally well to our use of the generalized Breit-Pauli Hamiltonian.

Bethe and Salpeter\(^{20}\) outline how the higher order terms can be calculated by quantum field theory using higher order perturbation theory for the electron's interaction with the virtual radiation field: "Transitions involving the emission and absorption of a single virtual photon by the same electron, plus renormalization terms, lead to the Lamb shift," which is of order \(\alpha^3\) \(\ln \alpha\). Terms of order \(\alpha^3\) can be obtained by fourth order perturbation theory which corresponds to the exchange of two photons. One of these terms "corresponds to the absorption of the first photon before the emission of the second one. Other terms of the same order of


magnitude also occur, for instance, a term representing the emission of two successive photons by one electron, followed by their absorption by the second electron."
1.3 Non-relativistic long range interaction energies

Let us discuss briefly some of the results of the usual non-relativistic treatment of the long range energy of interaction between two molecules a and b, in the quantum states A' and B', respectively. By long range, we mean an intermolecular separation, R, sufficiently large that the charge distributions of the two molecules do not overlap and yet not large enough to involve retardation effects. For these values of R the interaction energy, $E_{ab}$, and the wave function, $\Psi$, can be written in the form

$$E_{ab} = \sum_{s=1}^{\infty} \frac{C_s}{R^s}$$  \hspace{1cm} (1.3-1)

$$\Psi = \sum_{s=0}^{\infty} \frac{\Psi_s}{R^s}$$  \hspace{1cm} (1.3-2)


23. H. B. G. Casimir and D. Forder, Phys. Rev. 73, 360 (1948).

where the coefficients $C_s$ and $\psi_s$ are independent of $R$.

To calculate intermolecular energies it is not necessary to make expansions in inverse powers of the intermolecular separation; indeed, such expansions are not valid at short range. The $1/R$ expansion becomes meaningful when $R > (R_a + R_b)$. Here $R_a$ is the "radius" of molecule $a$, such that most of the charge distribution of $a$ lies within a sphere of radius $R_a$ about its center. Similarly $R_b$ is the "radius" of molecule $b$. The neglect of the small amount of charge not obeying the above requirements leads to terms in the interaction energy which decrease exponentially with increasing $R$ and are therefore negligible.

The advantage of the $1/R$ expansion is that the individual energy terms involve only the properties of the isolated molecules.

In this paper we neglect retardation effects and thus we assume $R < \lambda_0$, where $\lambda_0 = \hbar c |\delta E|^2$ is the wavelength corresponding to the transition with the largest dipole moment matrix element ($\delta E$ being the excitation energy). In atomic units, where $\lambda_0$ is in units of $a_0$ and $\delta E$ in units of $e^2/a_0$, we obtain

$$\lambda_0 = \frac{2\pi}{\alpha} |\delta E|^2 = 861 |\delta E|^2.$$ 

A typical value of $|\delta E|$ is 3/3 (corresponding to a H atom).

25. Strictly speaking, the interaction between particle $j$ on $a$ and particle $t$ on $b$ leads to $1/R^6$ type energy terms when integrated over those portions of configuration space for which $R > (r_{ij} + r_{kt})$, the coefficients of $1/R^6$ depending only "weakly" on $R$. The integration over those regions where $R < (r_{ij} + r_{kt})$ lead to terms which decrease exponentially with $R$. See J. S. Dahler and J. O. Hirschfelder, J. Chem. Phys. 25, 986 (1956).
2p $\rightarrow$ ls) is that $\lambda_0$ is generally of the order of 2300 a.u.

The effect of retardation begins $^{23,26}$ to become important at $R \sim \lambda_0/5$.

The non-relativistic Schrödinger equation for the bimolecular complex $a-b$ is

$$H_e \Psi = E_e \Psi$$  \hspace{1cm} (1.2-3)

where $H_e$ is given in Eq. (1.2-1). The non-relativistic Hamiltonian for the interaction of molecule $a$ with molecule $b$ can be written in the form

$$H_e = H_0(a) + H_0(b) + V_e$$  \hspace{1cm} (1.3-3)

where

$$H_0(a) = -\frac{1}{2} \sum_{j} \sum_{j'} \alpha_j \alpha_{j'} - \sum_{j} \sum_{\alpha} \frac{Z_{\alpha}}{r_{j\alpha}} + \sum_{\alpha} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} + \sum_{\alpha} \frac{1}{r_{\alpha\beta}}$$  \hspace{1cm} (1.3-4)

and $H_0(b)$ is defined similarly. Also,

$$V_e = -\sum_{\alpha} \sum_{\gamma} \frac{Z_{\alpha} Z_{\gamma}}{r_{\alpha\gamma}} - \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} + \sum_{\alpha} \sum_{\beta} \frac{1}{r_{\alpha\beta}}$$

$$+ \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \frac{Z_{\alpha} Z_{\beta} Z_{\gamma}}{r_{\alpha\beta\gamma}}$$  \hspace{1cm} (1.3-5)

Here $H_o(a)$ is the electronic Hamiltonian for the isolated molecule $a$, with eigenfunctions $\psi(A)$ and eigenvalues $\epsilon(A)$;

$$H_o(a)\psi(A) = \epsilon(A)\psi(A)$$  \hspace{1cm} (1.3-6)

Similar relations hold for the isolated molecule $b$. The intermolecular energy, $E_{ab}$, of the molecules in the states $A'$ and $B'$ is

$$E_{ab} = E_c - \epsilon(A') - \epsilon(B')$$  \hspace{1cm} (1.3-7)

Assuming $R > R_o + R_b$, the interaction potential $V_e$ can be expanded$^{27,28}$ in powers of $1/R$;

$$V_e = \sum_{m=1}^{\infty} \frac{V_m}{R^m}$$  \hspace{1cm} (1.3-8)

The expansion coefficients, $V_m$, represent the interaction of the various electrostatic multipoles of molecule $a$ with those of molecule $b$. For example, $V_1$ represents the charge-charge interaction, $V_2$ the charge-dipole interaction, $V_3$ the dipole-dipole interaction and charge-quadrupole interaction, etc. For the interaction of neutral molecules $V_1$ and $V_2$ are identically zero and the expansion for $V_e$ begins with the $1/R^3$ term.

The $V_m$ are discussed further in Appendix 1.A.

For a perturbation calculation of the long range interaction


energy of the molecules, the zero-th order problem corresponds to
infinite intermolecular separation, where $H_e$ becomes

$$H_o = H_o^{(a)} + H_o^{(b)} \quad (1.3-9)$$

The zero-th order Hamiltonian, $H_o$, has eigenfunctions $\Psi_{(A,B)}$ and eigenvalues $E_{(A,B)}$ given by

$$\Psi_{(A,B)} = \Psi_{(A)} \Psi_{(B)} \quad (1.3-10)$$

$$E_{(A,B)} = E_{(A)} + E_{(B)} \quad (1.3-11)$$

Hence our zero-th order wave function is $\Psi^{(0)} = \Psi_{(A')}(A') \Psi_{(B')} \Psi_{(B')}$ and the zero-th energy is $E^{(0)}_{e} = E_{(A')} + E_{(B')}$. Having chosen $H_o$, the perturbation on $H_o$ is given by the perturbation theory, we write

$$\Psi = \sum_{n=0}^{\infty} \Psi^{(n)} \quad (1.3-12)$$

and

$$E_{ab} = \sum_{n=1}^{\infty} E^{(n)}_{e} \quad (1.3-13)$$
Here $\psi^{(m)}$ is the $n$-th order perturbed wave function and $E_e^{(n)}$ is the $n$-th order perturbed energy. It should be emphasized that if either of the wave functions $\psi^{(A')}$ or $\psi^{(B')}$ is degenerate, then the zero order function $\psi^{(0)} = \psi^{(A')}\psi^{(B')}$ must be replaced by the proper linear combination of the degenerate zero-th order wave functions. 22

For long range interactions $\psi^{(m)}$ and $E_e^{(m)}$, for $m > 1$, can be written in the form

$$\psi^{(m)} = \sum_{m=n}^{\infty} \frac{\psi_m^{(n)}}{R^m}$$  \hspace{1cm} (1.3-14)

and

$$E_e^{(m)} = \sum_{m=n}^{\infty} \frac{D_m^{(n)}}{R^m}$$  \hspace{1cm} (1.3-15)

The coefficients $\psi_m^{(n)}$ and $D_m^{(n)}$ are independent of the intermolecular separation $R$. Substituting Eq. (1.3-15) into Eq. (1.3-13) and comparison with Eq. (1.3-1) yields the coefficients $C_s$ of $E_{ab} = \sum_s C_s / R^s$;

$$C_s = \sum_{m=s}^{\infty} D_m^{(s)}$$ \hspace{1cm} , $s \geq 1$  \hspace{1cm} (1.3-16)

For the interaction of two neutral non-degenerate molecules, for example, the expansion for $E_{ab}$ begins with the $1/R^6$ term; the usual induction and dispersion energies. 1,21 Similarly, Eqs. (1.3-2), (1.3-12) and (1.3-14) give the coefficients $\psi_s$ of $\psi = \sum_s \psi_s / R^s$;
We now derive explicitly the wave function, $\Psi$, through second order in $V_e$ and the energy, $E_e$, through third order in $V_e$, in terms of the expansion coefficients $V_m$.

The first order wave function $\Psi^{(1)}$ is the solution of the first order perturbation differential equation

$$(H_0 - E^{(0)}_e)\Psi^{(1)} + (V_e - E^{(1)}_e)\Psi^{(0)} = 0$$

(1.3-18)

with

$$\langle \Psi^{(0)} | \Psi^{(1)} \rangle = 0$$

(1.3-19)

For convenience all perturbed wave functions, $\Psi^{(m)}$, are taken to be real. The perturbation energies to third order in $V_e$ are given by.

29. The normalization of the $\Psi^{(m)}$ is the same as that used in refs. 22; namely, that the exact wave function $\Psi$ be normalized to unity through any given order in $V_e$. 
Let us now expand $\Psi^{(n)}$ in terms of the eigenfunctions of $H_0$.

\[ \Psi^{(n)} = \sum_{A,B} C(A,B) \Phi(A,B) \]  

(1.3-23)

Equation (1.2-19) yields $C(A',B') = 0$. The remaining $C$'s are determined from Eq. (1.3-18) and we obtain

\[ \Psi^{(n)} = \sum_{A,B} \langle A,B | V_e | A',B' \rangle \Phi(A) \Phi(B) \]  

(1.3-24)

The matrix elements in the numerator of Eq. (1.3-24) are defined by

\[ \langle A,B | V_e | A',B' \rangle = \int \psi_A^* \psi_B^* V_e \psi_{A'} \psi_{B'} d\tau_a d\tau_b \]  

(1.3-25)

30. Here the summation is understood to be over the continuum states as well as over the discrete states of the zero order problem.
The prime on the sum in Eq. (1.3-24) means that all terms with $A = A'$ and $B = B'$ are to be omitted. It should be emphasized that terms with $A = A'$ but with $B \neq B'$, for example, are to be included in the summation. Using the expansion for $\sqrt{e}$ given in Eq. (1.3-8),

$$
\psi^\prime = \sum_{m=1}^{\infty} \frac{\psi^{(m)}}{R^m}
$$

(1.3-26)

where

$$
\psi^{(m)} = \sum_{A,B} \langle A, B | V_m | A', B' \rangle \frac{\psi(A) \psi(B)}{(E^{(m)}_e - E(A, B))}
$$

(1.3-27)

Equations (1.3-20) - (1.3-22) may now be written in the form

$$
E^{(m)}_e = \sum_{m=1}^{\infty} \frac{D^{(m)}_m}{R^m}, \quad m = 1, 2, 3
$$

(1.3-28)

where

$$
D^{(1)}_m = \langle \psi^{(m)} | V_m | \psi^{(0)} \rangle
$$

(1.3-29)

$$
D^{(2)}_m = \sum_{s=1}^{m-1} \langle \psi^{(m)} | V_s | \psi^{(m-s)} \rangle
$$

(1.3-30)

$$
D^{(3)}_m = \sum_{s=1}^{m-1} \sum_{r=1}^{m-s-1} \left[ \langle \psi^{(m)} | V_s | \psi^{(m-r-s)} \rangle - D^{(1)}_r \langle \psi^{(r)} | V_s | \psi^{(m-r-s)} \rangle \right]
$$

(1.3-31)
Using the second order perturbation differential equation it is easy to show that

$$\psi^{(2)} = \sum_{m=2}^{\infty} \frac{\psi^{(1)}}{R^m} \quad (1.3-32)$$

where

$$\psi^{(m)} = \sum_{s=1}^{m-1} \left[ \frac{\sum' \sum \langle A^s B^s | V_{m-s} | A^s B' \rangle \langle A^s B | V_{m-s} | A^s B' \rangle \langle A^s B' | (E_{e} - E(A,B)) \rangle}{(E_{e} - E(A,B))^2} \right]$$

$$- D_s \sum' \sum' \langle A^s B^s | V_{m-s} | A^s B' \rangle \langle A^s B | V_{m-s} | A^s B' \rangle \langle A^s B' | (E_{e} - E(A,B)) \rangle$$

$$- \frac{1}{2} \sum' \sum' \langle A^s B^s | V_{m-s} | A^s B' \rangle \langle A^s B | V_{m-s} | A^s B' \rangle \langle A^s B' | (E_{e} - E(A,B)) \rangle \psi^{(n)}$$

$$\quad (1.3-33)$$

In specific problems the form of the results can often be simplified greatly by the use of group theory (see part II).
1.4. Relativistic Long Range Interaction Energies

In the Breit-Pauli approximation the relativistic Schrödinger equation for the bimolecular complex $a-b$ is given by

$$H\Psi = \left( H_e + x^2 H_{rel} \right) \Psi = E \Psi$$  \hspace{1cm} (1.4-1)

where $H_e$ and $H_{rel}$ are defined by Eqs. (1.2-1) and (1.2-5) respectively. We solve Eq. (1.4-1) for $E$, through order $\alpha^2$, using $H_e$ as the zero-th order Hamiltonian and $\alpha^2$ as the natural perturbation parameter. Thus

$$\Psi = \Psi^{(0)} + x^2 \Psi^{(1)} + \cdots, \quad E = E^{(0)} + \alpha^2 E^{(1)} + \cdots$$  \hspace{1cm} (1.4-2)

where

$$\Psi^{(0)} = \Psi, \quad E^{(0)} = E_e$$  \hspace{1cm} (1.4-3)

and

$$E^{(1)} = \langle \Psi | H_{rel} | \Psi \rangle$$  \hspace{1cm} (1.4-4)

The limitations of the use of the Breit-Pauli approximation correspond to the dots in Eq. (1.4-2) and are explained in Sec. 1.2. However, $E^{(1)}$ is given accurately by Eq. (1.4-4). When the molecules $a$ and $b$ are far apart, \(R > (R_a + R_b)\),
but not too far apart \( (R \ll \lambda_0) \), we can expand \( E^{(i)} \) in inverse powers of the intermolecular separation \( R \),

\[
E^{(i)} = E_0^{(i)} + E_a^{(i)} = E_0^{(i)} + \sum_{s=1}^{\infty} \frac{W_s}{R^s} \quad (1.4-5)
\]

Here \( E_0^{(i)} \) gives the relativistic energy of the isolated molecules \( a \) and \( b \), and \( E_a^{(i)} \) is the relativistic interaction energy. Thus the intermolecular energy (including both non-relativistic and relativistic terms) is given by

\[
E_{ab} = \sum_{s=1}^{\infty} \left[ C_s + \alpha_s W_s \right] / R^s \quad (1.4-6)
\]

Substituting Eq. (1.2-5) into Eq. (1.4-4) gives

\[
E^{(i)} = \sum_\sigma E_\sigma^{(i)} \quad ; \quad E_\sigma^{(i)} = \langle \Psi | H_\sigma | \Psi \rangle \quad (1.4-7)
\]

Here, as in Sec. 1, \( \sigma = LL, SS, SL, P, D \).

In order to obtain the relativistic long range interaction energy, the \( H_\sigma \) are expanded in powers of \( 1/R \), analogously to the expansion for \( V_e \);

\[
H_\sigma = H_\sigma^{(0)} + \sum_{m=1}^{\infty} \frac{H_\sigma^{(m)}}{R^m} \quad (1.4-8)
\]
Here

\[ H_{LL,1} = H_{SS,1} = H_{SS,2} = 0 \]

\[ H_{D,m} = 0, \quad m > 0 \]  \hspace{1cm} (1.4-9)

Note that \( H_{LL} \) and \( H_{SL} \) have non-vanishing terms of order \( 1/R \) and \( 1/R^2 \) respectively, which become the lead terms in the \( 1/R \) expansion of \( H \) for the interaction of neutral molecules. Also

\[ H_{\delta,0} = H_{\delta,0}^{(a)} + H_{\delta,0}^{(b)} \]  \hspace{1cm} (1.4-10)

where \( H_{\delta,0}^{(a)} \) is the Hamiltonian for the isolated molecule \( a \), corresponding to the relativistic correction \( \delta \). The expansion coefficients \( H_{\delta,m} \), for \( m > 0 \), represent the interaction of various orbital and spin magnetic multipoles of molecule \( a \) with those of molecule \( b \) and are derived in Appendix 1.A.

For example:

\( H_{LL,1} \) represents the \( \text{(orbital-current)-(orbital-current)} \) interaction; \( H_{LL,2} \) the \( \text{(orbital-current)-(orbital-dipole)} \) interaction; \( H_{LL,3} \) the \( \text{(orbital-dipole)-(orbital-dipole) \ and \ (orbital-current)-(orbital-quadrupole)} \) interaction.

\( H_{SS,3} \) gives the \( \text{(spin dipole)-(spin-dipole)} \) interaction.
$H_{SL,2}$ represents the (orbital-current)-(spin-dipole) interaction; $H_{SL,3}$ the (orbital-dipole)-(spin-dipole) and the (orbital-current)-(spin-quadrupole) interactions.

The $H_{\epsilon,m}$ are given explicitly, through $\mathcal{O}(1/R^2)$, in Appendix 1.B.

Let us now expand the $E^{(i)}$ in powers of $1/R$. Equations (1.3-2), (1.4-7) and (1.4-6) give

$$E^{(i)} = E^{(i)}_{\epsilon,0} + \sum_{s=1}^{\infty} \frac{W_{\epsilon,s}}{R^s}$$

(1.4-11)

where

$$E^{(ii)}_{\epsilon,0} = \langle \Psi^{(0)} | H_{\epsilon,0} | \Psi^{(0)} \rangle$$

(1.4-12)

and

$$W_{\epsilon,s} = \sum_{s=1}^{s-1} \sum_{m=0}^{s-1} \langle \Psi_{m} | H_{\epsilon,s} | \Psi_{s-\lambda-m} \rangle, \quad s > 0.$$  

(1.4-13)

Further, we note that certain terms in $W_{\epsilon,s}$ are identically zero, namely, those involving $H_{SL,1} = H_{SS,1} = H_{SS,2} = H_{p.p} \neq 0 = H_{\epsilon,1} \neq 0$. Here $E_{\epsilon,0}$ is the energy of the isolated molecules corresponding to the $\epsilon$-th relativistic correction.

Comparing Eq. (1.4-5) with Eqs. (1.4-7) and (1.4-11) gives $E^{(ii)}_{\epsilon}$ and the coefficients $W_{\epsilon}$ of $E^{(ii)}_{\epsilon} = \sum_{s} W_{\epsilon,s}/R^s$:

$$E^{(ii)}_{\epsilon} = \sum_{s} E^{(ii)}_{\epsilon,0}, \quad W_{\epsilon} = \sum_{s} W_{\epsilon,s}$$

(1.4-14)
Clearly the expression for the relativistic molecular interaction energy has a multitude of terms representing different types of interactions. The importance of the various terms depend on the charge and on the spin and orbital angular momentum states of the interacting molecules. In part II we consider in detail the interaction of two neutral non-degenerate atoms (l = 0, S = 0). The interaction energy, through order \( \alpha^2/R^6 \), has the form

\[
\mathcal{E}_{ab} = \frac{\alpha^2 W_4}{R^4} + \frac{C_6}{R^6} + \frac{\alpha^2 W_6}{R^6} + \ldots
\]  

(1.4-15)

Thus, even for this simple example, we have the interesting result that the interaction energy begins with a \( 1/R^4 \) term rather than the usual \( 1/R^6 \) van der Waals energy \( (C_6/R^6) \). The term \( W_4/R^4 \) corresponds to an (orbital-current)-(electrostatic-dipole) dispersion energy. Many other interesting types of energy terms occur for the interaction of charged and/or degenerate atoms and molecules.

The existence of long range relativistic interaction energies has been known for a long time, but they have not been studied systematically. Three of the orbital-magnetic interaction terms were obtained by Ma-royannis and Stephen. Using field theoretic techniques they obtained the interaction energies:

31. A long range magnetic interaction due to spin-spin coupling was discussed by Margenau, ref. 1; see also A. Dalgarno and R. McCarrol, Proc. Roy. Soc. A237, 383 (1956).

32. These authors also give the form of \( U_2, U_3, U_4 \) for large intermolecular separation \( (R \gg \lambda_0^2) \) where retardation becomes important.
Here, $\mu$ and $L$ are, respectively, the dipole moment and the orbital angular momentum operators for molecule $a$.

Equations (1.4-16)-(1.4-18) were obtained on the assumption that the molecules are rapidly rotating and have been averaged over all orientations. The energy $U_2$ is of particular interest because it is non-zero only for molecules without centers of inversion. It should be noted that $U_3$ and $U_4$ are of order $\alpha^2$ smaller than the interaction terms we derive in.
this work and that for the interaction of two non-degenerate atoms
\[ U_2 = U_3 = U_4 = 0. \] Further, terms of order \( \alpha^3 \) and \( \alpha^3 \ln \alpha \) (see Sec. 1.2) have yet to be derived.

Again we emphasize that the Breit-Pauli approximation cannot rigorously give terms of higher order than \( \alpha^2 \). However, it is clear that many interesting new interaction energies arise from our treatment. Indeed, these lower order (in \( \alpha \)) terms should dominate in problems of chemical interest.

In order to apply the theory of Secs. 1.3 and 1.4 we need the expansion coefficients for the 1/R-expansion of $H_{rel}$ and $V_e$ for $R > R_a + R_b$. To obtain these expansion coefficients it is desirable to use the algebra of irreducible spherical tensors. Excellent presentations of the required theory are given by M. E. Rose and A. R. Edmonds.

It is found that $H_{LL}$, $H_{SS}$ and $H_{SL}$ are expressible as a sum of terms representing the coupling of the magnetic multipole moments of the two molecules $a$ and $b$. All the relativistic Hamiltonians are expressed in irreducible tensorial form and thus the matrix elements of these Hamiltonians may be treated by the Wigner-Eckart theorem. The expansion coefficients for $V_e$ are well known and have been discussed by several authors (see Sec. 1.A-e).

Expansion Coefficients of $H_{rel}$

The relativistic Hamiltonians $H_\sigma$, for $\sigma = LL, SS, SL, p, D$ can be expanded in powers of 1/R;

33. The work in Appendix 1.A on the two center expansion of $H_{rel}$ together with the corresponding one center expansion, will be published in a paper by P. R. Fontana and W. J. Meath.


36. E. P. Wigner, Z. Phys. 43, 624 (1927); C. Eckart, Rev. Mod. Phys. 2, 305 (1930); see also refs. 34 and 35.

where

\( H_{s0} = H_{s0} + \sum_{m=1}^{\infty} \frac{H_{s0,m}}{R^m} \)  \hspace{2cm} (1.4-8)

and

\( H_{p,m} = H_{0,m} = 0 \), \hspace{1cm} m > 0 \), \hspace{2cm} (1.4-9)

\[ H_{s0} = H_{s0}^{(a)} + H_{s0}^{(b)} \]  \hspace{2cm} (1.4-10)

Here \( H_{s0}^{(a)} \) is the Hamiltonian for the isolated molecule \( a \), corresponding to the relativistic correction \( \sigma \). The coordinate system used in the problem is illustrated in Fig. 1.1-1.

The expansion coefficients of \( H_{LL} \) will be discussed in considerable detail. The derivation of the coefficients for the other Hamiltonians, being very similar to the derivation for \( H_{LL} \), will not be given in detail.

a. Expansion Coefficients of the Orbit-Orbit Hamiltonian, \( H_{LL} \)

The orbit-orbit Hamiltonian for the isolated molecule \( a \), say, is given by

\[ H_{LL,0}^{(a)} = \frac{1}{2} \sum_{k,j} \frac{1}{2} \left[ \frac{P_j P_k + P_k P_j}{R_{jk}} \left( \frac{P_j P_k}{R_{jk}} \right) \right] \]  \hspace{2cm} (1.4-11)
with an analogous equation for molecule b. For many purposes it is 
more convenient to write $H_{\text{LL, 0}}(a)$ as contractions of irreducible 
spherical tensors. We write

$$
\rho_j \cdot \rho_k = \sum_\omega (-1)^\omega \overline{T_\omega (\rho_j)} T_\omega (\rho_k) \tag{1.A-2}
$$

$$
\tau_{jk} \cdot \rho_j = \left( \frac{\mu_j \nu_j}{3} \right)^{1/2} \sum_\omega (-1)^\omega \overline{U_\omega (\tau_{jk})} T_\omega (\rho_j) \tag{1.A-3}
$$

where the solid spherical harmonic, $U_\omega (\xi)$, is defined by

$$
U_\omega (\xi) = r^\omega \overline{Y_\omega (\theta, \phi)} \tag{1.A-4}
$$

Here $\omega = 0, \pm 1$ and the spherical components, $T_\omega (\theta)$, of a vector 
$\mathbf{A}$ are defined in terms of the ordinary Cartesian components by

$$
T_\omega (\theta) = \frac{1}{(2\nu_\omega)^{1/2}} (A_x \mp i A_y) \tag{1.A-5}
$$

33. The phase convention we use for the spherical harmonics, $Y_\omega (\theta, \phi)$, is the same as that used, for example, by E. U. Condon and 
G. H. Shortley, "Theory of Atomic Spectra" (Cambridge University 
Press, London, 1935); refs. 34 and 35. Another commonly used 
phase convention is that of refs. 21 and 11, which differs 
from ours simply by a factor of $(-1)^m$.

39. The phase convention for the irreducible spherical tensors is 
defined by the phase convention for the $Y_\omega (\theta, \phi)$; see ref. 38.
Using Eq. (1.A-3) we write

$$\frac{1}{\mathcal{J}_k} (f_{j_k} \cdot \rho_j) \rho_k = \frac{4\pi}{3} \sum \sum (-1)^{\omega + \kappa} \chi_j^{\omega} \chi_j^{\kappa} \frac{T_j^1(p_j)}{T_k^1(p_k)}.$$  

(1.A-6)

The coupling rule for spherical harmonics gives

$$\sum \sum \chi_j^{\omega} \chi_j^{\kappa} \frac{3}{[4\pi(2l+1)]^{3/2}} C(11l; \omega \kappa) C(11l; 00) \nonumber$$

$$\times \chi_j^{\omega + \kappa} \chi_j^{\kappa} (\phi_j, \phi_j).$$  

(1.A-7)

In Eq. (1.A-7), $C(l_1, l_2, l_3; m_1, m_2)$, is a Clebsch-Gordon coefficient and $l = 0, 2$. It should be noted that

$$C(l_1, l_2, l_3; m_1, m_2, m_3, m_4) = 0$$  

(1.A-8)

unless

$$l_3 = l_1 + l_2, l_3 + l_2 - 1, \quad \left| l_1 - l_2 \right|$$  

(1.A-9)

40. In this work we use the phase convention for the Clebsch-Gordon coefficients given by the standard works of ref. 38. Closed expressions for these coefficients are available (see refs. 38) and they have been tabulated by Condon and Shortley. The 3-j symbols, which are closely related to the Clebsch-Gordon coefficients, have been tabulated in detail by M. Rotenberg, R. Bivins, N. Metropolis and J. K. Wooten, Jr., "The 3-j and 6-j Symbols" (The Technology Press, Cambridge, Massachusetts, 1950).
Equations (1.4-1), (1.4-2), (1.4-6) and (1.4-7) yield

\[
H_{LL,0}^{(a)} = \frac{-(\pi)^2}{3} \sum_{j, k} \frac{1}{r_j} \sum_{\omega, \kappa} (-1)^{\omega + \kappa} C(112j, \omega, \kappa)
\]

\[
\times Y_{2j}(U_{jk}, \phi_{jk}) T_{1}(\varphi_j) T_{1}(\varphi_k)
\]

(1.4-11)

where

\[
C(112j, \omega, \kappa) = \frac{1}{(\xi)^2} \left[ \frac{(2 + \omega + \kappa)(2 - \omega - \kappa)}{(1 + \omega)(1 - \omega)(1 + \kappa)(1 - \kappa)} \right]^{1/2}
\]

(1.4-12)

From the form of Eq. (1.4-11) it is clear that \(H_{LL,0}^{(a)}\) is an invariant, that is a tensor of zero rank. To show this explicitly one proceeds in the following manner. Let us construct the invariant

\[
T'_{1}(\varphi_j, \varphi_k) = \sum_{\omega} C(110j, \omega, -\omega) T_{1}(\varphi_j) T_{1}(\varphi_k)
\]

\[
= -\frac{1}{(3)^2} \sum_{\omega} (-1)^{\omega} T_{1}(\varphi_j) T_{1}(\varphi_k)
\]

(1.4-13)
and the second rank tensor

\[ T_{2}^{\kappa}(\rho_{j}\rho_{k}) = \sum_{\omega} C(112; -\omega, -\kappa + \omega) T_{1}(\rho_{j}) T_{1}(\rho_{k})^{\kappa + \omega} \]  

(1.\text{A}-14)

Substituting Eqs. (1.\text{A}-13) and (1.\text{A}-14) into Eq. (1.\text{A}-11) we obtain

\[ H_{\rho_{j}\rho_{k}}^{(\alpha)} = \sum_{\kappa} \frac{1}{s_{\kappa}} \left\{ \frac{2}{(3)^{\nu_{1}}} \sum_{\rho_{j}}^{c} (-1)^{\kappa} Y_{2}^{\kappa}(\hat{\omega}_{jk}, \phi_{jk}) T_{2}(\rho_{j}\rho_{k}) \right\} \]

(1.\text{A}-15)

Constructing the invariant

\[ \mathcal{W}_{0}^{\kappa}(\rho_{j}\rho_{k}\rho_{r}) = \sum_{\kappa} C(2, 0; \kappa, -\kappa) Y_{2}^{\kappa}(\hat{\omega}_{jk}) T_{2}(\rho_{j}\rho_{k})^{\kappa} \]

\[ = \frac{1}{(5)^{\nu_{1}}} \sum_{\kappa} (-1)^{\kappa} Y_{2}^{\kappa}(\hat{\omega}_{jk}) T_{2}(\rho_{j}\rho_{k})^{\kappa} \]  

(1.\text{A}-16)

we obtain

\[ H_{\rho_{j}\rho_{k}}^{(\alpha)} = \frac{2}{(3)^{\nu_{1}}} \sum_{\rho_{j}}^{c} \frac{1}{s_{\kappa}} \left\{ \frac{2}{(5)^{\nu_{1}}} \mathcal{W}_{0}^{\kappa}(\rho_{j}\rho_{k}\rho_{r}) - \left(\frac{2\pi}{3}\right)^{\nu_{1}} \mathcal{W}_{0}^{\kappa}(\rho_{j}\rho_{k}\rho_{r}) \right\} \]  

(1.\text{A}-17)

Equation (1.\text{A}-17) shows explicitly that $H_{\rho_{j}\rho_{k}}^{(\alpha)}$ is a scalar invariant.

From Eqs. (1.2-6), (1.4-8) and (1.4-10)

\[ \sum_{m}^{\infty} \frac{H_{\rho_{j}\rho_{k}}^{(\alpha)} m}{R_{m}^{4}} = \frac{1}{2} \sum_{\Lambda} \sum_{t} \frac{1}{\Lambda_{t}^{4}} \left[ \frac{R_{t}^{2}}{\Lambda_{t}^{2}} \rho_{t} + \frac{R_{t}}{\Lambda_{t}^{2}} (\Lambda_{t} \cdot \rho_{t}) \rho_{t} \right] \]  

(1.\text{A}-18)
Analogous to the derivation of Eq. (1.A-11), it is clear that

$$\sum_{m=1}^{\infty} \frac{H_{LL,m}}{R^m} = \sum_{k,t} \left\{ H_{LL}^{(1)}(k,t) + H_{LL}^{(2)}(k,t) \right\}$$

(1.A-19)

where

$$H_{LL}^{(1)}(k,t) = -\frac{2}{3} \sum_{R} \left( -i \right)^{\omega} T_{-}^{\omega}(p_{R}) T_{-}^{\omega}(p_{t})$$

(1.A-20)

$$H_{LL}^{(2)}(k,t) = \left( \frac{4\pi}{i^{ \omega}} \right) \sum_{R} \left( -i \right)^{\omega+\kappa} C^{(112, \omega, \kappa)}(R^{(\omega, \kappa)}) Y_{2}^{\omega+\kappa}(\omega_{R}, \phi_{R}) \times T_{-}^{\omega}(p_{R}) T_{-}^{\kappa}(p_{t})$$

(1.A-21)

Clearly

$$H_{LL,m} = \sum_{k,t} \left\{ H_{LL,1}^{(1)}(k,t) + H_{LL,1}^{(2)}(k,t) \right\}$$

(1.A-22)

To expand $H_{LL}^{(2)}(k,t)$ in powers of $1/R$ we must first expand

$$Y_{2}^{\omega+\kappa}(\omega_{R}, \phi_{R})$$

in spherical harmonics of $(\omega_{R}, \phi_{R})$ and

$(\omega_{t}, \phi_{t})$. This is easily done by generalizing the corresponding one center result of Rose and one obtains

$$Y_{\lambda}^{\mu}(\omega_{R}, \phi_{R}) = \sum_{k,t} \sum_{\lambda=0}^{\lambda} \sum_{\sigma=0}^{\sigma} A(\lambda, \mu, \sigma, \tau, \gamma, \omega, \phi, \omega_{R}, \phi_{R}) \times R^{\lambda-\sigma-\tau} Y_{\gamma}^{S}(\omega_{R}, \phi_{R}) Y_{\mu-\gamma}^{S}(\omega_{t}, \phi_{t})$$

(1.A-23)
where

\[ A(\lambda, \mu, \sigma, \tau; \delta; \xi, \eta) = (-1)^{\lambda-\sigma} \xi^\delta \eta^{-\tau} \]

\[
\chi \left[ \frac{4\pi (2\lambda+1)(\lambda+\mu)!(\lambda+1)!}{(2\tau+1)(2\tau+3)!(\lambda-\sigma-\tau)!} \right]^{1/2}
\]

(1.A-24)

Also needed is the two center expansion of \( \frac{1}{R_{12}} \) for \( m > 0 \).

Sack \[41\] has recently shown that \[42\]

\[
\frac{1}{R_{12}} \approx \sum_{l, l_2, l_3 = 0} \sum_{m = -l, s, s_2} \sum_{s, s_2} \left( \frac{G_{12}(l, l_2, m; s, s_2; \xi, \eta)}{R_{12} + \lambda_2 + 2s + 2s_2} \right) \times Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2)
\]

(1.A-25)

where

\[ G(l, l_2, l_3, m; s, s_2; \xi, \eta) = \frac{4\pi (-1)^{l_2} (-1)^{s_2} \gamma(l_2, l_3, m)}{K(l, l_2, l_3, m)} \times N(l, l_2, l_3; s, s_2; \xi, \eta) \]

(1.A-26)


42. This expression (for \( n=1 \)) agrees with the earlier work of refs. 27, 28 and 37.
\[ K(l_1, l_2, l_3, m) = \left[ \frac{\Gamma(l_1 + l_2 + l_3)}{\Gamma(l_1 + l_2 - l_3)!} \right] \left[ \frac{\Gamma(l_1 + l_3 - l_2)!}{\Gamma(l_1 + l_3)!} \right] \left[ \frac{\Gamma(l_2 + l_3 - l_1)!}{\Gamma(l_2 + l_3)!} \right] \\
\times \left[ \frac{(l_1 + l_2 + 1)(l_1 + l_3 + 1)(l_2 + l_3 + 1)}{(l_1 + l_2 + l_3 + 1)!} \right]^{\frac{1}{2}} \right] \\
\times C(l_1, l_2, l_3; m_1, m_2) \quad (1.3.27) \]

\[ N(s, l_1, l_2, l_3; j, a, b, c, d) = \frac{2^{l_1 + l_2 + l_3}}{\Gamma\left[ \frac{1}{2}(m + l_1 + l_2 + l_3) + s + 1 \right]} \left[ \frac{1}{\Gamma\left[ \frac{1}{2}(m + l_1 + l_2 + l_3 - 1) + s + 1 \right]} \Gamma_{l_1}^{l_2 + l_3} \right]^{\frac{1}{2}} \]

\[ \times \left[ \frac{1}{\Gamma\left[ \frac{1}{2}(m + l_1 + l_2 + l_3 - 1) + s + 1 \right]} \Gamma_{l_1}^{l_2 + l_3} \right]^{\frac{1}{2}} \] \\
\[ \quad (1.3.28) \]

Here \( \Gamma(x) \) is the Gamma function and \((2k)!! = 2 \cdot 4 \cdot \ldots \cdot 2k = 2^k k! \)

\((2k+1)!! = 1 \cdot 3 \cdot \ldots \cdot (2k+1) = 2^{k+1} k! \sqrt{2} / \Gamma(k+2) \), where \( k \) is an integer. For \( n=1 \) Eq. (1.3.23) simplifies greatly.

\[ \frac{1}{K_{l_2}} = \sum_{l_1, l_3} \sum_{l_1, l_2 = 0}^{l_2} \frac{C_1 \left( 1, l_1, l_2, l_3, m_1, m_2 \right)}{R^{l_1 + l_2 + l_3}} \left( \frac{1}{2} \right) \]

\[ \times \left( \frac{1}{2} \right)^{m_3} \left( \frac{1}{2} \right)^{m_4} \] \\
\[ \quad (1.3.29) \]
The results of Eqs. (1.A-23) and (1.A-25) now enable us to expand $\Omega_{\mu}^{(1)}(k,\tau)$ and $\Omega_{\mu}^{(2)}(k,\tau)$ in powers of $1/R$.

Using Eqs. (1.A-20) and (1.A-25)

$$I_{LL}^{(1)}(k,\tau) = \frac{2}{3} \sum_{\lambda_1, \lambda_2} \sum_{m, \omega} (-1)^{\omega} G(1, \lambda_1, \lambda_2, \lambda_2; m, o, o, (\lambda_1, \omega) / R,$$

$$\times Y_{\lambda_1}^{(1)}(\theta_k, \phi_k) Y_{\lambda_2}^{(1)}(\theta_k, \phi_k) \chi_{\lambda_1}^{(2)}(\phi_k) \chi_{\lambda_2}^{(2)}(\phi_k)) \right) / R.$$

Next define a tensor operator, $\Omega_{\mu}^{(1)}(l^1, \rho)$, of rank $u$;

$$\Omega_{\mu}^{(1)}(l^1, \rho) = \sum_{m} C(l1u; m, \nu-m) Y_{\nu}^{(m)}(\rho) \Gamma_{\nu}^{(m)}(\rho).$$

The inverse transformation to Eq. (1.A-32) is

$$Y_{\nu}^{(1)}(\rho) \Gamma_{\nu}^{(1)}(\rho) = \sum_{m} C(l1u; m, \nu-m) \Omega_{\mu}^{(1)}(l^1, \rho).$$
Thus

\[ H^{(n)}_{LL, m} = -\frac{\pi}{3} \sum \sum (-i)^{\omega} C(1, l_0, l_2, l_0 + l_2; m, j; 0, 0; r_k, r_t) \]
\[ \times C(0, l_j, l_0, m; \omega) C(1, j, q; m, -\omega) r_k^{-1} r_t^{-1} \]
\[ \times \Omega_{\omega}^{\omega, m} \Omega_{q}^{q, t} \]

\((1.A-34)\)

In general the summation is over the set of indices \(\ell \frac{3}{4}\), given by

\[ l_1, l_2 = 0, 1, \ldots, \infty; j, m, = -l_1, -l_1 + 1, \ldots, l_1, j; \omega = 0, \pm 1; \]
\[ \ell = l_1 + 1, l_1, \ldots, l_1 - 1; q = l_2 + 1, l_2, \ldots, l_2 - 1 \]

with

\[ l_1 + l_2 + 1 = m \]

\((1.A-35)\)

Equations (1.A-21), (1.A-23) and (1.A-25) give

\[ H^{(n)}_{LL} = -\left(\frac{\pi}{12}\right)^{1/2} \sum \sum \sum \sum \sum (-i)^{\omega + \kappa} \]
\[ \times G(1, l_0, l_2, l_0, j; m, s, g; 0, 0; r_k, r_t) A(2, \omega + \kappa; s, g, r_k, r_t) \]
\[ \times C(1, l_j, l_0, m; \omega) Y_{l_j}^{m, 0} Y_{l_0}^{q, 0} T_{(r_k)}^{-\omega} \]
\[ \times Y_{l_2}^{-m, \omega + \kappa - g} Y_{l_1}^{+l_1 + l_2 + 1, g, \kappa + \gamma} T_{(r_t)}^{-\kappa} / R \]

\((1.A-36)\)

43. Usually the summation will be restricted further by the conditions given by Eqs. (1.A-10).
Let us define

\[ D(m,\{x\}) = (-1)^{\omega + \kappa} G(m; l, m, s, \phi, \kappa, \alpha) A(2, \omega + \kappa, \alpha, \sigma, \tau, \phi; \phi, \kappa, \alpha) \]

\[ \times C_{\{l, m, \sigma, \tau, \phi; \omega, \kappa\}} \frac{(2l + 1)(2\sigma + 1)}{4\pi(2l + 1)} \times C_{\{l, \sigma, \tau, \phi; m, \omega - \kappa\}} \times C_{\{l, \sigma, \tau, \phi; 0, 0\}} \frac{(2l + 1)}{4\pi(2l + 1)} \times C_{\{l, \sigma, \tau, \phi; m, \omega + \kappa - \phi\}} \times C_{\{l, \sigma, \tau, \phi; 0, 0\}} \]

where \( \{x\} \) represents the set of summation indices on which \( D \)

depends. Then using the coupling rule for spherical harmonics and

Eq. (1.A-33) we obtain

\[ H_{LL, m}^{(2)} = \frac{(\frac{\mu}{15})^{\frac{1}{2}}}{\sum_{\{x\}, \mu, \nu} D(\{x\}, \mu, \nu)} \times C_{\{l, m, \omega + \kappa - m, \omega - \kappa\}} \Omega_{\omega + \phi + \kappa}^{m + \sigma - \omega - \kappa} \Omega_{\omega + \phi - \kappa}^{m - \sigma + \omega - \kappa} \]

In general the summation in Eq. (1.A-38) is over the set of

indices, \( \{x\} \), and \( \omega \) and \( \nu \).

\[ \{x\}: \ l_1, l_2, s, g = 0, 1, \ldots, \infty \]

\[ i = l_1 + l_2, l_1 + l_2 - 1, \ldots, l_2 - l_1 \]

\[ \text{l1+l2 even} \]

\[ m_1 = -l_1, l_1 + 1, \ldots, l_1, j \ ] \]

\[ \sigma = 0, 1, 2, j \ ] \]

\[ \tau = 0, 1, \ldots, (2 - \sigma) \]

\[ g = -\sigma - 1, \ldots, \sigma, j \ ] \]

\[ \phi, \kappa = 0, \pm 1 \]

\[ q = l_1 + \sigma, \phi, \phi + \sigma - 1, \ldots, l_2 - \sigma, j \]

\[ q_1 + l_1 + \sigma \text{ even} \]

\[ f = l_1 + \tau, l_1 + \tau - 1, \ldots, l_2 - \tau, j, \]

\[ f_1 = l_2 + \tau \text{ even} \]

(1.A-39)
with

\[ 1 + \frac{1}{2} + \frac{1}{2} + 2 \gamma + 2 \zeta + \xi = \eta \tag{1.A-40} \]

\[ u = q + 1, q, \ldots, q - 1 \quad \forall = f + 1, f, \ldots, f - 1 \tag{1.A-41} \]

Using Eqs. (1.A-22), (1.A-34) and (1.A-38) it is relatively easy to obtain the \( H_{ll,a} \), particularly for small \( m \). \( H_{ll,m} \) for \( m=1,2,3 \) is given explicitly in Appendix 1.4 even in irreducible tensorial form and in terms of Cartesian coordinates.

b. Expansion Coefficients of the Spin-Spin Hamiltonian, \( H_{ss} \)

The spin-spin Hamiltonian for the isolated molecule \( a \), say,

is given by

\[
H_{ss,0}^{(2)} = \sum_{R \neq J} \left\{ \frac{\hbar}{3} \langle \sigma_j^z \sigma_R^z \rangle \delta^{(3)}(\mathbf{r}_j - \mathbf{r}_R) + \frac{1}{3} \left[ \mathbf{r}_j^2 \cdot \mathbf{r}_R^2 - 3 \langle \mathbf{r}_j \cdot \mathbf{r}_R \rangle \langle \mathbf{r}_j \cdot \mathbf{r}_R \rangle \right] \right\}
\]

\[
(1.A-42)
\]

Analogous to the derivation of Eq. (1.A-11) it is easy to show that

\[
H_{ss,0}^{(2)} \sum_{R \neq J} \left[ \frac{-32 \pi \lambda}{3} \sum_{\omega_1} (-1)^{\omega_1} \mathbf{T}_j \langle \sigma_j \rangle \mathbf{T}_R \langle \sigma_R \rangle \right]
\]

\[
H_{ss,0}^{(2)} \sum_{R \neq J} \left[ \frac{-32 \pi \lambda}{3} \sum_{\omega_1} (-1)^{\omega_1} \mathbf{C}_{\omega_1}(\mathbf{r}_j, \mathbf{r}_R) \frac{\omega + \lambda}{\lambda} \mathbf{T}_j \langle \sigma_j \rangle \mathbf{T}_R \langle \sigma_R \rangle \right]
\]

\[
(1.A-43)
\]

To facilitate taking matrix elements of $H_{SS,0}^{(a)}$, it is often more convenient to write $H_{SS,0}^{(a)}$ in the form

$$H_{SS,0}^{(a)} = \sum_{\kappa \neq j} \left[ \frac{S T}{(3)^{1/2}} b(l_{jk}) T_0 (s_j s_k) - \left( \frac{2 \pi n}{5} \right)^{1/2} \sum_{\kappa} (-1)^K Y_2^{l_{jk}} (\theta_k, \phi_k) T_2 (s_j s_k) \right]$$

(1.A-44)

The tensors $T_0 (s_j s_k)$ and $T_2 (s_j s_k)$ are defined in Eqs. (1.A-13) and (1.A-12), respectively, and $b(l_{jk})$ is a scalar.

From Eqs. (1.2-7), (1.4-8) and (1.4-10)

$$\sum_{m=3}^{\infty} \frac{H_{SS,m}}{R_m^{\infty}} = \sum_{\kappa} \sum_{l=3}^{\infty} \frac{1}{\xi_{2l}} \left[ n_{\kappa 2l} (\bar{S}_l, \bar{S}_k) - 2 (\bar{S}_k, \bar{S}_l) (\bar{S}_l, \bar{V}_l) \right]$$

(1.A-45)

Expressed in irreducible tensorial form we obtain

$$\sum_{m=3}^{\infty} \frac{H_{SS,m}}{R_m^{\infty}} = \sum_{\kappa} \frac{H_{SS}(\kappa, t)}{R_{\kappa}^{\infty}} = \sum_{\kappa} \sum_{m=3}^{\infty} \frac{H_{SS,m}}{R_m^{\infty}}$$

(1.A-46)

where

$$H_{SS}(\kappa, t) = \left( \frac{2 \pi n}{5} \right)^{1/2} \sum_{\kappa} (-1)^K C(112, \omega, \kappa) Y_2^{l_{jk}} (\theta_k, \phi_k) T_1 (s_k) T_1 (s_l)$$

(1.A-47)

Following the same procedure that was used in the derivation of $H_{LL,a}$ we obtain

$$H_{SS,m} = \left( \frac{2 \pi n}{5} \right)^{1/2} \sum_{\xi_1^j} D(\xi_1^j, \chi_j) Y_2^{m_0, \xi_1^j} (\theta_k, \phi_k) T_1 (s_k)$$

$$\times Y_2^{m_0, \xi_2^j} (\theta_k, \phi_k) T_1 (s_k)$$

(1.A-48)
Here the summation is over the set of indices, \( \{ \mathbf{\lambda} \} \), given by Eq. (1.A-39) with

\[
M + l + J_x + 2s + 2g + 6 + \gamma = m
\]  

(1.A-49)

Equation (1.A-48) will often be useful as it stands since the spin and space variables of molecule \( a, \) say, are separated. Defining an irreducible tensor operator

\[
\sum_\mathbf{\mu} ^i \left( T^\mathbf{\mu} \right) _i
\]

of rank \( \mathbf{\mu} \) (see Eq. (1.A-32)) and proceeding as in the derivation of Eq. (1.A-38) we obtain

\[
H_{SS,m} = -\left( \frac{e^2}{\hbar} \right) \sum_\{\mathbf{\lambda},\mathbf{\mu},\mathbf{\nu}\} \mathbf{D}(\mathbf{\lambda},\mathbf{\mu},\mathbf{\nu}) r_{k}^{-}\frac{r_{k}^{-}}{2} C \left( r_{k}^{-},m,-g_{j}-\omega \right) x C \left( r_{j}^{+},m+y-m,-g_{j}-\omega \right) \sum_{\mathbf{\alpha}} \left( r_{\alpha}^{+}\right) \sum_{\mathbf{\nu}} \left( r_{\nu}^{+}\right) .
\]  

(1.A-50)

The restriction on the summation indices \( \mathbf{\lambda} \) and \( \mathbf{\nu} \) are given by Eq. (1.A-41). Using either Eq. (1.A-48) or Eq. (1.A-50) it is relatively easy to obtain the \( H_{SS,m} \), particularly for small \( m \).

\( H_{SS,3} \) is given explicitly in Appendix 1.B.

c. Expansion Coefficients of the Spin-Orbit Hamiltonian, \( H_{SL} \)

The spin-orbit Hamiltonian for the isolated molecule \( a, \) say,

\[
H_{SL}^{(a)} = \frac{1}{2} \sum_{\alpha} \sum_{j} Z_{\alpha} \left( r_{j}^{+} x^{P_{j}} \right) S_{j}
\]  

(1.A-51)
The irreducible tensor components of the vector \( \Sigma \times \rho \) are given by
\[
\Gamma_{i}^{\omega}(\Sigma \times \rho) = \left( \frac{\Omega \Omega}{2} \right) \frac{\theta}{2} \sum_{j} \Gamma_{i}^{\omega}(\Sigma \rho)
\]
(1.A-52)

where \( \Omega_{i}^{\omega}(\Sigma \rho) \) is defined by Eq. (1.A-52). Hence
\[
\begin{align*}
H_{\alpha}^{(1)} &= \frac{1}{2} \sum_{i} \sum_{j} \sum_{x} \sum_{y} \sum_{z} \sum_{w} (-1)^{i} \Gamma_{ij}^{\omega}(\Sigma_{j} \rho_{j}) \Gamma_{i}^{\omega}(\Sigma_{j}) \\
&= \frac{1}{2} \sum_{i} \sum_{j} (-1)^{i} \left[ \Gamma_{ij}^{\omega}(\Sigma_{j} \rho_{j}) - 2 \Gamma_{ij}^{\omega}(\Sigma_{j} \rho_{j}) \right] \Gamma_{i}^{\omega}(\Sigma_{j})
\end{align*}
\]
(1.A-53)

From Eqs. (1.A-52), (1.A-55), and (1.A-56) we obtain
\[
\sum_{n=2}^{\infty} \frac{H_{\alpha}^{(1)}}{R_{m}} = \sum_{i} \sum_{j} \sum_{k} \sum_{l} H_{i}^{(1)}(\alpha, k) + \sum_{i} \sum_{j} \sum_{l} H_{i}^{(1)}(\alpha, l) + \sum_{i} \sum_{j} \sum_{k} \sum_{l} \left[ H_{i}^{(1)}(\alpha, k) + H_{i}^{(1)}(\alpha, l) \right]
\]
(1.A-54)

where
\[
\begin{align*}
H_{i}^{(1)}(\alpha, k) &= \frac{Z_{v}}{2 \nu_{k}} \left( \Sigma_{k} \rho_{k} \right) \cdot \Sigma_{k} \\
H_{i}^{(1)}(\alpha, l) &= \frac{Z_{v}}{2 \nu_{l}} \left( \Sigma_{l} \rho_{l} \right) \cdot \Sigma_{l} \\
H_{i}^{(1)}(\alpha, k) &= \frac{1}{2 \nu_{k}} \left[ \left( \Sigma_{k} \rho_{k} \right) \cdot \Sigma_{k} - 2 \left( \Sigma_{k} \rho_{k} \right) \cdot \Sigma_{k} \right]
\end{align*}
\]
(1.A-55)

(1.A-56)

(1.A-57)

(1.A-58)
Analogous to the derivation of Eq. (1.47) it is clear that

$$H_{(i)}^{(')}(k, l, \xi) = \frac{2 \pi}{2 \pi k^2} \sum_{\omega} (-1)^{\omega} T_{\omega}(k, l, \xi) \tilde{H}(l, k, \omega) \tilde{H}(k, l, \omega).$$  

(1.59)

Let us define

$$\tilde{K}(k, l, \xi; \epsilon) = (-1)^{\omega} C(k, l, m, s; \frac{2 \pi}{\pi k^2}) A(k, l, m, s; \frac{2 \pi}{\pi k^2}) A(k, l, m, s; \frac{2 \pi}{\pi k^2})$$

$$\times C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2})$$

$$\times C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2})$$

(1.60)

where \{\epsilon\} is the set of summation indices on which \( K \) depends.

(see Eq. (1.53)). Then using Eqs. (1.42), (1.43), (1.45) and proceeding as in the derivation of \( H_{(i)}^{(')} \), it is easy to show that

$$H_{(i)}^{(')}(k, l, \xi) = \frac{2 \pi}{2 \pi k^2} \sum_{\omega} \tilde{H}(k, l, \xi; \epsilon) R_{\omega}^{(-g)}$$

$$\times \sum_{\omega} C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2})$$

$$\times C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2}) C(k, l, m, s; \frac{2 \pi}{\pi k^2})$$

(1.61)

Similarly one can readily show that
\[
H_{(x,t)}^{(2)} = - \frac{2}{c} \sum \tilde{K}(x,t,\{e\}) x \sum_{u=15..11}^{5+1} \frac{1}{c} \frac{2}{3} \sum_{\{e\}} \tilde{K}(x,t,\{e\}) \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \right. \\
\left. \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \right.
\]
\[
(1.A-62)
\]

\[
H_{(x,t)}^{(3)} = - \frac{1}{c} \frac{2}{3} \sum \tilde{K}(x,t,\{e\}) \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \\
\left. \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \right.
\]
\[
(1.A-63)
\]

\[
H_{(x,t)}^{(4)} = + \frac{1}{c} \frac{2}{3} \sum \tilde{K}(x,t,\{e\}) \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \\
\left. \left[ \frac{\partial}{\partial \xi} \sum_{u=15..11}^{5+1} C(q_{1u}, m-g, \omega - k) Y_{g}^{\omega} (\phi_k, \phi_e) \Omega_{u}^{\xi} (\epsilon_{e} \phi_e) T_{1}(S_{e}) \right] \right.
\]
\[
(1.A-64)
\]
The first summation in Eqs. (1.A-61)-(1.A-64) is over the set of indices, \( \{ \ell \}, \) given by\(^{43}\)

\[
\ell, \ell_2, s, g = 0, 1, \ldots, \infty; \quad \ell = \ell_1 + \ell_2, \quad \ell + \ell_2 - 1, \quad 1 - \ell + \ell_2 |,
\]

\( \ell + \ell_2 \) even \( \; m = -\ell, -\ell + 1, \ldots, \ell; \quad \sigma = 0, 1; \quad \tau = 0, 1; \quad (1-61); \)

\( q = -\delta - 6 + 1, \ldots, \delta; \quad \omega, \kappa = 0, \pm 1; \quad \delta = \ell_1 + \ell_2 + \ell_2 - 1, \ldots, 1 - \ell - \ell_2 |,
\]

\( \ell + \sigma + q \) even \( \; \delta = \ell_1 + \tau, \ell_2 + \tau - 1, \ldots, 1 - \ell - \ell_2 |, \ell_2 + \tau + q \) even,

(1.A-65)

with

\[ 2 + \ell_1 + \ell_2 + 2 s + q + \sigma + \tau = m \quad (1.A-66) \]

Using Eq. (1.A-58) and Eqs. (1.A-61)-(1.A-64) it is relatively easy to obtain the \( H_{SL,m} \); particularly for small \( m \).\(^{45,46}\) \( H_{SL,m} \), for \( m = 2, 3 \), is given explicitly in Appendix 1.B.

d. Expansion Coefficients of \( H_p \) and \( H_D \)

\[
H_{p,0}^{(a)} = H_{p}^{(a)} = - \frac{1}{8} \sum_{k=1}^{\ell} P_{k}^{(4)} \quad (1.A-67)
\]

45. The one-center expansion for \( H_{SL} \) has been derived recently by M. Blume and R. E. Watson, Proc. Roy. Soc. A270, 127 (1962).

46. In Eqs. (1.A-61)-(1.A-64) one could couple the spin and space tensors to form a new spin-space tensor. However, for most purposes it will be more convenient to use the results as they stand.
\[ H_{p,m} = 0 \quad , m > 0 \]  \hspace{1cm} (1.A-68)

\[ H_{D,0}^{(a)} = \frac{\mu}{2} \left\{ \sum_{k} \sum_{\lambda} Z_{k} |(\lambda_{k})|^{2} - 2 \sum_{k > j} \delta(\lambda_{k}) \right\} \]  \hspace{1cm} (1.A-69)

\[ H_{D,m} = 0 \quad , m > 0 \]  \hspace{1cm} (1.A-70)

\( H_{p}^{(a)} \) and \( H_{D,0}^{(a)} \) are of course scalars and analogous equations hold for molecule \( b \).

e. Expansion Coefficients of the Non-Relativistic Interaction

Potential \( V_{e} \)

The expansion coefficients for \( V_{e} \) are well known. \(^{27,28,37}\)

For convenience we write \( V_{e} \) in the form

\[ V_{e} = \sum_{l, q} \frac{e_{e} e_{q}}{r_{e q}} \]  \hspace{1cm} (1.A-71)

Here \( \frac{e_{e} e_{q}}{r_{e q}} \) is the Coulombic interaction between a particle (nuclei or electrons) of charge \( e_{l} \) in molecule \( a \) and another particle of charge \( e_{q} \) in molecule \( b \). Then for \( R > R_{a} + R_{b} \) we may write

\[ V_{e} = \sum_{m \geq 1} \frac{V_{m}}{R^{m}} \]  \hspace{1cm} (1.A-72)

where

\[ V_{m} = \sum_{l, q} e_{e} e_{q} \sum_{l_{k} \lambda_{l}} \sum_{m_{l}} G_{l_{k}, \lambda_{l}}(l_{k}, \lambda_{l}, l_{k} + l_{l}, j_{l} + j_{l}, \ldots, m_{l}; 0, 0; r_{e}, r_{q}) \times Y_{l_{k}, \lambda_{l}}^{(m_{l})} Y_{l_{l}, \lambda_{l}}^{(m_{l})} \]  \hspace{1cm} (1.A-73)
The significance of the expansion coefficients \( \psi_m \) is well known.\(^1\) They represent the interaction of the various electrostatic multipoles of molecule a with those of molecule b.

\[
\lambda, \nu \geq 0, 1, \ldots, \infty, \quad m = -\lambda, -\lambda + 1, \ldots, \lambda
\]

\[1 + \lambda + \nu = mn\]  

\[G(1; \lambda, \nu, \lambda, \mu, j, m, o, o, r, r)\] is given by Eq. \((1.A-30)\).
Appendix 1.B: Summary of the Expansion Coefficients of $H_{\text{rel}}$

The expansion coefficients of $H_{\text{rel}}$ are derived in general in Appendix 1.A. Here the $H_{\alpha,\beta}$ are given explicitly for $\delta = 1.13, 1.5$, and $\gamma = 0$ through $O(1/R^3)$, both in irreducible tensorial form and in terms of Cartesian coordinates. The coefficients $H_{\alpha,\beta}$ are given explicitly in Appendix 1.A.

Expansion Coefficients $H_{\text{rel}}$ in irreducible Tensorial Form

In order to simplify the results we adopt the following notations:

\[
S_{\ell}^{(m)} = \sum_{\kappa} \xi_{\ell}^{m} (\xi_{\kappa})^* ; \quad \Omega_{\ell}^{m} = \sum_{\kappa} \xi_{\ell}^{m} (\xi_{\kappa})^* ; \quad \Gamma_{\ell}^{m} = \sum_{\kappa} \xi_{\ell}^{m} (\xi_{\kappa})^* \]

\[
D_{\ell}^{m}(a) = (\xi_{\ell}^{m})^{1/2} \sum_{\kappa} \Omega_{\ell}^{m} \xi_{\kappa}^{m} \rho_{\kappa} = \sum_{\kappa} T_{\ell}^{m} (\xi_{\kappa} \rho_{\kappa}) \]

\[
L_{\ell}^{m}(a) = \sum_{\kappa} T_{\ell}^{m} (\xi_{\kappa} \rho_{\kappa}) = \sum_{\kappa} T_{\ell}^{m} (\xi_{\kappa} \rho_{\kappa}) = \frac{i}{2 \ell} D_{\ell}^{m}(a) \]

\[
\Omega_{\ell}^{m}(a) = \sum_{\kappa} \left\{ T_{\ell}^{m} (\xi_{\kappa}^{2} \rho_{\kappa}) + \left( \frac{\ell}{2} \right)^{1/2} \xi_{\kappa}^{2} \sum_{\kappa} \xi_{\ell}^{m} (\rho_{\kappa}) \right\} \]

\[
\gamma_{\ell}^{m}(a) = \sum_{\kappa} T_{\ell}^{m} (\xi_{\kappa}^{2} \rho_{\kappa}) \quad \gamma_{\ell}^{m}(a) = \sum_{\kappa} T_{\ell}^{m} (\xi_{\kappa}^{2} \rho_{\kappa}) \]

(1.5)
where
\[ T_{l}^{m}(r_{i}^{a} r_{j}^{b}) = \left( \frac{\hbar}{\sin \theta} \right)^{2} \sum_{\bar{\alpha}} \Omega_{l}^{m} \left( \bar{r}_{i}^{a} \bar{r}_{j}^{b} \right) \] (1.8-6)

\[ \left[ T_{l}^{m}(r_{i}^{a} r_{j}^{b}) T_{l'}^{m'}(r_{i}^{a} r_{j}^{b}) \right]_{\alpha} = \sum_{\bar{\alpha}} T_{l}^{m}(r_{i}^{a} r_{j}^{b}) T_{l'}^{m'}(r_{i}^{a} r_{j}^{b}) \] (1.8-7)

with analogous definitions for molecule \( b \). In Eq. (1.8-7) the tensor \( T_{l}^{m}(r_{i}^{a} r_{j}^{b}) \) is a function of the coordinates of electron \( i \).

The tensors \( \Omega_{l}^{m} \) are defined by Eq. (1.8-32) and the tensors \( T_{l}^{m} \) are given explicitly in Cartesian coordinate form in Appendix 1.C.

We also make use of a permutation operator \( P_{ab} \), which permutes all indices associated with molecule \( a \) with the corresponding indices of molecule \( b \):
\[ P_{ab} f(a, b) = f(b, a) \] (1.8-8)

**Expansion Coefficients of the Orbit-Orbit Hamiltonian, \( H_{LL} \):**

\[ H_{LL,1} = -\frac{1}{2} \left[ 1 + P_{ab} \right] \left[ \Omega_{i}^{o}(a) \Omega_{i}^{o}(b) - \Omega_{i}^{r}(a) \Omega_{i}^{r}(b) \right] \] (1.8-9)

\[ H_{LL,2} = +\frac{1}{2} \left[ 1 - P_{ab} \right] \left[ i \Omega_{i}^{o}(a) \Omega_{i}^{o}(b) - i \Omega_{i}^{r}(a) \Omega_{i}^{r}(b) - \frac{1}{2} \Omega^{o}(a) \Omega^{o}(b) \right] \] (1.8-10)

\[ H_{LL,3} = C_{LL,3} + \Xi_{LL,3} + C_{LL,3} \] (1.8-11)
where

\[ C_{LL,3} = -\frac{1}{4} \left[ 1 + \rho_{ab} \right] \left[ L^0_{(a)} L^0_{(b)} + L^0_{(a)} L^0_{(b)} \right] \quad (1.8-12) \]

\[ F_{LL,3} = \frac{3}{4} \left[ 1 + \rho_{ab} \right] \left[ \frac{1}{2} \left( D^0_{(a)} D^0_{(b)} - D^0_{(a)} D^1_{(b)} \right) \right] \quad (1.8-13) \]

\[ G_{LL,3} = \frac{1}{2(15)^{1/2}} \left[ 1 + \rho_{ab} \right] \left[ \begin{array}{c} \rho^0_{(a)} - 3(5)^{1/2} \rho^1_{(a)} - 3 \rho^2_{(a)} \ End{array} \right] \quad (1.8-14) \]

Expansion Coefficients of the Spin-Spin Hamiltonian, \( H_{SS} \)

\[ H_{SS,1} = 0 \quad H_{SS,2} = 0 \quad (1.8-15) \]

\[ H_{SS,3} = -\left[ 1 + \rho_{ab} \right] \left[ S^0_{(a)} S^0_{(b)} + S^1_{(a)} S^1_{(b)} \right] \quad (1.8-16) \]

Expansion Coefficients of the Spin-Orbit Hamiltonian, \( H_{SL} \)

\[ H_{SL,1} = 0 \quad (1.8-17) \]

\[ H_{SL,2} = \frac{1 - \rho_{ab}}{c} \left[ \begin{array}{c} \frac{1}{2} (\tilde{Z}_{(a)} - \tilde{m}_{(a)}) \tilde{T}_1 (\tilde{e}_c) \tilde{T}_1 (\tilde{e}_b) - \tilde{T}_1 (\tilde{e}_c) \tilde{T}_1 (\tilde{e}_b) \\ \right] \quad (1.8-18) \]

\[ + \tilde{Q}^0_{(a)} S^0_{(b)} - \tilde{Q}^1_{(a)} S^1_{(b)} \]
\[
\mathbf{H}_{s_{1,3}} = \mathbf{C}_{s_{1,3}} + \mathbf{F}_{s_{1,3}} + \mathbf{G}_{s_{1,3}}
\]

where

\[
\mathbf{C}_{s_{1,3}} = \frac{1}{2} \left[ 1 + \mathbf{P}_a \right] \mathbf{L}_{s_{1,3}}^2 \left[ \mathbf{S}_{s_{1,3}}^0 + \mathbf{S}_{s_{1,3}}^1 + \mathbf{S}_{s_{1,3}}^2 \right]
\]

\[
\mathbf{F}_{s_{1,3}} = \left[ 1 + \mathbf{P}_b \right] \left( \frac{(\mathbf{Z}_{s_{1,3}} - \mathbf{S}_{s_{1,3}}^0)}{2} \mathbf{L}^2 \mathbf{L}^3 \left[ \mathbf{T}_{s_{1,3}}^0 - \mathbf{T}_{s_{1,3}}^1 \right] \right)
\]

\[
\mathbf{G}_{s_{1,3}} = \frac{1}{2} \left[ 1 + \mathbf{P}_b \right] \left[ 2 \mathbf{\Omega}^a \mathbf{L}_{s_{1,3}}^2 \mathbf{L}_{s_{1,3}}^3 \left( \mathbf{T}_{s_{1,3}}^0 - \mathbf{T}_{s_{1,3}}^1 \right) \mathbf{T}_{s_{1,3}}^0 \right]
\]

\[
-\frac{1}{2} \left[ 1 + \mathbf{P}_b \right] \sum_x \mathbf{Z}_x \left[ \mathbf{T}_{s_{1,3}}^0 \mathbf{L}_{s_{1,3}}^2 \mathbf{L}_{s_{1,3}}^3 \left( \mathbf{T}_{s_{1,3}}^0 - \mathbf{T}_{s_{1,3}}^1 \right) \mathbf{T}_{s_{1,3}}^0 \right]
\]

\[
+2 \mathbf{\Omega}^a \mathbf{L}_{s_{1,3}}^2 \mathbf{L}_{s_{1,3}}^3 \left( \mathbf{T}_{s_{1,3}}^0 - \mathbf{T}_{s_{1,3}}^1 \right) \mathbf{T}_{s_{1,3}}^0 \right)
\]

\[
\]
The $H_{ij,m}$, $\sigma = \text{LL, SS, SI}$ and $m \neq 0$, represent the interaction of various orbital and spin magnetic multipoles of molecule a with those of molecule b. We have written the $H_{ij,3}$ in the form

$$H_{ij,3} = C_{ij,3} + F_{ij,3} + G_{ij,3}.$$  

Here $C_{ij,3}$ is the coefficient of the $1/R^3$ term that one would expect from the usual magnetic dipole-dipole interaction:

$$H_{ij}^{(\text{int})} = \frac{k^2}{R^3} \left[ M_i^{(a)} \cdot M_j^{(b)} \right] - \frac{3}{R} M_i^{(a)} R_i^{(a)} M_j^{(b)}.$$  

(1.8-24)

where $L^{(a)}$ and $S^{(a)}$ are, respectively, the electronic orbital and spin angular momentum operators for molecule a. Thus $F_{ij,3}$ and $G_{ij,3}$ may be regarded as correction terms to the semi-classical result of Eq. (1.3-21). It should be noted that $F_{ij,3} = G_{ij,3} = 0$.

b. Expansion Coefficients of $H_{ij,3}$ in Cartesian Coordinate Form

To simplify the results we use the following notation:

$$S^{(a)} = \sum_{R} m_{a}^{R} S_{R}^{(a)}; \quad Q^{(a)} = \sum_{R} m_{a}^{R} Q_{R}^{(a)}; \quad R^{(a)} = \sum_{R} m_{a}^{R} R_{R}^{(a)}$$  

(1.8-26)

$$L^{(a)} = \sum_{R} m_{a}^{R} L_{R}^{(a)} = \sum_{R} m_{a}^{R} R_{R}^{(a)} \times \frac{1}{R_{R}} \frac{C_{df}}{a} = \sum_{R} C_{R} \frac{d_{a}}{R_{R}}.$$  

(1.8-27)

with similar equations for molecule b. Using the results of Eqs. (1.8-9)-(1.8-23) and Appendix G we obtain the following results for the non-zero expansion coefficients through $O(1/R^3)$.

47. Magnetic multipole moments have recently been discussed by M. Mizushima, Phys. Rev. 134, A883 (1964).
\[ H_{L_{L_1}} = -\frac{i}{2} \left[ \tilde{Q}^{(a)} \cdot \tilde{Q}^{(b)} + \tilde{Q}_{\pm}^{(a)} \tilde{Q}_{\pm}^{(b)} \right] \]  
(1.B-28)

\[ H_{L_{L_2}} = \frac{i}{2} \left[ -i \tilde{p}_{ab} \left[ \tilde{L}_{a}^{(a)} \tilde{Q}^{(b)}_{\pm} - \tilde{L}_{a}^{(a)} \tilde{Q}^{(b)}_{\pm} + \tilde{r}_{a} \tilde{r}_{a} \tilde{p}_{ab} \tilde{L}_{a}^{(b)}} \right] \]  
(1.B-29)

\[ H_{L_{L_3}} = C_{L_{L_3}} + F_{L_{L_3}} + G_{L_{L_3}} \]  
(1.B-30)

where

\[ C_{L_{L_3}} = \frac{1}{4} \left[ \tilde{L}_{a}^{(a)} \tilde{L}_{a}^{(b)} - 3 \tilde{L}_{a}^{(a)} \tilde{L}_{a}^{(b)}} \right] \]  
(1.B-31)

\[ F_{L_{L_3}} = \left[ 1 + \tilde{p}_{ab} \right] \]  
(1.B-32)

\[ G_{L_{L_3}} = \left[ 1 + \tilde{p}_{ab} \right] \]  
(1.B-33)
$$H_{ss,3} = \mathcal{S}^{(a)} \mathcal{S}^{(b)} - 3 \mathcal{S}^{(a)} \mathcal{S}^{(b)}$$  \hspace{1cm} (1.B-33)$$

$$H_{s^2,2} = \left[1 - \mathcal{P}_{ab}\right] \left[\frac{1}{2} \left(Z_{a^\alpha} - \eta_{a}\right) \left[p_{a} s_{y} - p_{a} s_{x}\right]_{b} + \mathcal{Q}^{(a)}_{x} s_{y}^{(b)} - \mathcal{Q}^{(a)}_{y} s_{x}^{(b)}\right]$$  \hspace{1cm} (1.B-34)$$

$$H_{s_{1,3}} = C_{s_{1,3}} + F_{s_{1,3}} = G_{s_{1,3}}$$  \hspace{1cm} (1.B-35)$$

where

$$C_{s_{1,3}} = \frac{1}{2} \left[1 + \mathcal{P}_{ab}\right] \left[\mathcal{L}^{(a)} s_{x}^{(b)} - 3 \mathcal{L}^{(a)} s_{x}^{(b)}\right]$$  \hspace{1cm} (1.B-36)$$

$$F_{s_{1,3}} = \frac{1}{2} \left[1 + \mathcal{P}_{ab}\right] \left[\left(Z_{a^\alpha} - \eta_{a}\right) \left[p_{a} s_{y} - 3 z_{a} s_{x} + 3 z_{a} s_{x}\right]_{b} + 6 \left[z_{a} p_{a}\right] s_{y}^{(b)} - 6 \left[z_{a} p_{a}\right] s_{x}^{(b)} - 3 \mathcal{L}^{(a)} s_{y}^{(b)} + 3 \mathcal{L}^{(a)} s_{x}^{(b)}\right]$$  \hspace{1cm} (1.B-37)$$

$$G_{s_{1,3}} = \frac{1}{2} \left[1 + \mathcal{P}_{ab}\right] \left[\left(p_{a} s_{x} - p_{a} s_{x}\right)_{b} + \mathcal{Q}^{(a)}_{x} \left[p_{a} s_{y} - p_{a} s_{y}\right]_{b} - 2 \mathcal{Q}^{(a)}_{x} \left[p_{a} s_{x} - p_{a} s_{x}\right]_{b}\right]$$

$$- 2 \mathcal{Q}^{(a)}_{x} \left[p_{a} s_{y} + p_{a} s_{y}\right]_{b} + 2 \mathcal{Q}^{(a)}_{x} \left[p_{a} s_{x} + p_{a} s_{x}\right]_{b} - 2 \mathcal{Q}^{(a)}_{x} \left[p_{a} s_{y} - p_{a} s_{y}\right]_{b}\right]$$

$$- \frac{1}{2} \left[1 + \mathcal{P}_{ab}\right] \sum_{d} Z_{d} \left[X_{x} \left[p_{a} s_{y} - p_{a} s_{y}\right]_{b} + X_{x} \left[p_{a} s_{x} - p_{a} s_{x}\right]_{b}\right]$$

$$- 2 \mathcal{Z}_{x} \left[p_{a} s_{y} - p_{a} s_{y}\right]_{b}\right]$$  \hspace{1cm} (1.B-38)$$
Appendix I.C: Some Useful Irreducible Spherical Tensors.

In Appendix I.B the expansion coefficients of $H_{el}$ through $O(1/R^3)$ are given in irreducible tensor form. In this appendix we give the relevant spherical tensors explicitly in terms of Cartesian coordinates.

An irreducible spherical tensor $T_{l}^{m}$ of rank $l$ has $(2l+1)$ components, $T_{l}^{m}$, with $m = -l, -l+1,..., l$, which satisfy the commutator relations:

\[ [J_x \pm iJ_y, T_{l}^{m}] = i[(l\pm m)(l \mp m + 1)]^{1/2} T_{l}^{m \mp 1} \]  \hspace{1cm} (I.C.1)

\[ [J_z, T_{l}^{m}] = m T_{l}^{m} \]  \hspace{1cm} (I.C.2)

Here $\mathbf{J}$ is an angular momentum operator, $\mathbf{J} = \sum_{k=\pm 1}^{\pm l} i \mathbf{J}_k$, and we are primarily concerned with $\mathbf{J} = \mathbf{L}$ and $\mathbf{J} = \mathbf{S}$. For a tensor operator of rank one, $A$, the irreducible spherical components are given by Eq. (I.A-5).

Now let $T_{l_1}^{m_1}(R_1)$ and $T_{l_2}^{m_2}(R_2)$ be spherical tensors of rank $l_1$ and $l_2$ respectively. The symbols $R_1$ and $R_2$ represent the variables on which the tensors depend. Then a tensor of rank $l$ can be constructed from these two tensors according to the rule:

48. The tensors given are proportional to the tensors defined by Eq. (I.A-32); see Eqs. (I.B-1)-(I.B-6).

49. This definition of irreducible tensors is due to G. Racah, Phys. Rev. 61, 186 (1942); 62, 438 (1942); 63, 367 (1943). Irreducible tensors may also be defined by their transformation properties under rotations, see for example, refs. 34 and 35. The two definitions are equivalent.
Using Eq. (1.C-3) one can construct irreducible tensor operators of any desired rank. Equations (1.C-4) and (1.C-5) provide a convenient check on the tensors so obtained.

The irreducible tensors relevant to the results of Appendix I.B can be written down by comparison with the following tensors:

\[ T^0_{\ell} (AB) = -\frac{1}{(2\ell)!} A \cdot B \] (1.C-4)

\[ T^1_{\ell} (AB) = \frac{1}{2} (A_x B_x - A_y B_y + i A_z B_z - i A_y B_z + i A_y B_x + i A_x B_y) \] (1.C-5)

\[ T^2_{\ell} (AB) = \frac{1}{2} (A_x B_x - A_y B_y - i A_z B_z + i A_y B_z + i A_z B_y + i A_x B_x) \] (1.C-6)

\[ T^3_{\ell} (AB) = \frac{1}{(2\ell)!} (A_x B_x - A_y B_y + i A_z B_z + i A_y B_z + i A_z B_y + i A_x B_x) \] (1.C-7)

\[ T^4_{\ell} (AB) = \frac{1}{(2\ell)!} (A_x B_x + A_y B_y - i A_z B_z - i A_y B_z - i A_z B_y - i A_x B_x) \] (1.C-8)

\[ T^5_{\ell} (AB) = \frac{1}{(2\ell)!} (A_x B_x + A_y B_y + i A_z B_z + i A_y B_z + i A_z B_y + i A_x B_x) \] (1.C-9)

\[ T^6_{\ell} (AB) = \frac{1}{(2\ell)!} (A_x B_x + 3 A_y B_y + 3 A_z B_z) \] (1.C-10)

50. Here \( T^\ell_{\ell} (AB) \) is the irreducible spherical tensor of rank \( \ell \) formed by coupling the components of the first rank tensors \( T^\ell_1 (A), T^\ell_1 (B) \). The tensors \( T^\ell_{\ell} (AB) \) were taken from ref. 8 (see also L. F. Curtiss, J. Chem. Phys. 24, 225 1956) and were checked by Eq. (1.C-3). The other tensors were constructed by using Eq. (1.C-3) and checked with Eqs. (1.C-1) and (1.C-2).
\[ T_2^{(A'B')} = \frac{1}{2} \left( A_x B_x + A_y B_y - A_z B_z \right) \] 
\[ T_2^{(A'B')} = \frac{1}{2} \left( A, x B, y - A, x B, y - A, y B, x \right) \] 

\[ T_3^{(A'B')} = -\frac{3}{15} \left( \frac{1}{2} A^t B^t - A^t B^t - A^t A^t B^t - A^t A^t B^t \right) \] 

\[ T_1^{(A'B')} = \frac{3}{30} \left[ -\frac{1}{2} A^t B^t - A^t B^t - A^t A^t B^t - A^t A^t B^t \right] \] 

\[ T_2^{(A'B')} = \frac{1}{6} \left[ \frac{1}{2} A^t B^t - A^t B^t + A^t A^t B^t - A^t A^t B^t \right] \] 

\[ T_3^{(A'B')} = \frac{1}{6} \left[ \frac{2}{3} A^t B^t + \frac{1}{2} A^t B^t - 2 A^t B^t + A^t A^t B^t - 4 A^t A^t B^t \right] \]
\[ T^\circ_j(A^i B_i) = -\frac{i}{(10)^2} \left[ A^x B^y + 3 A^x A^2 B_x + 2 A^x A^2 B_x + 2 A^x A^2 B_y \right] \]  
(1.6-19)  

\[ T^{-1}_j(A^i B_i) = -\frac{i}{(30)^2} \left[ \frac{3}{2} A^x A^y B_x + \frac{1}{2} A^x A^y B_x + 2 A^x B^x + A^x A^y B_y - 4 A^x A^y B_y \right] \]  
(1.6-20)
Appendix 1.D: The Breit-Fauli Hamiltonian with External Fields

If the molecule under consideration is acted upon by external fields the results of Sec. 1.2 must be modified in the following manner. Let \( \Phi_j^{(e)} \) be the external electrostatic potential, \( E_j^{(e)} \) the external electric field strength, \( B_j^{(e)} \) the external magnetic field strength, and \( \mathcal{A}_j^{(e)} \) the external vector potential — all at the position of electron \( j \). Then the non-relativistic Hamiltonian, \( \tilde{H}_e \), of Sec. 1.2 is to be replaced by:

\[
\tilde{H}_e = \tilde{H}_e - \sum_j \Phi_j^{(e)} \tag{1.D.1}
\]

Furthermore, the following terms should be added to \( H_{\text{rel}} \):

\[
H_1 = -\frac{1}{2} \sum_j \left( \frac{E_j^{(e)} \rho_j}{E_j^{(e)} + \rho_j} \right)^2 + \frac{1}{2} \sum_j \rho_j \left( \frac{E_j^{(e)}}{E_j^{(e)} + \rho_j} \right)^2 \tag{1.D.2}
\]

\[
H_2 = \sum_j \frac{B_j^{(e)}}{\rho_j} \cdot \mathcal{A}_j^{(e)} + \sum_j \frac{B_j^{(e)}}{\rho_j} \cdot \mathcal{A}_j^{(e)} \tag{1.D.3}
\]

The Hamiltonian \( H_1 \) gives the effect of external electric fields while \( H_2 \) gives the interaction with an external magnetic field.

As was mentioned in Sec. 1.2, the Breit-Fauli Hamiltonian is to be used in the context of an expectation value with respect to the exact non-relativistic wavefunction, which is now the eigenfunction of \( \tilde{H}_e \) of Eq. (1.D.1).

Equations (1.D.2) and (1.D.3) are straightforward generalizations of the corresponding terms in ref. 11, p. 181, and have been discussed by Hirschfelder, Curtiss, and Bird. We give them here for completeness and clarity.
RELATIVISTIC INTERMOLECULAR FORCES; THE LONG RANGE INTERACTION OF NEUTRAL, NON-DEGENERATE ATOMS (NEGLECTING RETARDATION)

2.1 Introduction

The long range interaction between two neutral non-degenerate atoms is considered (neglecting retardation), as an example of the general theory of relativistic intermolecular forces discussed in part I. The interaction energy, through $O(\alpha^2/R^6)$, has the form

$$E_{a-b} = E_{ab} + \alpha^2 \epsilon^{(ii)}_{a-b} = \alpha^2 \frac{W_4}{R^4} + \frac{C_6}{R^6} + \alpha^2 \frac{W_6}{R^6} + \ldots \quad (2.1-1)$$

Here $E_{ab}$ is the usual non-relativistic interaction energy, which through $O(1/R^6)$, is equal to the well known London dispersion energy, $C_6/R^6$. The (orbital-current)-(electrostatic-dipole) dispersion energy, $\alpha^2 W_4/R^4$, is of $O(\alpha^2)$ smaller than the London energy. Nevertheless, since this relativistic dispersion energy is of longer range than the van der Waals energy, it may be significant in low energy atomic and molecular beam scattering problems. The energy $\alpha^2 W_6/R^6$ contains several new types of interaction energies. However, this relativistic dispersion energy will probably be of little importance in most problems since it has the same $1/R$ dependence, but is of $O(\alpha^2)$ smaller, than the London dispersion energy.
The results of the usual treatment of long range atomic interaction energies are discussed briefly in Sec. 2.2 in order to have them available for comparison with the new relativistic energies which are derived in Sec. 2.3. Order of magnitude estimates for all the interaction energies occurring in Eq. (2.1-1) for the interaction of various rare gas atoms, are calculated in Sec. 2.4.

In the expressions for long range molecular interaction energies one must deal with rather complicated expressions involving integrals of the type:

\[ \langle A', B'|T|A, B \rangle = \int \psi^*(A') \psi^*(B') \mathcal{T} \psi(A) \psi(B) \, d\mathbf{r}_A \, d\mathbf{r}_B \]  

(2.1-2)

Here \( \psi(A) \) is a non-relativistic eigenfunction of the isolated molecule \( a \), say, characterized by a set of quantum numbers \( A \), and \( \mathcal{T} \) is a perturbation Hamiltonian. Fortunately, for long range problems (where the charge distributions of the interacting molecules \( a \) and \( b \) do not overlap) all the \( \mathcal{T} \) can be written as a sum of products of irreducible spherical tensor operators of the molecules \( a \) and \( b \) (see Appendices 1.A, B, C), symbolically;

\[ \mathcal{T} = \sum \mathcal{T}_{\ell_1, m_1}^{\ell_2, m_2} \mathcal{H}^{\ell_1}_{\ell_2} (a) \mathcal{H}^{\ell_2}_{m_2} (b) \]  

(2.1-3)

Thus the matrix element of Eq. (2.1-2) factorizes into a sum over products of integrals involving the isolated molecules \( a \) and \( b \).
For the interaction of two atoms a and b (i.e. the problem at hand) the non-relativistic eigenfunctions \( \psi(a) \) and \( \psi(b) \) represent states of sharp angular momentum (both spin and orbital). Thus one may use the Wigner-Eckart theorem to simplify matrix elements of the type \( \langle A',B' | T | A,B \rangle \) and hence the usually complicated general results of part 1. Since it is necessary to use the Wigner-Eckart theorem repeatedly in obtaining the results of Secs. 2.2 and 2.3 we discuss the relevant details of the theorem in Appendix 2.A.

**Notation:** The basic notation is the same as that introduced in Sec. 1.1. The following modifications are convenient. The nuclei of atom a and atom b have nuclear charges \( Z_a \) and \( Z_b \), respectively. The interatomic separation, \( R \), is defined as the distance between the two nuclei, a and b. The geometry of the problem is given in Fig. 1.1. Again all results are in atomic units; energy \( \sim e^2/a_o \), length \( \sim a_o \).

Let \( L(a) \) and \( S(a) \) be the electronic spin and orbital angular momentum operators for the atom a. Then the set of quantum numbers \( A \), characterizing the states of the atom a, is

1. For the interaction of two atoms, point a in Fig. 1.1 is the nucleus of atom a and similarly for point b.
given by

\[ A = l_a, l, m_a, m_s, s_a \]  \hspace{1cm} (2.1-5)

where

\[ L_z^{(A)} \psi(A) = L_z l (l_z + 1) \psi(A) \] \hspace{1cm} \[ L_z^{(a)} \psi(a) = M_a \psi(A) \]

\[ S_z^{(a)} \psi(a) = S_z (s_a + 1) \psi(a) \] \hspace{1cm} \[ S_z^{(a)} \psi(a) = s_a \psi(A) \]  \hspace{1cm} (2.1-6)

Here \( k_a \) denotes the remaining quantum numbers required for the specification of the states of the atom. The set of quantum numbers, \( S \), is defined in an analogous manner. The non-degenerate ground state of atom \( a \), say, is denoted by \( A' = 1, 0, 0, 0 \equiv 0 \). For convenience we define the following energy difference corresponding to the transition \( A' \rightarrow A \):

\[ \Delta E(A) = \Delta E_a(l, l, s) = E(A') - E(l_a, l, s_a) \]  \hspace{1cm} (2.1-7)

and it should be noted that the non-relativistic energy \( E(A) \) is independent of the quantum numbers \( M_a \) and \( s_a \).
2.2 Non-relativistic Long Range Interaction Energy between two Neutral Non-degenerate Atoms

An expression is derived for the usual long range interaction energy $E_{ab}$, between two neutral non-degenerate atoms, which is accurate through $0(1/R^8)$ (see Sec. 1.3 for the general treatment). The results, which are well and $E_{1.3}$ are given here to have them available for comparison with the relativistic interaction energies to be derived in Sec. 2.3.

The interaction potential, $V_e$, is expanded in powers of $1/R$ in Appendix 1-A-e. For the interaction of two neutral atoms the expansion for $V_e$ simplifies considerably, with the result

$$V_e = \sum_{m=3}^{\infty} \frac{V_m}{R^m}$$

$$(2.2-1)$$

$$V_m = \sum_{k} \sum_{t} \sum_{l_1=1}^{l} \sum_{m_1=3}^{l_1} G(1; l_1, m_1, \ldots, l_1, m_1, 0, 0; \phi_k, \phi_t)$$

$$\times Y_{l_1}^{m_1}(\phi_k) Y_{m_1-l_1-1}^{m_1}(\phi_k)$$

$$(2.2-2)$$

where $l_0$ is the lesser of $l_1$ and $m - l_1 - 1$ and the coefficient $G$ is given by Eq. (1.A-30).


For the interaction of two neutral non-degenerate atoms the first order contribution to the interaction energy is zero since the electrostatic perturbation, $V_e$, does not connect $S$ states;

$$E_e^{(1)} = \sum_{n=1}^{\infty} \frac{\langle A', B' | V_m | A, B \rangle}{R^{m}} = 0 \quad (2.2-3)$$

Thus, since $V_1 = V_2 = 0$, the formalism of Sec. 1.3 gives the following result for the non-relativistic interaction energy through $O(1/R^6)$.

$$E_{ab} = \frac{C_6}{R^6} + \frac{C_8}{R^8} + \cdots \quad (2.2-4)$$

The lead term in the $1/R$ expansion of the interaction energy is the usual London dispersion energy. The coefficient, $C_6$, is given by

$$C_6 = \langle \psi^{(0)} | V_3 | \psi^{(0)} \rangle \quad (2.2-5)$$

where in general

$$\langle \psi^{(0)} | V_m | \psi^{(0)} \rangle = \sum_{A, B} \frac{\langle A', B' | V_m | A, B \rangle \langle A, B | V_L | A', B' \rangle}{(\Delta E(A) + \Delta E(B))} \quad (2.2-6)$$

4. The coefficient $C_6$ is easily shown to be identically zero by symmetry considerations.

The coefficient \( V_3 \) of the \( 1/R^3 \) term in the expansion of \( v_e \) is

\[
V_3 = \left[ \mathbf{r}(a) \cdot \mathbf{r}(b) - 3 \mathbf{r}(a) \cdot \mathbf{r}(b) \right]
\]

\[
= -\left[ r_1^{0}(a) r_1^{0}(b) + r_1^{0}(a) r_1^{0}(b) + 2 r_1^{0}(a) r_1^{0}(b) \right]
\]  \hspace{1cm} (2.2-7)

Here, \( \mathbf{r}(a) \) is the electronic dipole moment operator of atom \( a \) and the irreducible tensorial components, \( r_1^m(a) \), are defined in the usual manner (see Eq. (1.4-5)). From symmetry considerations, the expression for \( C_6 \) may be written in the form \(^6\)

\[
C_6 = 6 \sum_{k_a} \sum_{k_b} \left| \langle 0 | r_1^{0} | k_a, l_a, 0 \rangle \right|^2 \left| \langle 0 | r_1^{0} | k_b, l_b, 0 \rangle \right|^2 \frac{(\Delta E_{e}(k_{a}) + \Delta E_{e}(k_{b}))}{(\Delta E_{e}(k_{a}) + \Delta E_{e}(k_{b}))}
\]  \hspace{1cm} (2.2-8)

where

\[
\left< k', l', M' | r_1^{0} | k, l, M \right> = \left< k_{a}', l_{a}', M_{a}' | r_1^{0} | k_{a}, l_{a}, M_{a} \right> .
\]  \hspace{1cm} (2.2-9)

Let us define the mean oscillator strength \( f(k, l) \) for the transition \( (k = 1, L = 0) \rightarrow (k, L = 1) \):

\[
f(k, l) = -\frac{2}{3} \Delta E_{e}(k_{a}) \sum_{M=-1}^{1} \left| \left< 0 | r_1^{0} | k_{a}, l_{a}, M \right> \right|^2
\]

\[
= -2 \Delta E_{e}(k_{a}) \left| \left< 0 | r_1^{0} | k_{a}, l_{a}, 0 \right> \right|^2
\]  \hspace{1cm} (2.2-10)

6. In all expressions involving matrix elements of spin free or scalar spin operators, the spin quantum numbers \( S = 0 \) and \( \sigma = 0 \) are suppressed.
Equations (2.2-8) and (2.2-10) give:

\[
C_6 = \frac{3}{2} \sum_{K_a} \sum_{K_b} \frac{f_K^{(a)} f_K^{(b)}}{(\Delta E_a(K_a) + \Delta E_b(K_b)) \Delta E_a(K_a) \Delta E_b(K_b)}
\]

(2.2-11)

From Eq. (2.2-8) it follows that \( C_6 \) has the same sign as 
\((\Delta E_a(K_a) + \Delta E_b(K_b))\). Hence for the interaction of two 
ground state atoms \( C_6 \) is negative, and the long-range dispersion energy is 
attractive.

\[
C_8 \text{ The energy } C_8 \text{ is the usual dipole-quadrupole dispersion energy.}^{2,3} \text{ The coefficient } C_8 \text{ is given by}
\]

\[
C_8 = \langle \psi^{(o)}| V_4 | \psi^{(i)} \rangle + \langle \psi^{(o)}| V_3 | \psi^{(i)} \rangle + \langle \psi^{(o)}| V_2 | \psi^{(i)} \rangle
\]

(2.2-12)

The last two terms in Eq. (2.2-12) vanish because of symmetry considerations. The coefficient \( V_4 \) in the 1/\( R \)-expansion of \( V_e \) is given by

\[
V_4 = \frac{3}{(2)^{1/2}} \left\{ \frac{1}{2} - P_{ab} \right\} \left\{ Q_{2a}^{(a)} Q_{2b}^{(b)} + Q_{2a}^{(a)} Q_{2b}^{(b)} + (3)^{1/2} r_{ab} \langle Q_{2a}^{(a)} Q_{2b}^{(b)} \rangle \right\}
\]

(2.2-13)

where

\[
Q_{2a}^{(a)} = \sum \tilde{T}_{e2} \tilde{T}_{e2}^* \text{; } P_{ab} g(a,b) = g(b,a)
\]

(2.2-14)
and the second rank tensor, \( T_2^{m}(\alpha \beta) \), is defined by Eqs. (1.C.8)-(1.C.12). The tensor \( Q_2^m(b) \) is proportional to the m-th component of the electrostatic quadrapole moment operator of atom b. Using the Wigner-Eckart theorem (see Appendix 2.A) it is easy to show that

\[
C_g = \frac{4\xi}{2} \left\{ 1 + P_{ab} \right\} \sum_{k_a} \sum_{k_b} |\langle 0 | Q_2^m | k_a, 0 \rangle|^2 \frac{1}{(\Delta E_a(k_a) + \Delta E_b(k_b))^2}
\]

\[
= -\frac{4\xi}{4} \left\{ 1 + P_{ab} \right\} \sum_{k_a} \sum_{k_b} \frac{f^{(a)}(k_a)}{\Delta E_a(k_a)(\Delta E_a(k_a) + \Delta E_b(k_b))}
\]

\[
= \text{f}(2.2-15)
\]

From Eq. (2.2-15) it is clear that for the interaction of two ground state atoms the dipole-quadrapole interaction energy is attractive.
2.3 Relativistic Long Range Interaction Energy between two Neutral Non-degenerate Atoms

The general treatment of relativistic long range interaction energies, through $O(\alpha^2)$, as discussed in Sec. 1.4. Here we derive an expression for the relativistic interaction energy $E_{ab}^{(i)}$, between two neutral non-degenerate atoms, which is accurate through $O(\alpha^2/R^6)$.

It is convenient to write the relativistic interaction energy, through $O(\alpha^2)$, as a sum of contributions from the various Hamiltonians comprising $H_{rel}$ (see Eq. (1.5)):

$$E_{ab}^{(i)} = \sum_{\sigma} E_{ab}^{(i)}(\sigma)$$

where

$$E_{ab}^{(i)}(\sigma) = \sum_{m=1}^{\infty} \frac{W_{\sigma,m}}{R^m}$$

and

$$W_{\sigma,m} = \sum_{l=0}^{m-l} \sum_{m=0}^{l} \langle \psi_m | H_{\sigma,l} | \psi_{m-l-m} \rangle$$

Certain terms in $W_{\sigma,m}$ are identically zero, namely, those involving

$$H_{SS,2} = H_{SL,2} = H_{P,l>0} = H_{D,l>0} = 0$$

(2.2)
For the interaction of neutral atoms, \( V_1 = V_2 = 0 \), and from Eqs. (1.3-17), (1.3-26) and (1.3-32) it is clear that

\[
\psi_0 = \psi^{(0)} \quad \psi_1 = \psi^{(1)} = 0
\]

(2.3-5)

\[
\psi_m = \psi^{(m)}_m \quad \text{for} \quad m = 3, 4, 5, \quad \psi_6 = \psi^{(1)}_6 + \psi^{(2)}_6
\]

(2.3-6)

Further, for the interaction of two non-degenerate atoms, it can be shown (see Appendix 2.B) that

\[
\langle \psi_0 | H_{\epsilon, l} | \psi_0 \rangle \equiv 0 \quad \text{for} \quad l > 0, \quad \sigma \equiv \sigma
\]

(2.3-7)

Using Eqs. (2.3-3), (2.3-5) and (2.3-7) we obtain

\[
W_{6,m} = \sum_{l=0}^{m} \sum_{m-l=0}^{m-1} \langle \psi_m | H_{\epsilon, 2} | \psi_{m-1-l} \rangle \quad \text{for} \quad m \geq 2
\]

(2.3-8)

\[
W_{6,1} = W_{6,2} = 0
\]

(2.3-9)

The natural perturbation parameter, \( \alpha^2 \), which is used to order the relativistic corrections in a perturbation sense, is suppressed in the equations given here. In actual fact \( \epsilon_{ab}^{(1)} \), being of \( O(\alpha^2) \), is multiplied by \( \alpha^2 \) in the final results.
a. Contribution of the Orbit-Orbit Hamiltonian, $H_{LL}$

The contribution, through $O(1/R^6)$, to $E^{(1)}_{ab}$ from the orbit-orbit Hamiltonian is

$$E^{(1)}_{ab}(LL) = \sum_{m=2}^{6} \frac{W_{LL,m}}{R^m}$$

(2.3-10)

Let us consider each of the coefficients $W_{LL,m}$ appearing in Eq. (2.3-10) separately.

From Eq. (2.3-8), making use of the Hermitian character of $H_{LL,0}$, we find

$$W_{LL,3} = 2 \langle \psi_3^{*(n)} | H_{LL,0} | \psi^{*(n)} \rangle$$

(2.3-11)

where in general

$$\langle \psi_m^{*(n)} | H_{LL,0} | \psi^{*(n)} \rangle = \sum_{A,B} \frac{\langle \psi_m^{*(n)} | H_{LL,0} | \psi^{*(n)} \rangle}{\Delta \epsilon(A) + \Delta \epsilon(B)}$$

(2.3-12)

Since $H_{LL,0}$ is the sum of the orbit-orbit Hamiltonians for the two isolated atoms $a$ and $b$, it is clear that

$$W_{LL,3} = 0$$

(2.3-13)

7. In this work, as mentioned in part I, we assume all the $\psi^{*(n)}$ are real.
From Eq. (2.3-8), omitting terms of the type given by Eq. (2.3-11) which are zero,

\[ W_{LL,4} = 2 \left< \Psi'_3 \left| H_{LL,4} \right| \Psi'^{(s)} \right> \]  \hspace{1cm} (2.3-14)

Equations (1.4-9), (3.2-7), and (2.3-12) then yield

\[
W_{LL,4} = \sum_{A,B} \left[ \begin{array}{c}
\left< A' r^{(a)}_{1} A \right> \left< B' r^{(b)}_{1} B \right> \\
+ \left< A' r^{(a)}_{1} A \right> \left< B' r^{(b)}_{1} B \right> \\
+ 2 \left< A' r^{(a)}_{1} A \right> \left< B' r^{(b)}_{1} B \right>
\end{array} \right] \frac{2 \left< A | Q^{(a)}_{1} | A' \right> \left< B | Q^{(b)}_{1} | B' \right>}{\Delta E(A) + \Delta E(B)}
\]

(2.3-15)

Here \( Q^{m}_{1}(b) \) are the irreducible tensorial components of the current operator \( Q_{1}(b) \); \( Q_{1}(b) = \sum_{\phi} \phi \). The interaction energy \( W_{LL,4}/R^{4} \) is an (orbital-current)-(electrostatic-dipole) dispersion energy. From symmetry considerations it follows that

\[
W_{LL,4} = 2 \sum_{A,B} \sum' \left< 0 | r^{(a)}_{1} A, 0 \right> \left< 0 | r^{(b)}_{1} B, 0 \right> \left< 0 | r^{(a)}_{1} A, 0 \right> \left< 0 | r^{(b)}_{1} B, 0 \right> \left< 0 | r^{(a)}_{1} A, 0 \right> \left< 0 | r^{(b)}_{1} B, 0 \right> \frac{\Delta E_{a}(A,1) + \Delta E_{b}(B,1)}{(\Delta E_{a}(A,1) + \Delta E_{b}(B,1))}
\]  \hspace{1cm} (2.3-16)

Making use of the commutator relation

\( i \left[ H_{0}^{(a)}, r^{(a)}_{1} \right] = Q^{(a)}_{1} \)  \hspace{1cm} (2.3-17)
it is easy to show that

\[ W_{LL,5} = -2 \sum_a \sum_b \frac{\Delta E_a(k_i) \Delta E_b(k_i) |\Psi_{L}^{(a)}(k_i,0)\psi_{L}^{(a)}|^2 |\Psi_{L}^{(b)}(k_i,0)\psi_{L}^{(b)}|^2}{(\Delta E_a(k_i) + \Delta E_b(k_i))} \]  

(2.3-18)

The coefficient \( W_{LL,5} \) may be expressed in terms of the average oscillator strengths, \( \bar{f}(k_i) \), or Eq. (2.2-10):

\[ W_{LL,5} = -\frac{1}{2} \sum_a \sum_b \frac{f^{(a)}(k_i) f^{(b)}(k_i)}{(\Delta E_a(k_i) + \Delta E_b(k_i))} \]  

(2.3-19)

From Eq. (2.3-18), it is apparent that \( W_{LL,5} \) is positive for the interaction of two ground state atoms and thus the (orbital-current)- (electrostatic-dipole) dispersion energy is repulsive. Since this \( 1/R^4 \) dispersion energy is of longer range than the usual London dispersion energy, \( C_6 R^6 \), it may be of considerable importance in atomic and molecular collision processes. This new interaction energy, which is of \( O(\alpha^2) \), is compared to the London dispersion energy in Sec. 2.4 for the interaction of various rare gas atoms.

The strong similarity between the expressions for the coefficients \( C_6 \) and \( W_L \) should be noted (compare Eqs. (2.2-11) and (2.3-19)).

From Eq. (2.3-9), omitting terms of the type given by Eq. (2.3-11) which vanish,

\[ W_{LL,5} = 2 \langle \Psi_l^{(a)} | H_{LL,5} | \Psi_l^{(a)} \rangle + 2 \langle \Psi_l^{(a)} | H_{LL,5} | \Psi_l^{(a)} \rangle \]  

(2.3-20)
The expansion coefficients $H_{LL,1}$ and $H_{LL,2}$ are given by Eqs. (1.B-9) and (1.B-10) and from symmetry considerations it is easy to show

$$W_{LL,5} = 0 \quad (2.3-21)$$

$W_{LL,6}$ From Eqs. (2.3-6) and (2.3-8), omitting terms which are zero from symmetry considerations we obtain

$$W_{LL,6} = W_{LL,4;2} + W_{LL,3;3} + W_{LL,6;0} \quad (2.3-22)$$

where

$$W_{LL,4;2} = 2 \left< \psi^{(1)}_{4} \right| H_{LL,2} \left| \psi^{(0)} \right> \quad (2.3-23)$$

$$W_{LL,3;3} = 2 \left< \psi^{(0)}_{3} \right| H_{LL,3} \left| \psi^{(0)} \right> \quad (2.3-24)$$

$$W_{LL,6;0} = 2 \left< \psi^{(3)}_{6} \right| H_{LL,0} \left| \psi^{(0)} \right> + \left< \psi^{(1)}_{3} \right| H_{LL,0} \left| \psi^{(0)} \right> \quad (2.3-25)$$

We will consider each of the contributions to $W_{LL,6}$ separately.

$W_{LL,4;2}$ Using Eqs. (1.B-10), (2.2-13) and (2.3-12) yields
\[ W_{\text{LL},4;2} = \frac{3}{(2)^3} \sum_{A,B} \left[ \langle A' | r_{\text{a}}^2 | A \rangle \langle B' | Q_{\text{b}}^{\text{o}} | B \rangle + \langle A' | r_{\text{a}}^2 | A \rangle \langle B' | Q_{\text{b}}^{\text{t}} | B \rangle \right] + (3)^2 \langle A' | r_{\text{a}}^2 | A \rangle \langle B' | Q_{\text{b}}^{\text{t}} | B \rangle - \langle A' | r_{\text{a}}^2 | A \rangle \langle B' | r_{\text{b}}^{\text{t}} | B \rangle - (3)^2 \langle A' | r_{\text{a}}^2 | A \rangle \langle B' | r_{\text{b}}^{\text{t}} | B \rangle \]

\[ = \frac{1}{\Delta \varepsilon(A) + \Delta \varepsilon(B)} \left[ i\langle A | L_{\text{a}}(\alpha) | A' \rangle \langle B | Q_{\text{b}}^{\text{o}} | B' \rangle - i\langle A | L_{\text{a}}(\alpha) | A' \rangle \langle B | Q_{\text{b}}^{\text{t}} | B' \rangle \right] \]

\[ \times \left[ - (6)^2 \langle A | D_{\text{a}}^{\text{o}} | A' \rangle \langle B | Q_{\text{b}}^{\text{t}} | B' \rangle - i\langle A | Q_{\text{a}}^{\text{t}} | A' \rangle \langle B | L_{\text{b}}^{\text{o}} | B' \rangle + i\langle A | Q_{\text{a}}^{\text{t}} | A' \rangle \langle B | L_{\text{b}}^{\text{t}} | B' \rangle + (6)^2 \langle A | Q_{\text{a}}^{\text{o}} | A' \rangle \langle B | D_{\text{b}}^{\text{t}} | B' \rangle \right] \]

(2.3-26)

Applying the selection rules (see Ap. ind. x 2 A.) for the tensor operators involved in the expression for \( W_{\text{LL},4;2} \) gives:

\[ W_{\text{LL},4;2} = q \left[ 1 + \rho_{\text{ab}} \right] \sum_{\mathbf{k}_a} \sum_{\mathbf{k}_b} \sum_{\mathbf{r}_a} \int_{\mathbf{r}_b} \left[ \langle 0 | l_{\mathbf{r}_a}^{\text{o}} | 0 \rangle \langle 0 | r_{\mathbf{r}_a}^{\text{t}} | 0 \rangle \langle 0 | Q_{\mathbf{r}_b}^{\text{o}} | 0 \rangle \langle 0 | Q_{\mathbf{r}_b}^{\text{t}} | 0 \rangle \right] \left( \Delta \varepsilon_{\mathbf{k}_a}(\mathbf{r}_a) + \Delta \varepsilon_{\mathbf{k}_b}(\mathbf{r}_b) \right) \]

(2.3-27)

It is easy to show that

\[ + \frac{i}{\hbar} \left[ H_0(\alpha), Q_{\text{a}}^{\text{o}}(\alpha) \right] = D_{\text{a}}^{\text{t}}(\alpha) \]

(2.3-28)

and similarly for atom b. Equations (2.3-17), (2.3-27) and (2.3-28) give
From Eq. (2.3-29) it is clear that for the interaction two ground state atoms the dispersion energy $W_{LL,4;2}/R^6$ is repulsive. There is a strong similarity between the coefficients $C_\text{B}$ and $W_{LL,4;2}$ (compare Eqs. (2.2-15) and (2.3-29)).

From Eqs. (1.8-11) and (2.3-24)

$$W_{LL,3;3} = 2 \langle \psi^{(i)} | C_{LL,3} | \psi^{(i)} \rangle + 2 \langle \psi^{(i)} | F_{LL,3} | \psi^{(j)} \rangle + 2 \langle \psi^{(i)} | G_{LL,3} | \psi^{(i)} \rangle$$

(2.3-30)

where $C_{LL,3}$, $F_{LL,3}$, and $G_{LL,3}$ are given by Eqs. (1.8-12) - (1.8-14).

Using the selection rules for the irreducible tensors involved in the expression for $W_{LL,3;3}$ it is easy to show that the first two terms in Eq. (2.3-30) vanish identically and that the non-zero contribution from the last term gives
\[ W_{L_{1,1};3} = -\frac{3i}{(15)^\frac{1}{2}} \sum_{\hat{a}} \sum_{\hat{b}} \left\{ 1 + p_{\hat{a} \hat{b}} \right\} \frac{\Delta E_{a}(k,1) \gamma_{0} \gamma_{\hat{a}} \gamma_{\hat{b}} \gamma_{10} \Gamma_{\hat{a} \hat{b}}}{(\Delta E_{a}(k,1) + \Delta E_{b}(k,1))} \]

Here \( \gamma_{0} \) is the first rank tensor defined by

\[ \gamma_{0}^{(a)} = -\frac{3}{(15)^\frac{1}{2}} \sum_{j} \left\{ \Gamma_{j}^{0} \left( \gamma_{j} \gamma_{\rho j} \right) - 2 \gamma_{j}^{+} \Gamma_{j} \left( \rho_{j} \right) \right\} \]  

Using Eqs. (2.3-17) and (2.2-10) we obtain

\[ W_{L_{1,1};3} = \frac{6i}{(15)^\frac{1}{2}} \sum_{\hat{a}} \sum_{\hat{b}} \left\{ 1 + p_{\hat{a} \hat{b}} \right\} \frac{\Delta E_{b}(k,1) \gamma_{0} \gamma_{\hat{a}} \gamma_{\hat{b}} \gamma_{10} \Gamma_{\hat{a} \hat{b}}}{(\Delta E_{a}(k,1) + \Delta E_{b}(k,1))} \]

\[ = -\frac{3i}{(15)^\frac{1}{2}} \sum_{\hat{a}} \sum_{\hat{b}} \left\{ 1 + p_{\hat{a} \hat{b}} \right\} \frac{\Delta E_{b}(k,1) \gamma_{0} \gamma_{\hat{a}} \gamma_{\hat{b}} \gamma_{10} \Gamma_{\hat{a} \hat{b}}}{(\Delta E_{a}(k,1) + \Delta E_{b}(k,1))} \]

(2.3-33)

\[ W_{L_{1,1};6;0} \]  

Let us define the following quantity: \( ^{6} \)
From Eqs. (1.3-27), (1.3-33), (1.4-10) and (2.3-25), using the Wigner-Eckart theorem, it can be shown that

$$W(H_{s,0}) = \left[ 1 + \frac{\mathcal{P}_{ab}}{6} \right] \sum_{k_a, k_b} \sum' \frac{\sum' \langle 0| H_{s,0} | 0 \rangle \langle k'_a, 0 | k, 0 \rangle \langle k, 0 | k'_b, 0 \rangle \langle k'_b, 0 | 0 \rangle \langle k, 0 | H_{s,0} | 0 \rangle}{(\Delta E_a(k_a) + \Delta E_b(k_b)) \Delta E_a(k, 0) \Delta E_b(k, 0)} \frac{f(a)}{f(b)}$$

$$W_{L_L, b; 0} = W(H_{L_L, 0}) \quad (2.3-35)$$

The interaction energy, $W_{L_L, b; 0}/R^6$, arises in our treatment because the relativistic Hamiltonians for the isolated atoms are not included in the zero-th order perturbation Hamiltonian (see Eq. (1.3-9)). This term appears to correct for the non-relativistic nature of our zero-th order wave functions.
Order of magnitude estimates for \( W_{LL,6;0} \), \( W_{LL,3;3} \) and \( W_{LL,4;2} \), for various rare gas interactions, are given in Sec. 2.4.

b. Contribution of the Spin Hamiltonians, \( H_{SS} \) and \( H_{SL} \).

The contribution, through \( C(1/R^6) \), to \( E_{ab}^{(ii)} \) from the spin-spin Hamiltonian, \( H_{SS} \), is given by

\[
E_{ab}^{(ii)} = \sum_{m=3}^{6} \frac{W_{SS,m}}{R^m},
\]

where from Eqs. (2.3-4) and (2.5-8)

\[
W_{SS,m} = \sum_{l=0}^{m-2} \sum_{m=0}^{m-l} \langle \Psi_m | H_{SS;l} | \Psi_{m-l-m} \rangle
\]

In the coefficients \( W_{SS,n} \), terms of the type given by Eq. (2.3-12) appear, which are identically zero,

\[
\langle \Psi_m | H_{SS,q} | \Psi_{m+l} \rangle = 0
\]

This integral vanishes for \( q = 0 \) since \( H_{SS,0} = H_{SS,0}^{(SS)} + H_{SL,0}^{(SL)} \).

For \( q \neq 0 \), \( H_{SS,q} \) is given symbolically (see Eq. (1.4-48)) by

\[
H_{SS,q} = \sum_{k} \sum_{\omega} \sum_{\omega} \xi(k, t, \omega, \kappa) T_{\omega}(S_{\omega}) T_{\omega}(S_{\omega})
\]
and thus is not diagonal in the spin quantum numbers. Since the operator $V_n$ appearing in Eq. (2.3-12) is diagonal in the spin quantum numbers Eq. (2.3-38) holds for $q \neq 0$. Using Eq. (2.3-38) it is easy to show that the only non-zero $W_{S_S, n}$, $n \leq 6$, is given by

$$W_{S_S, 6} = 2 \langle \psi_6^{(1)} | H_{SS, 0} | \psi_6^{(0)} \rangle + \langle \psi_3^{(1)} | H_{SS, 0} | \psi_3^{(0)} \rangle$$

(2.3-40)

It should be noted that $W_{S_S, 0}$, $n = 0$, is comprised of two terms (see Eq. (1.4-44)), one of which is a scalar in both spin and space variables. The other term is a sum of products of second rank spin tensors with second rank space tensors. Hence it is easy to show that

$$W_{S_S, 6} = W(\Delta_{S_S, 0}) = W_{S_S, 6, 0}$$

(2.3-41)

where

$$\Delta_{S_S, 0}^{(a)} = \frac{-8\pi}{3} \sum_{R > j}^{m_0} \frac{S_j \cdot S_R}{R^2} S_j^{(3)} \delta(S_{j} R)$$

(2.3-42)

and $W(\Delta_{S_S, 0})$ is defined by Eq. (2.3-36). The energy $W_{S_S, 6}/R^6$ corrects for the non-relativistic nature of our zero-th order wave functions (see discussion for $W_{LL, 6, 0}$).

The relativistic Hamiltonian, $H_{SL}$, makes no contribution to $\mathcal{E}_{ab}^{(1)}$. This is a direct consequence of the spin structure of $H_{SL, q}$ for all $q$. 

The contribution, through \( O(1/R^6) \), to \( E_{ab}^{(1)} \) from the Hamiltonian's \( H_\sigma \), for \( \sigma = p \) and \( D \), is given by:

\[
E_{ab}^{(1)}(\sigma) = \sum_{m=3}^{6} \frac{W_{\sigma,m}}{R^m}, \quad \sigma = p, D, \tag{2.3-43}
\]

where from Eqs. (2.3-44) and (2.3-8):

\[
W_{\sigma,m} = \sum_{m=0}^{n} \langle \Psi_m | H_{\sigma,0} | \Psi_{n-m} \rangle \tag{2.3-44}
\]

\[m \neq 1, 2, m-1, m+2\]

It is easy to show that the only non-vanishing \( W_{\sigma,n}, m \leq 6 \), is given by:

\[
W_{\sigma,6} = W(H_{\sigma,0}) \equiv W_{\sigma,6,0}, \quad \sigma = p, D, \tag{2.3-45}
\]

where \( W(H_{\sigma,0}) \) is defined by Eq. (2.3-34). The energies \( W_{p,6}/R^6 \) and \( W_{D,6}/R^6 \) again appear to correct for the non-relativistic nature of our zero-th order basis set.
2.4 Estimates for the Relativistic Interaction Energies.

Combining the results of Secs. 2.2 and 2.3 we find that the interaction energy, through terms of \( \Theta(\alpha^2/R^4) \), is given by

\[
E_{ab} = \frac{\alpha^2 W_4}{R^4} + \frac{C_6}{R^6} + \frac{\alpha^2 W_6}{R^6},
\]

(2.4-1)

where

\[
W_4 = W_{LL,4}
\]

(2.4-2)

\[
W_6 = W_{LL,4} + W_{LL,4} + W_{6,0}
\]

(2.4-3)

and

\[
W_{6,0} = \sum \frac{W_6}{W_{6,0}}
\]

(2.4-4)

Here we give order of magnitude estimates for the coefficients involved in Eq. (2.4-1) for various ground state rare gas interactions.

\( W_4 \) and \( C_6 \) The dipole polarizability \(^8\) of atom \( a \), in it ground state, is given by

\[
\alpha_d^{(a)} = \sum_{k,1} \frac{f_k^{(a)}}{[\Delta E_a(k,1)]^2}
\]

(2.4-5)

The van der Waals coefficient, $C_6$, may be written as:

$$C_6 = \frac{3\hbar}{2} \sum_a \sum_b \frac{\int f(a) f(b) \Delta E_a(k_{ij}) \Delta E_b(k_{ij})}{(\Delta E_a(k_{ij}) + \Delta E_b(k_{ij}))^2}$$

(2.4-6)

Applying Unsöld's approximation to Eq. (2.4-6) and using Eq. (2.4-5), yields London's formula for $C_6$:

$$C_6 = -\frac{3\hbar}{2} \frac{\alpha_d(a) \alpha_d(b)}{\Delta_a + \Delta_b}$$

(2.4-7)

In a similar manner one obtains the following approximation for $W_4$:

$$W_4 = \frac{1}{2} \frac{\Delta_a^2 \Delta_b^2 \alpha_d(a) \alpha_d(b)}{\Delta_a + \Delta_b}$$

(2.4-8)

The results of Eqs. (2.4-7) and (2.4-8) are identical with those obtained from the harmonic oscillator model (see below). It is often found that choosing the average energies, $\Delta$, equal to the first ionization potentials, $I$, of the interacting atoms gives good estimates for $C_6$. Values for $C_6$ and $W_4$ obtained from Eqs. (2.4-7) and (2.4-8), with $\Delta_a = I_a$ and $\Delta_b = I_b$, are given in Table I for various rare gas interactions. The estimates for $C_6$ agree (to within 0-30 per cent.) with the accurate theoretical values of the van der Waals coefficient, $C_6^K$.

10. The approach discussed here is similar to that used in ref. 2.
11. The energy levels for the rare gas atoms are listed by C. Moore, N.B.S. Circular 467, vol. 1, 1949.
Table I

Estimates of $W_4$ for Rare Gas Interactions. All quantities are in atomic units. The (orbital-current)-(electrostatic-dipole) dispersion energy is given by $\alpha^2 W_4/R^4$ and the van der Waals energy is given by $C_6/R^6 (\alpha_{4}(\alpha), C_K^6$ and $I_a$ from refs. 8, 12 and 14, respectively).

<table>
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<tr>
<th>Interaction a-b</th>
<th>Accurate theoretical values</th>
<th>Oscillator with $\Delta = 1$ Eqs. (2.4-7), (2.4-8)</th>
<th>Oscillator with $\Delta^K$ Eqs. (2.4-7), (2.4-8)</th>
<th>Unsöld with $\Delta^K$ Eqs. (2.4-9), (2.4-10)</th>
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<td>$-C_6^K$</td>
<td>$\Delta_a$</td>
<td>$-C_6$</td>
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</tr>
<tr>
<td>A-A</td>
<td>11.080</td>
<td>65.4</td>
<td>0.5790</td>
<td>53.3</td>
</tr>
</tbody>
</table>
determined by A. E. Kingston. Values for \( W_4 \) are also listed in Table I, for \( \Delta = \Delta^K \), the value of \( \Delta \) obtained by requiring Eq. (2.4-7) to give \( C_6 = C_6^K \) for like atom interactions.

A second set of approximation formulae may be obtained for \( W_4 \) and \( C_6 \) which do not involve the polarizabilities of the interacting atoms. Applying Unsöld's approximation in Eq. (2.3-19) and using the Reiche-Thomas-Kuhn sum rule, \( \sum_{k_a} \frac{f(k, l)}{C_6} = M_a \), yields

\[
W_4 = \frac{1}{2} \frac{M_a M_b}{\Delta_a + \Delta_b} \tag{2.4-9}
\]

Here \( M_a \) is the number of electrons in atom \( a \). The corresponding approximation for \( C_6 \) is given by

\[
C_6 = -\frac{3}{2} \frac{M_a M_b}{(\Delta_a + \Delta_b) \Delta_a \Delta_b} \tag{2.4-10}
\]

If the average energies, \( \Delta \), are chosen to be the first ionization potentials of the interacting atoms, Eq. (2.4-10) gives poor approximations to \( C_6 \). Instead, we choose \( \Delta = \Delta^K \), the value of \( \Delta \) obtained by requiring Eq. (2.4-10) to give Kingston's value for \( C_6 \) for like atom interactions. Values of \( W_4 \) computed from Eq. (2.4-9) with \( \Delta = \Delta^K \) are given in Table I.

\[
\frac{W_6}{W_{LL,4;2}} \quad \text{and} \quad \frac{W_6}{W_{LL,3;3}}
\]


are easily obtained from the frequently used harmonic oscillator model. In this approximation each electron in atom a, say, is represented by a 3-dimensional harmonic oscillator of fundamental frequency \( \nu_a \). The energy \( \hbar \nu_a = \Delta_a \) is usually set equal to the first ionization potential \( I_a \). The wave functions for the atom are assumed to be products of harmonic oscillator wave functions, one for each electron. The coefficients of the various interaction energies are given in terms of \( \Delta \) and the polarizabilities, \( \alpha_d \), of the interacting atoms. If this model is used to calculate approximations for \( C_6 \) and \( W_4 \), one would obtain Eqs. (2.4-7) and (2.4-8). The results for \( W_{LL,4;2} \) and \( W_{LL,3;3} \) are:

\[
W_{LL,4;2} = \frac{1}{4} \Delta_a \Delta_b \left( \alpha_d(a) \alpha_d(b) \frac{1}{\Delta_a + 2\Delta_b} \right) 
\]
\[
W_{LL,3;3} = -\frac{3}{4} \Delta_a \Delta_b \left( \alpha_d(a) \alpha_d(b) \frac{1}{\Delta_a + \Delta_b} \right) 
\]

The values of \( C_6 \), \( W_{LL,4;2} \) and \( W_{LL,3;3} \), obtained from the oscillator model with \( \Delta = 1 \), are compared in Table II for various rare gas interactions.

Finally, the coefficient, \( W_{6;0} = \sum_d W_{d,6;0} \) can be estimated by applying Unsöld's approximation to Eq. (2.3-34);

TABLE II

Estimates for $W_{LL,4;2}$ and $W_{LL,3;3}$ for Rare Gas Interactions.

All quantities are in atomic units. The relativistic dispersion energies are given by $\alpha^2 W_{LL,4;2} + W_{LL,3;3} R^6$ and the van der Waals energy by $C_6/R^6$. The harmonic oscillator model is used with $\Delta = 1$.

<table>
<thead>
<tr>
<th>Interaction a-b</th>
<th>$-C_6$</th>
<th>$W_{LL,4;2}$</th>
<th>$-W_{LL,3;3}$</th>
<th>$W_{LL,4;2} + W_{LL,3;3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-He</td>
<td>1.298</td>
<td>2.345</td>
<td>1.172</td>
<td>1.173</td>
</tr>
<tr>
<td>He-Ne</td>
<td>2.33</td>
<td>3.96</td>
<td>1.98</td>
<td>1.99</td>
</tr>
<tr>
<td>Ne-A</td>
<td>8.12</td>
<td>12.3</td>
<td>6.02</td>
<td>6.27</td>
</tr>
<tr>
<td>Ne-Ne</td>
<td>4.21</td>
<td>6.68</td>
<td>3.34</td>
<td>3.34</td>
</tr>
<tr>
<td>Ne-A</td>
<td>14.8</td>
<td>20.5</td>
<td>10.2</td>
<td>10.4</td>
</tr>
<tr>
<td>A-A</td>
<td>53.3</td>
<td>67.7</td>
<td>30.9</td>
<td>30.9</td>
</tr>
</tbody>
</table>
The choice of the average energies made in Eq. (2.4-13) tends to overestimate each term in $W_{\delta, \sigma; \pi}$. We have evaluated these coefficients for the He-He interaction using the simple approximate ground state helium wave function

\[ \Psi_{1,2} = \begin{bmatrix} 1 + \rho_{ab} \end{bmatrix} \]

The integrals for $\sigma = SS, Sl, p, \text{ and } D$ are easily done. The evaluation of the integrals involving $H_{11,0}^{(a)}$ is discussed in Appendix 2.C where a one-center expansion for this Hamiltonian is

15. The integrals, $\langle 0 | H_{11,0} | 0 \rangle$, for all $\sigma$ are discussed by H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One-and Two-Electron Atoms" (Academic Press, New York, 1957).
derived. The results are (for \( Z = 2 \))

\[
\begin{align*}
W_{LL,6j0} &= 3.204 \quad ; \quad W_{5s,6j0} = -6.311 \\
W_{SL,6j0} &= 0 \quad ; \quad W_{p,6j0} = 67.523 \\
W_{D,6j0} &= -47.342 \quad ; \quad W_{6j0} = 17.073
\end{align*}
\]  

(2.4-15)

For the rare gas interactions considered here, the relativistic interaction energy, \( \alpha^2 \left( W_{LL,4;2} + W_{LL,3;3} \right) / R^6 \), is of order \( \alpha^2 \sim 5 \times 10^{-5} \) times smaller than the magnitude of the van der Waals energy (see Table II). For the He-He interaction the dispersion energy \( \alpha^2 W_{6;0} / R^6 \) is of order \( 10 \alpha^2 \sim 5 \times 10^{-4} \) times smaller than the magnitude of the London energy and one would expect this to be true for the other rare gas interactions as well. On the other hand, for sufficiently large values of \( R \), the (orbital-current)-(electrostatic-dipole) dispersion energy is not negligible since it is of longer range than the van der Waals energy (see below).

From these considerations we conclude, that in the generalized Breit-Pauli approximation, the interaction energy for ground state rare gas atoms is given through \( O(\alpha^2/R^6) \) by

16. As mentioned previously the Unsöld's approximation for \( W_{6j0} \) probably overestimates the magnitude of this coefficient. One would expect \( W_{6j0} \) to be of the same order of magnitude as the other coefficients of \( O(\alpha^2/R^6) \). It should be noted that there is a strong possibility of severe cancellation in the coefficients of \( O(\alpha^2/R^6) \).
where,

\[ \beta = - \frac{W_4}{C_b} \]  

(2.4-17)

For the interaction of the rare gas atoms considered in Table I, the ratio of the (orbital-current)-electrostatic-dipole dispersion energy, \( E_4 \), to the van der Waals energy, \( E_6 \), given by

\[ \frac{E_4}{E_6} = -\beta \alpha^2 R^2 \]  

(2.4-18)

This ratio is tabulated as a function of \( R \) in Table III for \( \beta = 1 \). These order of magnitude results suggest that the relativistic dispersion energy, \( \alpha^2 W_4 / R^4 \), might be significant in low energy atomic and molecular beam scattering experiments.

17. In general one would expect that the results obtained from Eq. (2.4-9) tend to overestimate \( W \), while the results from Eq. (2.4-8) tend to underestimate this coefficient.

18. It should be pointed out that this \( 1/R^4 \) dispersion energy could be partially shielded by other effects, for example higher order relativistic energies arising with large coefficients. Also, as discussed in part I, we have neglected correction factors due to retardation effects and to the coupling between electronic and nuclear motion. It has been shown that the nuclear-electronic coupling is negligible for atoms in non-degenerate states (see for example A. Dalgarno and R. McCarroll, Proc. Roy. Soc. A227, 363 (1955)).
TABLE III

Values of $E_4/E_6 = -\beta \chi^2 R^2$ as a Function of $R$ for $\beta = 1$. Here $E_4$ is the (orbital-current)-(electrostatic-dipole) dispersion energy and $E_6$ is the London energy. All quantities are in atomic units.

<table>
<thead>
<tr>
<th>$R$</th>
<th>$-E_4/E_6$</th>
<th>$R$</th>
<th>$-E_4/E_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.00533</td>
<td>60</td>
<td>0.192</td>
</tr>
<tr>
<td>20</td>
<td>0.0213</td>
<td>70</td>
<td>0.261</td>
</tr>
<tr>
<td>30</td>
<td>0.0479</td>
<td>80</td>
<td>0.341</td>
</tr>
<tr>
<td>40</td>
<td>0.0852</td>
<td>90</td>
<td>0.431</td>
</tr>
<tr>
<td>50</td>
<td>0.133</td>
<td>100</td>
<td>0.533</td>
</tr>
</tbody>
</table>

As an example of the results of part I we have discussed the interaction of two neutral non-degenerate atoms. Applications to other interacting systems will give dispersion energies similar to those derived here and will yield other types of interaction energies as well (see I, Sec. 1.4).
Appendix 2.A. The Wigner-Eckart Theorem

In the derivation of the various interaction energies of Secs. 2.2 and 2.3 the Wigner-Eckart theorem is used repeatedly to simplify the general results of part I. The purpose of this Appendix is to discuss the Wigner-Eckart theorem and its usefulness in the calculation of long range interaction energies.

Let \( T^m_l \) be a component of an irreducible spherical tensor operator of rank \( l \), \( m = -l, -l + 1, \ldots, l \), which is defined with respect to the angular momentum operator \( \mathbf{J} \). (see Appendix 1.C)

Let us consider the matrix elements of \( T^m_l \) with respect to the eigenfunctions, \( \Psi(J, \omega) \), of \( J^2 \) and \( J_z \):

\[
J^2 \Psi(J, \omega) = J(J+1) \Psi(J, \omega) \quad (2.A-1)
\]

\[
J_z \Psi(J, \omega) = \omega \Psi(J, \omega) \quad (2.A-2)
\]

Such matrix elements appear repeatedly in the treatment of long range interaction energies between atoms. In the work of Secs. 2.2 and 2.3 we are specifically concerned with \( J = L, S \).

One of the first steps in reducing the general results of part I to the expressions obtained in Secs. 2.2 and 2.3 is to


determine the selection rules for the irreducible tensor operators, $T_{2}^{m}$. This is easily accomplished by the Wigner-Eckart theorem which states that

$$\langle k', J', \omega' | T_{2}^{m} | k, J, \omega \rangle = C(J \parallel J', \omega \parallel m \parallel \omega') \langle k', J' \parallel T_{2} \parallel k, J \rangle .$$

(2.A-3)

The quantity $\langle k', J' \parallel T_{2} \parallel k, J \rangle$ is called the reduced matrix element of the set of tensors $T_{2}^{m}$ and is independent of $\omega', m$ and $\omega$. A useful alternate expression for Eq. (2.A-3) is

$$\langle k', J', \omega' | T_{2}^{m} | k, J, \omega \rangle = (-1)^{l+m}(\frac{2J'+1}{2J+1})^{\frac{1}{2}} C(J \parallel J,-\omega', m, -\omega) \times \langle k', J' \parallel T_{2} \parallel k, J \rangle .$$

(2.A-4)

The section rules for the irreducible tensor operators arise from the conditions under which the Clebsch-Gordan coefficients in Eq. (2.A-3) vanish. The $C(J \parallel J'; \omega m; \omega')$ vanish unless

$$\omega' = \omega + m$$

(2.A-5)

$$J' = J + \lambda, J + \lambda - 1, \ldots, |J - \lambda|$$

(2.A-6)

$$|\omega| \leq J, |m| \leq \lambda, |\omega'| \leq J'$$

(2.A-7)
Also the following relations are useful

\[ C(J, l, J', 000) = 0 \quad , \text{unless } j + l + j' \text{ even} \quad (2.6) \]

\[ C(J, 0, J', \omega, 0, \omega') = \delta_{j, j'} \delta_{\omega, \omega'} \quad (2.9) \]

The selection rules for \( J^m \), with \( m = 1, 0, -1 \), are \(^{20}\)

\[ \langle R, J', \omega' | J^m | R, J, \omega \rangle = \delta_{J, J'} \delta_{\omega, \omega'} (\omega + m)^m (J(J + 1))^1/2 \]

\[ \times C(J, 0, J', \omega + m, \omega') \quad (2.10) \]

The Wigner-Eckart theorem permits a further simplification over that afforded by the selection rules for the \( \gamma^m \). Namely, all non-zero matrix elements of the type given by Eq. (2.3), for fixed \( J', l \) and \( J \), may be written in terms of a single unknown quantity, the reduced matrix element. The reduced matrix element may be determined by calculating the left hand side of Eq. (2.3) once only, for some convenient choice of \( \omega \), \( m \) and \( \omega' \).
Appendix 2.B: On the Vanishing of \( \langle \psi^{(\sigma)} | H_{\sigma, \ell} | \psi^{(\sigma)} \rangle \), for \( \ell > 0 \).

In the discussion of the relativistic interaction energy given in Sec. 2.3 we make use of the following theorem:

\[
\langle \psi^{(\sigma)} | H_{\sigma, \ell} | \psi^{(\sigma)} \rangle = 0 \quad \text{for all} \quad \sigma, \ell > 0 \quad (2.B-1)
\]

where \( \psi^{(\sigma)} \) is given by

\[
\psi^{(\sigma)} = \varphi(A') \varphi(B) \quad (2.B-2)
\]

and \( \varphi(A') \) and \( \varphi(B') \) are real.

For the orbit-orbit Hamiltonian, \( H_{LL} \), the theorem is most easily shown without recourse to the explicit form of the expansion coefficients \( H_{LL, m} \).

From Eq. (1.A-18) it is easy to show that

\[
\sum_{m=1}^{\infty} \frac{H_{LL, m}}{R^m} = -\frac{1}{2\ell} \sum_{k} \sum_{t} \mathcal{B}(k, t) \cdot \frac{\mathcal{B}(k, t)}{R^{k_t}} \quad (2.B-3)
\]

\[
\mathcal{B}(k, t) = \frac{1}{k_t} \left[ \frac{\mathcal{B}(k, t)}{R^{k_t}} + \mathcal{B}(k, t) \cdot \nabla_R \right] \quad (2.B-4)
\]

where

\[
(\varphi_{\sigma} \cdot \mathcal{B}(k, t)) = 0 \quad (2.B-5)
\]
Consider the integral
\[ I = \langle \Psi^{(a)} | B(k, t) \cdot \vec{p}_t | \Psi^{(a)} \rangle \]
\[ = \frac{1}{2} \langle \Psi^{(a')} | \Psi^{(b')} | \vec{p}_t \cdot B(k, t) + B(k, t) \cdot \vec{p}_t | \Psi^{(a')} | \Psi^{(b')} \rangle \]
(2.B-6)

Integrating over the electronic coordinates of atom \( a \) gives
\[ I = \frac{1}{2} \langle \Psi^{(b')} | \vec{p}_t \cdot \vec{E}(t) + \vec{E}(t) \cdot \vec{p}_t | \Psi^{(b')} \rangle \]
(2.B-7)

where
\[ F(t) = \langle \Psi^{(a')} | B(k, t) | \Psi^{(a')} \rangle \]
(2.B-8)

Since \( F(t) \) is a function of the position coordinates of electron \( t \), the operator \( (\vec{p}_t \cdot \vec{E}(t) + \vec{E}(t) \cdot \vec{p}_t) \) is a purely imaginary Hermitian operator of atom \( b \). Since \( \Psi^{(b')} \) is chosen to be real, the integral \( I \) vanishes. Thus from Eq. (2.B-3) we obtain

\[ \sum_{m=1}^{\infty} \frac{\langle \Psi^{(a')} | H_{LL, m} | \Psi^{(a')} \rangle}{R^m} = 0 \]
(2.B-9)

21. It is well known that for a real atomic wave function \( \Psi \), of the orbital form, the expectation value of \( H^{(a)} \) vanishes (see for example H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron atoms" (Academic Press, New York, 1957), p. 189; A. Froman, Rev. Mod. Phys. 32, 317 (1960)). This theorem is analogous to the result of Eq. (2.B-9).
Since Eq. (2.B-9) holds for all $R$, we obtain the result of Eq. (2.B-1) for $\sigma = LL$.

The expansion coefficients $H_{SS,m}$ and $H_{SL,m}$ for $m > 0$, both contain rank one spin tensor operators of the atoms $a$ or $b$. Thus since the states $A'$ and $B'$ represent non-degenerate states of the atoms $a$ and $b$ ($\mathbf{S}_a = \mathbf{S}_b = \sigma_a = \sigma_b = 0$), Eq. (2.B-1), for $\sigma = SS, SL$, follows from the Wigner-Eckart theorem.

The theorem is trivial for $H_p$ and $H_d$ since $H_{p,m} = H_{d,m} = 0$, for $m > 0$. 


Appendix 2.C: A One-Center Expansion for the Atomic Orbit-Orbit Hamiltonian

Integrals involving the atomic orbit-orbit coupling Hamiltonian occur in the expression for $W_{LL,6;0}$. Here we derive a one-center expansion for $H_{LL,0}^{(a)}$ which facilitates the calculation of these integrals and which may be useful in other contexts as well. The integrals involving $H_{LL,0}^{(a)}$, which occur in the Unsöld's approximation for $W_{LL,6;0}$, are evaluated for the He-He interaction. For convenience we will denote the orbit-orbit Hamiltonian for atom $a$, say, by $H_{LL}$ in this Appendix.

The operator $H_{LL}$, for two electrons, can be written in the form

$$H_{LL} = \frac{1}{2} (Q_1 + Q_2) \quad (2.C-1)$$

where

$$Q_1 = \frac{1}{r_{12}} \mathbf{\nabla}_1 \cdot \mathbf{\nabla}_2 \quad (2.C-2)$$

$$Q_2 = \frac{1}{r_{12}^3} (r_{12} \cdot \mathbf{\nabla}_1) \mathbf{\nabla}_2 = -\left(\mathbf{\nabla}_1 \frac{1}{r_{12}}\right) \cdot (r_{12} \cdot \mathbf{\nabla}_1) \mathbf{\nabla}_2 \quad (2.C-3)$$

The one-center expansion for $\frac{1}{r_{12}}$ is given by\(^2\textsuperscript{3}\)

$$\frac{1}{r_{12}} = \sum_{k,q} \frac{4\pi}{(2k+1)} Y^q_{k} \left( \theta^1, \phi^1 \right) Y^q_{k} \left( \theta^2, \phi^2 \right) Y^p_k \frac{r_2^p}{r_2^{k+1}}$$

(2.C-4)

where $Y^q_{k}$ is the spherical harmonic $Y^q_{k} \left( \theta_c, \phi_c \right)$. The corresponding one-center expansion for the operator $Q_1$ is given in spherical tensor form by

$$Q_1 = \frac{(4\pi)}{3} \sum_{k,q,p} (-1)^p Y^q_{k} \left( \theta^1, \phi^1 \right) Y^q_{k} \left( \theta^2, \phi^2 \right) Y^p_k \frac{\partial}{\partial \theta^1} Y^p_k \left( \theta^1, \phi^1 \right) \frac{\partial}{\partial \phi^1} Y^p_k \left( \theta^1, \phi^1 \right).$$

(2.C-5)

Here $Y^q_{k} \left( \theta^1, \phi^1 \right)$ is the solid harmonics obtained by replacing the components of $\Sigma$ in $Y^q_{k} \left( \omega \right) = r^2 Y^q_{k} \left( \omega, \phi \right)$ by the components of the gradient operator in $r$-space.

Using the gradient formula\(^2\textsuperscript{0}\), the $k$-th component of the first rank tensor $(\frac{\partial}{\partial \theta^1}, \frac{1}{r_{12}})$ is given by\(^2\textsuperscript{2}\)

$$\left( \frac{\partial}{\partial \theta^1}, \frac{1}{r_{12}} \right) = -4\pi \sum_{k,k',q} (-1)^q C(k,k',0,0) C(k,k',0,-k) Y^q_{k} \left( \theta^1, \phi^1 \right) Y^q_{k} \left( \theta^2, \phi^2 \right) A_{k,k'}$$

(2.C-6)

where

$$A_{k,k'} = \frac{(2k+1)}{(2k'+1)} \frac{r_2^{k-k'-1}}{r_2^{k+k'+1}} E \left( r_1 - r_2 \right)$$

$$A_{k,k'} = \frac{(2k+1)}{(2k'-1)} \frac{r_1^{k'-k-1}}{r_2^{k+k'+1}} E \left( r_2 - r_1 \right)$$

(2.C-7)

The $k$-th spherical component of the vector $\langle \mathbf{r}_1 \cdot \nabla \rangle \nabla_k$ is
\[ (\mathbf{r}_1 \cdot \nabla) \nabla_k^\omega = \frac{1}{2} \sum_\omega \frac{(-1)^\omega}{j_1(j_1+1)} Y_1^\omega (\mathbf{r}_1) Y_1^\omega (\nabla_x) Y_j^\omega (\nabla_k) \] \hspace{1cm} (2.C-8)

Finally, we require the one-center expansion of $\j_Y^\omega (\mathbf{r}_1)$, which has been derived by Rose 24:
\[ \j_Y^\omega (\mathbf{r}_1) = (2\pi)^{1/2} \sum_{L=0}^1 \sum_{M} (-1)^L \frac{C(L,1-L,1jM,\omega-M)}{[(2L+1)! (3-2L)!]} X Y_{(2)}^M Y_{(1)}^{\omega-M} \] \hspace{1cm} (2.C-9)

Combining the results of Eqs. (2.C-6) - (2.C-9) we obtain the one-center expansion for the operator $Q_2$
\[ Q_2 = \frac{(4\pi)^3}{3} \sum_{k,k',k''} \sum_{L=0}^1 \sum_{\omega,k} (-1)^{g_L+\omega+\kappa} \frac{C(L,1-L,1jM,\omega-M)}{[(2L+1)! (3-2L)!]} \] \[ X C(k,k';00) C(k,k';g,\kappa) X Y_{(1)}^{\kappa-q} Y_{(1)}^{\omega-M} Y_{(2)}^{-\omega} Y_{(2)}^{q} Y_{(2)}^{M} Y_{(2)}^{-\kappa} \] \hspace{1cm} (2.C-10)


25. The spherical tensors of the same argument could be coupled together in Eq. (2.C-10). However, it is often more convenient not to do this until after $Q_2$ has operated on a function.
The one center expansion for $H_{11}$ is given by Eqs. (2.C-1), (2.C-5) and (2.C-10). For the He-He interaction the approximate expression for $W_{LL,6;0}$, given by Eq. (2.C-13), contains the following integrals:

\begin{align}
\langle 0 | r^6 H_{LL} | 10 \rangle &= I_1 + I_2 \\
\langle 0 | r^6 H_{LL} | 10 \rangle &= I_3 + I_4 + I_5 + I_6
\end{align}

(2.C-11) 

\[ (2.C-12) \]

where

\begin{align}
I_1 &= \langle 0 | z_1 Q z_2 | 10 \rangle \\
I_2 &= \langle 0 | z_1 Q_1 z_2 | 10 \rangle \\
I_3 &= \langle 0 | z_1 z_2 Q | 10 \rangle \\
I_4 &= \langle 0 | z_1 z_2 Q | 10 \rangle \\
I_5 &= \langle 0 | z_1 z_2 Q | 10 \rangle \\
I_6 &= \langle 0 | z_1 z_2 Q | 10 \rangle
\end{align}

(2.C-13)

\begin{align}
| 10 \rangle &= \psi_{1,2} = Z_2^3 e^{-Z_2 (r_1 + r_2)} \frac{1}{n}
\end{align}

(2.C-14)

Here we evaluate the integral $I_2$ explicitly. The other integrals are easier and can be treated in an analogous manner. The following properties of the Clebsch-Gordon coefficients, $C(a b c; \alpha \beta \gamma)$ and the Racah coefficients, $W(a b c d; e f)$ are useful:

\[ \sum_{\alpha} C(abc;\alpha,\gamma-\alpha) C(abd;\alpha,\gamma-\alpha) = \delta_{c,d} \quad (2.C-15) \]

\[
(2e+1)(2f+1) \frac{1}{2} W(abcdef;efj) = \sum_{\alpha,\beta} C(abe;\alpha,\beta) C(edc;\alpha+\beta,\gamma-\alpha-\beta) \\
\times C(bdf;\beta,\gamma-\alpha) C(afc;\alpha,\gamma-\alpha) \\
(2.C-16)\]

\[
C(abe;\alpha,\beta) C(edc;\alpha+\beta,\delta) = \sum_{f} (2e+1)(2f+1) \frac{1}{2} W(abcdef;ef) \\
\times C(bdf;\beta,\delta) C(afc;\alpha,\beta+\delta) \\
(2.C-17)\]

\[
\sum_{e} (2e+1)(2f+1) W(abcdef;ef) W(abcd;eg) = \delta_{fg} \\
(2.C-18)\]

Letting \( Q_2 \) operate on the product \((2, \psi(1, 2))\), the integral \( I_2 \) may be written as

\[ I_2 = I_2^{(1)} + I_2^{(2)} \quad (2.C-19) \]

where
\[ I^{(1)}_{2} = -Z_{a} \frac{(4\pi)^{3}}{3} (2)^{\nu_{2}} \sum_{l, k, \ell} \sum_{\ell = 0, M, \omega, \kappa} (-1)^{j + L + \omega + \kappa} \frac{C(L, l, j, l, M, \omega - M)}{[(2L + 1)! (3L - 2L)!]^{1/2}} \]

\[ \times C(k|k'; 00) C(k|k'; q, l) \]

\[ \times \int Y_{1}^{q} Y_{1}^{q} Y_{l}^{q} Y_{l}^{q} Y_{l}^{q} Y_{l}^{q} Y_{l}^{q} Y_{l}^{q} Y_{l}^{q} \int_{k, l}^{2L - 2L} A_{k, l}^{q} \]

(2.C-20)

and

\[ I^{(2)}_{2} = Z_{a} \frac{(4\pi)^{4}}{4} (2)^{\nu_{2}} \sum_{l, k, \ell} \sum_{\ell = 0, \omega, \kappa} (-1)^{j + L + \omega + \kappa} \frac{C(L, l, j, l, M, \omega - M)}{[(2L + 1)! (3L - 2L)!]^{1/2}} \]

\[ \times C(k|k'; 00) C(k|k'; q, -\kappa) \]

\[ \times \int Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} Y_{1}^{q} \int_{k, l}^{2L - 2L} A_{k, l}^{q} \]

(2.C-21)

Integrating over the angles in Eq. (2.C-20) yields

\[ I^{(1)}_{2} = Z_{a} \frac{(4\pi)^{4}}{3} (2)^{\nu_{2}} \sum_{l, k, \ell} \sum_{\ell = 0, l} (-1)^{j} C(l, l, k; -\omega, \omega + q) C(1, 1, k, l, -\omega, \omega + q) \]

\[ \times C(k, k; q, -q) C(l, k; q, -q) C(1, 1, l, 00) C(k|k'; 00) \]

\[ \times C(l|k'; 00) \frac{(2k' + 1)^{k}}{[(2k + 1)!(2 - 2k)!(2k + 1)]^{1/2}} \Theta(k, k') \]

(2.C-22)

27. We have made use of the symmetry relations for the Clebsch-Gordan coefficients, see for example refs. 20 and 2b.
where
\[ \Theta(k,k') = \int_0^\infty \int_0^\infty r_1^{k+k'} r_1^{4-k} A_{k,k'} \Psi_{1,2}^2 \, dr_1 \, dr_2. \] \tag{2.C-23}

Using Eq. (2.C-15) and summing over \( m \) and \( q \) gives
\[ I_{2}^{(1)} = \frac{Z}{4\pi^3/6} \sum_{k=0}^{\infty} \sum_{k'} \left[ \frac{(2k'+1)}{(2k+1)(2-2k)(2k+1)} \right]^{1/2} \times C_{1,1-k,k';0,0} \sqrt{C_{1,k',00}}^2 \Theta(k,k'). \] \tag{2.C-24}

Integrating over the angles in Eq. (2.C-21):
\[ I_{2}^{(2)} = -\frac{Z}{4\pi^3/9} \sum_{k=0}^{\infty} \sum_{k'} \left[ \frac{(2k'+1)}{(2k+1)(2-2k)(2k+1)} \right]^{1/2} \times C_{1,1-L,L_1-M_1,\omega_1,\omega-M} \times C_{1,1-L,L_2-M_2,\omega_2,\omega-M} \times C_{k,k',M,M} \times C_{k,k',0,0} \left[ \frac{(2k'+1)(2k+1)}{(2L+1)(2-2L)} \right]^{1/2} \times N(L,k,k'). \] \tag{2.C-25}

where
\[ N(L,k,k') = \int_0^\infty \int_0^\infty r_1^{k+k'} r_1^{4-k} A_{k,k'} \Psi_{1,2}^2 \, dr_1 \, dr_2. \] \tag{2.C-26}
Summing over \( \omega, \kappa, \mu \) and using Eqs. (2.C-15) and (2.C-16) yields

\[
I_1^{(2)} = -\frac{2^2}{3} (4\pi r^2)^2 \sum_{\kappa, \kappa'} \sum_{L=0}^{L=0} \sum_{p} W(L, \kappa; \kappa') C(\kappa, \kappa'; \omega, 0, 0) \times \n(1, l, 0) C(L, \kappa, 00) C(L, \kappa', 00) \\
\times (2\kappa + 1) \left[ \frac{(2\kappa + 1)(2\kappa' + 1)}{(2L + 1)(2L' + 1)} \right]^{1/2} N(L, \kappa, \kappa'). 
\]

(2.C-27)

Applying Eq. (2.C-17) one can express the product \( \{ C(L, \kappa, 0) C(\kappa, \omega, 0, 0) \} \) in terms of the Racah coefficients \( N(L, \kappa, \kappa') \) then summing over \( p \) and using Eq. (2.C-18) one obtains finally

\[
I_2^{(2)} = -\frac{2^2}{3} (4\pi r^2)^2 \sum_{\kappa, \kappa'} \sum_{L=0}^{L=0} \sum_{p} C(1, l, 1, 0, 0) \left[ C(L, \kappa, 00) C(L, \kappa', 00) \right]^2 \\
\times \left[ \frac{(2\kappa + 1)(2\kappa' + 1)}{(2L + 1)(2L' + 1)} \right]^{1/2} N(L, \kappa, \kappa'). 
\]

(2.C-28)

The techniques illustrated in the evaluation of \( I_2 \) apply equally well to the calculation of the other integrals defined in Eq. (2.C-13). The results for these integrals are:

\[
I_1 = -\frac{2^2}{3} (4\pi r^2)^2 \int_0^\infty \int_0^\infty \frac{r_1^2 r_2^2 \Psi_{(1, 2)}^2}{r_1^5} dr_1 dr_2 \\
+ \frac{2^2}{3} (4\pi r^2)^2 \sum_{\kappa} \left[ C(L, \kappa, 00) \right]^2 M(\kappa) 
\]

(2.C-29)
where

\[ M(k) = \int_0^\infty r_1^2 r_2^2 \frac{\psi_{l_1}(r_1) \psi_{l_2}(r_2)}{r_1^{k+1}} dr_1 dr_2 \quad (2.C-30) \]

\[ I_3 = \frac{(4\pi)^2}{9} Z_a^2 \int_0^\infty \int_0^\infty r_1^4 r_2^2 \psi_{l_1}^2(r_1) dr_1 dr_2 \quad (2.C-31) \]

\[ I_4 = -Z_a^2 \frac{(4\pi)^2}{3}(\frac{2}{3})^{1/2} \sum_k \sum_{L=0}^{k/2} C(1-L,1,0;0,0) \{ C(k,k;0,0) \}^2 \]

\[ \times \left[ \frac{2^{R+1}}{(2L)!(2-2L)!} \right]^{1/2} S(k,L) \quad (2.C-32) \]

\[ S(k,L) = \int_0^\infty \int_0^\infty r_1^{L-k} r_2^{L+2} A_{k,L} \psi_{l_2}^2(r_1) dr_1 dr_2 \quad (2.C-33) \]

\[ I_5 = Z_a^2 \frac{(4\pi)^2}{3} \sum_k \{ C(1,k,0;0,0) \}^2 \frac{M(k)}{k} \quad (2.C-34) \]

\[ I_6 = I_2^{(k)} \quad (2.C-35) \]

The values of the radial integrals appearing in \( I_1, \ldots, I_6 \) are:

\[ \Theta(1,0) = -\frac{9}{2\pi^2} (3)^{1/2} \quad ; \quad \Theta(0,1) = \frac{2}{(3)^2(4)^{3/2}} \pi^2 \]

\[ \Theta(1,2) = \frac{(3)^{1/2}}{3\pi^2} \quad ; \quad \Theta(1,2) = \frac{(3)^{1/2}}{4\pi^2} \]
\[ N(0,0,1) = \frac{3\,3}{(3)^2\pi^2\Pi^3 Z_a} \quad N(1,1,0) = -3N(0,0,1) \]

\[ N(0,2,1) = -\left(\frac{5}{3}\right)^{\frac{1}{2}} \frac{15}{(4)^{\frac{1}{2}}\Pi^2 Z_a} \quad N(1,1,2) = -\frac{3}{5}N(0,2,1) \]

\[ N(1,3,2) = \frac{(21)^{\frac{1}{2}}}{5}N(0,2,1) \]

\[ \int_0^\infty \int_0^\infty \frac{r_1^3 r_2^2}{r_3^5} \Psi^2_{(1,2)} \, dr_1 \, dr_2 = \frac{25}{2(4)^{\frac{1}{2}}\Pi^2} \]

\[ M(0) = \frac{3\,3}{2(4)^{\frac{1}{2}}\Pi^2 Z_a} \quad M(1) = \frac{15}{2(4)^{\frac{1}{2}}\Pi^2 Z_a} \]

\[ \int_0^\infty \int_0^\infty \frac{r_1^4 r_2^2}{r_3^5} \Psi^2_{(1,2)} \, dr_1 \, dr_2 = \frac{3}{(4)^{\frac{1}{2}}\Pi^2 Z_a} \]

\[ S(1,0) = \frac{3}{(5)^{\frac{1}{2}}}N(0,2,1) \quad S(2,1) = N(0,2,1) \]

\[ S(0,1) = N(0,0,1) \]

Finally, evaluating the Clebsch-Gordan coefficients in the expressions for the integrals \( I_1 \), \( I_6 \) we obtain:

\[ I_1 = -\frac{Z_a}{8} \quad I_2 = -\frac{Z_a}{12} \]

\[ I_3 = \frac{Z_a}{12} \quad I_4 = -\frac{Z_a}{12} \]

\[ I_5 = 13\frac{Z_a}{6(4)^2} \quad I_6 = 7\frac{Z_a}{6(4)^2} \]  \hspace{1cm} (2.6.36)