RELATIVISTIC INTERMOLECULAR FORCES*

by

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ABSTRACT

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The generalized Breit-Pauli Hamiltonian is used to give a systematic treatment of magnetic and other relativistic intermolecular energies through $O(\alpha^2)$ (where α 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 α^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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I

RELATIVISTIC INTERMOLECULAR FORCES; GENERAL THEORY

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 $\alpha \sim 1/137$ 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,[1] 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[2] (see Sec. 1.4). One of these energies, of $\Theta(\alpha^2/R^6)$, 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,[3]

$$H = H_e + \alpha^2 H_{rel} \qquad (1.2\text{-}2)$$

where

$$H_{rel} = H_{LL} + H_{SS} + H_{SL} + H_P + H_D' \qquad (1.2\text{-}3)$$

Here H_e is the usual non-relativistic electronic Hamiltonian (we assume the Born-Oppenheimer approximation) and the term linear in α^2 gives the effects of orbit-orbit, spin-spin, and spin-orbit coupling and other relativistic effects. If Ψ 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

$$\mathcal{E}^{(1)} = \alpha^2 \langle \Psi | H_{rel} | \Psi \rangle \qquad (1.2\text{-}4)$$

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[1] H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

[2] C. Mavroyannis and M. J. Stephen, Mol. Phys. 5, 629 (1962).

[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, Ψ, can be written in the form

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

$$\Psi = \sum_{s=0}^{\infty} \frac{\Psi_s}{R^s} \qquad (1.3\text{-}2)$$

In Sec. 1.4 H_{rel} is expanded in powers of 1/R. Then using Eq. (1.3-2) and (1.2-4) we obtain

$$\mathcal{E}^{(1)} = \mathcal{E}_0^{(1)} + \mathcal{E}_{ab}^{(1)} = \mathcal{E}_0^{(1)} + \sum_{s=1}^{\infty} \frac{W_s}{R^s}. \qquad (1.4\text{-}5)$$

Here $\mathcal{E}_0^{(1)}$ gives the relativistic energy of the isolated molecules a and b and $\mathcal{E}_{ab}^{(1)}$ is the relativistic interaction energy (all accurate through $O(\alpha^2)$). The interaction energy (including non-relativistic and relativistic effects) is then given by

$$\mathcal{E}_{ab} = \sum_{s=1}^{\infty} \left(C_s + \alpha^2 W_s \right) / R^s \qquad (1.4\text{-}6)$$

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 $\mathcal{O}(1/R^3)$ 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 ν nuclei and n 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 $\underline{s}_j$ and $\underline{p}_j = 1/i \, \underline{\nabla}_j$, 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 $\underline{r}_{jk} = \underline{r}_j - \underline{r}_k$.

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 ν_a nuclei[4] in molecule a by α and β; the n_b electrons in b by u and t; the ν_b nuclei in b by γ and δ. 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.

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[4] Note that α is also used to denote the fine structure constant. No confusion will result in the context in which this symbol is used here.

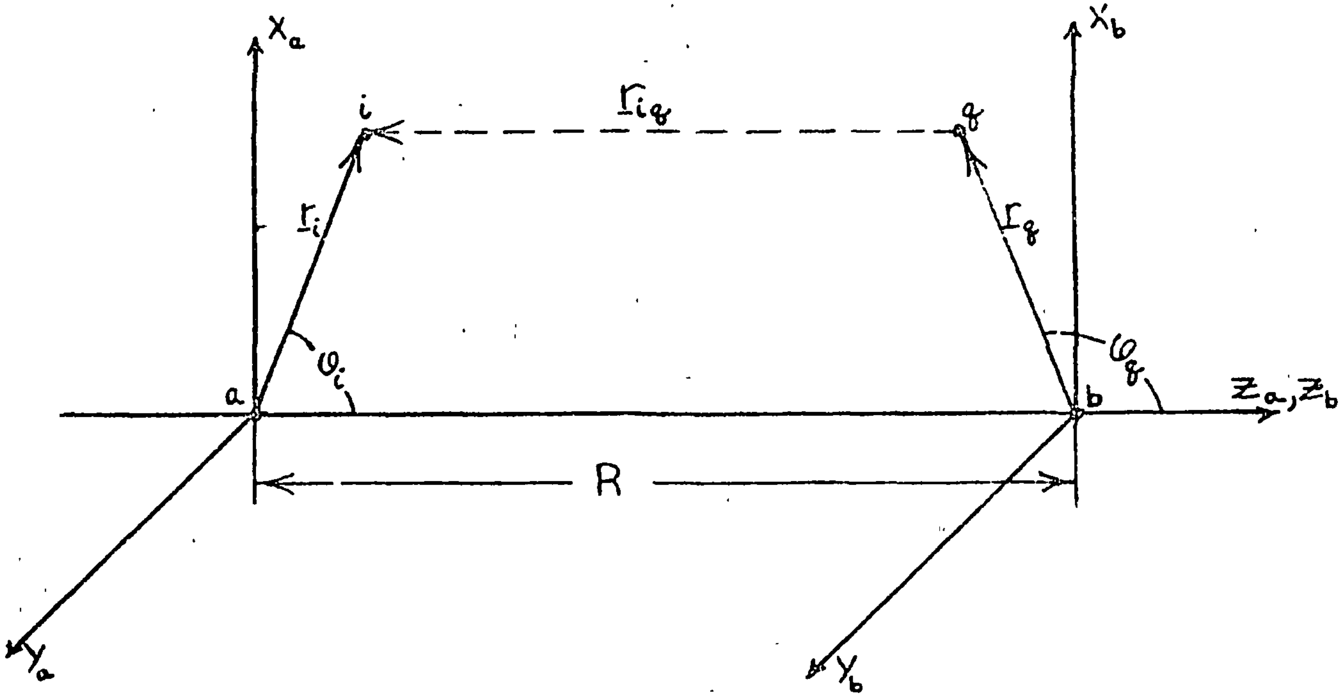

Fig. 1.1-1: Coordinate system used for the computation of molecular interaction energies. Point a is the origin of a right hand coordinate system in molecule a, and i is the location of a charge (nuclear or electronic) in this molecule. Point b is the origin of a right hand coordinate system in molecule 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)[5] the Hamiltonian for the system is assumed to be

$$H_e = -\frac{1}{2}\sum_{j}^{n}\nabla_j^2 - \sum_{j}^{n}\sum_{\beta}^{\nu}\frac{Z_\beta}{r_{j\beta}} + \sum_{k>j}^{n}\frac{1}{r_{jk}} + \sum_{\beta>\alpha}^{\nu}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \qquad (1.2\text{-}1)$$

However, in addition to the non-relativistic Hamiltonian, 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 $\mathcal{O}(\alpha^2)$, can be obtained by using the generalized Breit-Pauli approximation.[6] The generalized Breit-Pauli Hamiltonian has the form

$$H = H_e + \alpha^2 H_{rel} \qquad (1.2\text{-}2)$$

If Ψ and E_e are the electronic non-relativistic wave function

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[5] For a discussion of the approximations introduced by the Born-Oppenheimer approximation, see for example A. Dalgarno and R. McCarroll, Proc. Roy. Soc. A237, 383 (1956); A239, 413 (1957); D. W. Jepson and J. O. Hirschfelder, J. Chem. Phys. 32, 1323 (1960); A. Fröman, J. Chem. Phys. 36, 1490 (1962); W. R. Thorson, J. Chem. Phys. 37, 433 (1962).

[6] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "The Molecular Theory of Gases and Liquids" (John Wiley and Sons, Inc., New York, 1954), p. 1044.

and energy for the system,

$$H_e \Psi = E_e \Psi \quad , \qquad (1.2\text{-}3)$$

then the relativistic correction to E_e, correct through $\mathcal{O}(\alpha^2)$, is[7]

$$\mathcal{E}^{(1)} = \alpha^2 \langle \Psi | H_{rel} | \Psi \rangle \quad . \qquad (1.2\text{-}4)$$

For most practical purposes, this accuracy is sufficient.[8,9] Our paper is specifically concerned with the determination of molecular interaction energies with accuracy through $\mathcal{O}(\alpha^2)$.

The Breit-Pauli Hamiltonian,[10] accurate through $\mathcal{O}(\alpha^2)$, is derived for a two electron atom by Bethe and Salpeter.[11] 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 α^4, α^6, etc. Of course, one cannot obtain corrections of odd order in α 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.

[8] R. McWeeny, "Interpretation of Spin Hamiltonian Parameters", Preprint, March, 1964, Quantum Theory Group, University of Keele, to be published in "Advances in Quantum Chemistry" (edited by P. O. Löwdin, Academic Press, New York, 1965), vol. II.

[9] G. G. Hall and A. T. Amos, "Molecular Orbital Theory of the Spin Properties of Conjugated Molecules", Preprint, May 1964, Quantum Mechanics Group, Department of Mathematics, University of Nottingham.

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

[11] H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms" (Academic Press, New York, 1957), p. 170 et. seq.

generalization to a molecular system is given by Hirschfelder, Curtiss and Bird:[6,12,13]

$$H_{rel} = H_{LL} + H_{SS} + H_{SL} + H_{p} + H'_{D} \,, \tag{1.2-5}$$

$$H_{LL} = -\frac{1}{2}\sum_{k>j} \frac{1}{r_{jk}^3}\left[r_{jk}^2 \underline{p}_j \cdot \underline{p}_k + \underline{r}_{jk}\cdot(\underline{r}_{jk}\cdot\underline{p}_j)\underline{p}_k\right] \tag{1-2.6}$$

$$H_{SS} = \sum_{k>j}\left\{-\frac{8\pi}{3}(\underline{S}_j\cdot\underline{S}_k)\,\delta^{(3)}(\underline{r}_{jk}) + \frac{1}{r_{jk}^5}\left[r_{jk}^2\,\underline{S}_j\cdot\underline{S}_k - 3(\underline{S}_j\cdot\underline{r}_{jk})(\underline{S}_k\cdot\underline{r}_{jk})\right]\right\} \tag{1.2-7}$$

$$H_{SL} = \frac{1}{2}\sum_{\beta,j}\frac{Z_\beta}{r_{j\beta}^3}(\underline{r}_{j\beta}\times\underline{p}_j)\cdot\underline{S}_j - \frac{1}{2}\sum_{k\neq j}\frac{1}{r_{jk}^3}\left[(\underline{r}_{jk}\times\underline{p}_j)\cdot\underline{S}_j - 2(\underline{r}_{jk}\times\underline{p}_k)\cdot\underline{S}_j\right] \tag{1.2-8}$$

$$H_{p} = -\frac{1}{8}\sum_{j} p_j^4 \tag{1.2-9}$$

$$\begin{aligned} H'_{D} = {} & \pi\sum_{j}\left[\sum_{\beta} Z_\beta\,\delta^{(3)}(\underline{r}_{j\beta}) - \sum_{k\neq j}\delta^{(3)}(\underline{r}_{jk})\right] \\ & + \frac{i}{4}\sum_{j}\left[\sum_{\beta}\frac{Z_\beta}{r_{j\beta}^3}(\underline{r}_{j\beta}\cdot\underline{p}_j) - \sum_{k\neq j}\frac{1}{r_{jk}^3}(\underline{r}_{jk}\cdot\underline{p}_j)\right] \,. \end{aligned} \tag{1.2-10}$$

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12. A. Sessler, J. H. Van Vleck, W. Kleiner, H. A. Bethe, J. C. Slater and W. Pauli contributed to the derivation of this form of the Hamiltonian.

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;[14] they are of order α^2/M, where M is a nuclear mass. Also we have assumed that no external electric or magnetic fields are present.[15] The additional terms arising from the effects of external fields are discussed in Appendix 1.D.

The significance of the various terms in the generalized Breit-Pauli Hamiltonian of Eq. (1.2-5) have been discussed by several authors in detail:[6,11,16]

H_{LL} corresponds to the classical electromagnetic[17] coupling of the electrons through the interaction of the magnetic fields

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[14] The effects of nuclear spin are discussed, for example, in the review articles refs. 3 and 9.

[15] The terms arising in the Breit-Pauli Hamiltonian due to the presence of external fields are discussed in ref. 6 and 11.

[16] In particular, the spin Hamiltonians have been discussed and used frequently in problems of chemical interest. See for example the review articles, refs. 8 and 9, and the references given there. In addition see: A. Froman, Phys. Rev. 112, 870 (1958); H. F. Hameka, J. Chem. Phys. 37, 2209 (1962); M. Blume and R. E. Watson, Proc. Roy. Soc. A271, 565 (1963); J. S. Griffith, Phys. Rev. 132, 316 (1963); S. H. Glarum, J. Chem. Phys. 39, 3141 (1963); A. D. McLachlan, Molec. Phys. 6, 441 (1963); R. D. Sharma, J. Chem. Phys. 38, 2350 (1963); M. Blume, A. J. Freeman and R. E. Watson, Phys. Rev. 134, A320 (1964); Lue-Yung Chow Chiu, J. Chem. Phys. 40, 2276 (1964); S. Korde and E. Duval, J. Chem. Phys. 41, 315 (1964); Huang Wu-Han, Lin Fu-Cheng and Zhu Ji-Kang, Proc. Phys. Soc. 84, 661 (1964). The other terms in the Breit-Pauli Hamiltonian do not seem to be used as frequently as the spin Hamiltonians. However, see for example: A. Fröman, Rev. Mod. Phys. 32, 317 (1960); E. Clementi, J. Chem. Phys. 38, 2248 (1963); H. Hartman and E. Clementi, Phys. Rev. 133, A1295 (1964). R. Christoffersen has recently calculated the orbit-orbit coupling in H_2 using the Wang function (to be published in J. Chem. Phys.).

[17] See for example J. D. Jackson, "Classical Electrodynamics" (John Wiley and Sons Inc., New York, 1962), p. 411.

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'_D 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'_D can be replaced by the more useful Hamiltonian H_D;[18]

$$H_D = \frac{\pi}{2}\left[\sum_{\beta}\sum_{j} Z_\beta\, \delta^{(3)}(\underline{r}_{j\beta}) - 2\sum_{k>j} \delta^{(3)}(\underline{r}_{jk})\right] , \qquad (1.2\text{-}11)$$

provided that Ψ obeys the boundary conditions associated with stationary states.

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[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 α^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 α^3 can be obtained by fourth order perturbation theory which correspond 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

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[19] Reference 11, p. 173.

[20] Reference 11, p. 174.

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[21,22] 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[2,23,24] effects. For these values of R the interaction energy, E_{ab}, and the wave function, Ψ, can be written in the form

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

$$\Psi = \sum_{s=0}^{\infty} \frac{\Psi_s}{R^s} , \tag{1.3-2}$$

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21. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "The Molecular Theory of Gases and Liquids" (John Wiley and Sons Inc., New York, 1954), p. 916 et seq.

22. In this treatment we make use of the formalism of Rayleigh-Schrödinger perturbation theory. See for example the review articles: A. Dalgarno, in "Quantum Theory" (edited by D. R. Bates, Academic Press, New York, 1961), vol. I, chap. 5; J. O. Hirschfelder, W. Byers Brown and S. T. Epstein, in "Advances in Quantum Chemistry" (edited by P. O. Löwdin, Academic Press, New York, 1964), p. 225 et seq.

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

24. M. R. Aub, E. A. Power and S. Zienau, Phil. Mag. 2, 571 (1957); E. A. Power and S. Zienau, Nuovo Cim. 6, 7 (1957), I. E. Dzialoshinskii, J. exp. theor. Phys. 3, 977 (1957); A. D. McLachlan, Proc. Roy. Soc. A271, 387 (1963); M. J. Stephen, J. Chem. Phys. 40, 669 (1964).

where the coefficients C_s and Ψ_s are independent of R.

To calculate intermolecular energies it is <u>not</u> 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 <u>most</u> 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.[25] 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[2,23,24] and thus we assume $R \ll \lambda_0$ where $\lambda_0 = hc|\Delta\epsilon|^{-1}$ is the wavelength corresponding to the transition with the largest dipole moment matrix element ($\Delta\epsilon$ being the excitation energy). In atomic units, where λ_0 is in units of a_0 and $\Delta\epsilon$ in units of e^2/a_0, we obtain

$$\lambda_0 = \frac{2\pi}{\alpha}|\Delta\epsilon|^{-1} = 861|\Delta\epsilon|^{-1} .$$

A typical value of $|\Delta\epsilon|$ is 3/8 (corresponding to, H atom,

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[25] Strictly speaking, the interaction between particle j on a and particle t on b leads to $1/R^n$ type energy terms when integrated over those portions of configuration space for which $R > [r_{aj} + r_{bt}]$, the coefficients of $1/R^n$ depending only "weakly" on R. The integration over those regions where $R < [r_{aj} + r_{bt}]$ lead to terms which decrease exponentially with R. See J. S. Dahler and J. O. Hirschfelder, J. Chem. Phys. <u>25</u>, 986 (1956).

2p ⟷ 1s) s that λ_0 is generally of the order of 2300 a_0 . 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

$$H_e \Psi = E_e \Psi \qquad , \qquad (1.2\text{-}3)$$

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

$$H_e = H_0(a) + H_0(b) + V_e \qquad , \qquad (1.3\text{-}3)$$

where

$$H_0(a) = -\frac{1}{2}\sum_j^{n_a} \nabla_j^2 - \sum_j^{n_a}\sum_\alpha^{\nu_a} \frac{Z_\alpha}{r_{j\alpha}} + \sum_{\beta>\alpha}^{\nu_a} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \sum_{k>j}^{n_a} \frac{1}{r_{jk}} \qquad (1.3\text{-}4)$$

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

$$V_e = -\sum_k^{n_a}\sum_\gamma^{\nu_b} \frac{Z_\gamma}{r_{k\gamma}} - \sum_t^{n_b}\sum_\alpha^{\nu_a} \frac{Z_\alpha}{r_{t\alpha}} + \sum_k^{n_a}\sum_t^{n_b} \frac{1}{r_{kt}} + \sum_\alpha^{\nu_a}\sum_\gamma^{\nu_b} \frac{Z_\alpha Z_\gamma}{r_{\alpha\gamma}} \qquad (1.3\text{-}5)$$

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[26] Reference 21, p. 967.

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

$$H_o(a)\varphi(A) = \epsilon(A)\varphi(A) \qquad (1.3\text{-}6)$$

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

$$E_{ab} = E_e - \epsilon(A') - \epsilon(B') \qquad (1.3\text{-}7)$$

Assuming $R > R_a + R_b$, the interaction potential V_e can be expanded[27,28] in powers of $1/R$;

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

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-quadrapole 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

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27. B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 46, 626 (1950).
28. R. J. Buehler and J. O. Hirschfelder, Phys. Rev. 83, 628 (1951); 85, 149 (1952).

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

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

The zero-th order Hamiltonian, H_o, has eigenfunctions $\varphi(A,B)$ and eigenvalues $\epsilon(A,B)$ given by

$$\varphi(A,B) = \varphi(A)\varphi(B) \tag{1.3-10}$$

$$\epsilon(A,B) = \epsilon(A) + \epsilon(B) \tag{1.3-11}$$

Hence our zero-th order wave function is $\Psi^{(0)} = \varphi(A')\varphi(B')$ and the zero-th energy is $E_e^{(0)} = \epsilon(A') + \epsilon(B')$.

Having chosen H_o, the perturbation on H_o is given by the V_e of Eq. (1.3-8). Following the formalism of the Rayleigh-Schrödinger[22] perturbation theory, we write

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

and

$$E_{ab} = \sum_{n=1}^{\infty} E_e^{(n)} \tag{1.3-13}$$

Here $\Psi^{(n)}$ 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 $\varphi(A')$ or $\varphi(B')$ is degenerate, then the zero order function, $\Psi^{(0)} = \varphi(A')\,\varphi(B')$, must be replaced by the proper linear combination of the degenerate zero-th order wave functions.[22]

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

$$\Psi^{(n)} = \sum_{m=n}^{\infty} \frac{\Psi_m^{(n)}}{R^m} \qquad (1.3\text{-}14)$$

and

$$E_e^{(n)} = \sum_{m=n}^{\infty} \frac{D_m^{(n)}}{R^m} \qquad (1.3\text{-}15)$$

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 $E_{ab} = \sum_s C_s/R^s$;

$$C_s = \sum_{m=1}^{s} D_s^{m} \quad , \qquad s \geqslant 1 . \qquad (1.3\text{-}16)$$

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 Ψ_s of $\Psi = \sum_s \Psi_s/R^s$;

$$\Psi_0 = \Psi^{(0)}$$

$$\Psi_s = \sum_{m=1}^{s} \Psi_s^{(m)} \quad , \quad s \geq 1 . \qquad (1.3\text{-}17)$$

We now derive explicitly the wave function, Ψ , 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 ,

$$\left(H_0 - E_e^{(0)}\right)\Psi^{(1)} + \left(V_e - E_e^{(1)}\right)\Psi^{(0)} = 0 \qquad (1.3\text{-}18)$$

with[29]

$$\langle \Psi^{(0)} | \Psi^{(1)} \rangle = 0 \quad . \qquad (1.3\text{-}19)$$

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

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[29] The normalization of the $\Psi^{(n)}$ is the same as that used in refs. 22; namely, that the exact wave function Ψ be normalized to unity through any given order in V_e .

$$E_e^{(1)} = \langle \Psi^{(0)} | V_e | \Psi^{(0)} \rangle \qquad (1.3\text{-}20)$$

$$E_e^{(2)} = \langle \Psi^{(0)} | V_e | \Psi^{(1)} \rangle \qquad (1.3\text{-}21)$$

$$E_e^{(3)} = \langle \Psi^{(1)} | V_e | \Psi^{(1)} \rangle - E_e^{(1)} \langle \Psi^{(1)} | \Psi^{(1)} \rangle \qquad (1.3\text{-}22)$$

Let us now expand $\Psi^{(1)}$ in terms of the eigenfunctions of H_0,[30]

$$\Psi^{(1)} = \sum_{A,B} C(A,B)\, \varphi(A,B) \qquad (1.3\text{-}23)$$

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

$$\Psi^{(1)} = \sum_{A,B}{}' \frac{\langle A,B | V_e | A',B' \rangle}{(E_e^{(0)} - \epsilon(A,B))} \varphi(A)\varphi(B) \qquad (1.3\text{-}24)$$

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

$$\langle A,B | V_e | A',B' \rangle = \int \varphi^*(A)\varphi^*(B)\, V_e\, \varphi(A')\varphi(B')\, d\tau_a\, d\tau_b \qquad (1.3\text{-}25)$$

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[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 V_e given in Eq. (1.3-8),

$$\Psi^{(1)} = \sum_{m=1}^{\infty} \frac{\Psi_m^{(1)}}{R^m} \qquad (1.3\text{-}26)$$

where

$$\Psi_m^{(1)} = \sum_{A,B}{}' \frac{\langle A,B|V_m|A',B'\rangle\, \varphi(A)\varphi(B)}{(E_e^{(0)} - \epsilon(A,B))} \qquad (1.3\text{-}27)$$

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

$$E_e^{(n)} = \sum_{m=n}^{\infty} \frac{D_m^{(n)}}{R^m} \quad , n = 1,2,3 \qquad (1.3\text{-}28)$$

where

$$D_m^{(1)} = \langle \Psi^{(0)}|V_m|\Psi^{(0)}\rangle \qquad (1.3\text{-}29)$$

$$D_m^{(2)} = \sum_{s=1}^{m-1} \langle \Psi^{(0)}|V_s|\Psi_{m-s}^{(1)}\rangle \qquad (1.3\text{-}30)$$

$$D_m^{(3)} = \sum_{s=1}^{m-2}\sum_{r=1}^{m-s-1} \left[\langle \Psi_r^{(1)}|V_s|\Psi_{m-r-s}^{(1)}\rangle - D_r^{(1)}\langle \Psi_s^{(1)}|\Psi_{m-r-s}^{(1)}\rangle\right]. \qquad (1.3\text{-}31)$$

Using the second order perturbation differential equation[22] it is easy to show that

$$\Psi^{(2)} = \sum_{m=2}^{\infty} \frac{\Psi^{(2)}_{m}}{R^{m}} \qquad (1.3\text{-}32)$$

where

$$\Psi^{(2)}_{m} = \sum_{s=1}^{m-1} \left[\sum_{A'',B''}{}' \sum_{A,B}{}' \frac{\langle A,B|V_s|A'',B''\rangle\langle A'',B''|V_{m-s}|A',B'\rangle}{\left(E_e^{(0)}-\epsilon(A'',B'')\right)\left(E_e^{(0)}-\epsilon(A,B)\right)} \varphi(A)\varphi(B) - D_s^{(1)} \sum_{A,B}{}' \frac{\langle A,B|V_{m-s}|A',B'\rangle}{\left(E_e^{(0)}-\epsilon(A,B)\right)^2} \varphi(A)\varphi(B) - \frac{1}{2}\sum_{A,B}{}' \frac{\langle A',B'|V_s|A,B\rangle\langle A,B|V_{m-s}|A',B'\rangle}{\left(E_e^{(0)}-\epsilon(A,B)\right)^2} \Psi^{(0)} \right] \qquad (1.3\text{-}33)$$

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

$$H\Psi = (H_e + \alpha^2 H_{rel})\Psi = \mathcal{E}\Psi \quad , \qquad (1.4\text{-}1)$$

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 $\mathcal{E}$, through order α^2, using H_e as the zero-th order Hamiltonian and α^2 as the natural perturbation parameter. Thus

$$\Psi = \Psi^{(0)} + \alpha^2\Psi^{(1)} \cdots \; ; \quad \mathcal{E} = \mathcal{E}^{(0)} + \alpha^2 \mathcal{E}^{(1)} + \cdots \quad , \qquad (1.4\text{-}2)$$

where

$$\Psi^{(0)} = \Psi \qquad ; \qquad \mathcal{E}^{(0)} = E_e^{(0)} \qquad (1.4\text{-}3)$$

and

$$\mathcal{E}^{(1)} = \langle \Psi | H_{rel} | \Psi \rangle \qquad (1.4\text{-}4)$$

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, $\mathcal{E}^{(1)}$ 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 $\mathcal{E}^{(1)}$ in inverse powers of the intermolecular separation R,

$$\mathcal{E}^{(1)} = \mathcal{E}_0^{(1)} + \mathcal{E}_{ab}^{(1)} = \mathcal{E}_0^{(1)} + \sum_{s=1}^{\infty} \frac{W_s}{R^s} \quad . \tag{1.4-5}$$

Here $\mathcal{E}_0^{(1)}$ gives the relativistic energy of the isolated molecules a and b, and $\mathcal{E}_{ab}^{(1)}$ is the relativistic interaction energy. Thus the intermolecular energy (including both non-relativistic and relativistic terms) is given by

$$\mathcal{E}_{ab} = \sum_{s=1}^{\infty} [C_s + \alpha^2 W_s]/R^s \quad . \tag{1.4-6}$$

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

$$\mathcal{E}^{(1)} = \sum_{\sigma} \mathcal{E}_{\sigma}^{(1)} \quad ; \quad \mathcal{E}_{\sigma}^{(1)} = \langle \Psi | H_{\sigma} | \Psi \rangle \quad . \tag{1.4-7}$$

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

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

$$H_{\sigma} = H_{\sigma,0} + \sum_{m=1}^{\infty} \frac{H_{\sigma,m}}{R^m} \quad . \tag{1.4-8}$$

Here

$$\mathcal{H}_{SL,1} = \mathcal{H}_{SS,1} = \mathcal{H}_{SS,2} = 0$$

$$\mathcal{H}_{P,m} = \mathcal{H}_{D,m} = 0 \qquad , m > 0 . \qquad (1.4\text{-}9)$$

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

$$\mathcal{H}_{\sigma,0} = \mathcal{H}_{\sigma,0}^{(a)} + \mathcal{H}_{\sigma,0}^{(b)} \qquad , \qquad (1.4\text{-}10)$$

where $H_{\sigma,0}^{(a)}$ is the Hamiltonian for the isolated molecule a, corresponding to the relativistic correction σ. The expansion coefficients $\mathcal{H}_{\sigma,m}$, 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 (orbital-current)-(orbital-current) interaction; $H_{LL,2}$ the (orbital-current)-(orbital-dipole) interaction; $H_{LL,3}$ the (orbital-dipole)-(orbital-dipole) and (orbital-current)-(orbital-quadrapole) interaction.

$H_{SS,3}$ gives the (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-quadrapole) interactions.

The $H_{\sigma,m}$ are given explicitly, through $\mathcal{O}(1/R^3)$, in Appendix 1.B.

Let us now expand the $\mathcal{E}_\sigma^{(1)}$ in powers of $1/R$. Equations (1.3-2), (1.4-7) and (1.4-8) give

$$\mathcal{E}_\sigma^{(1)} = \mathcal{E}_{\sigma,0}^{(1)} + \sum_{s=1}^{\infty} \frac{W_{\sigma,s}}{R^s} \tag{1.4-11}$$

where

$$\mathcal{E}_{\sigma,0}^{(1)} = \langle \Psi^{(0)} | H_{\sigma,0} | \Psi^{(0)} \rangle \tag{1.4-12}$$

and

$$W_{\sigma,s} = \sum_{\ell=0}^{s} \sum_{m=0}^{s-\ell} \langle \Psi_m | H_{\sigma,\ell} | \Psi_{s-\ell-m} \rangle \quad , s > 0 \tag{1.4-13}$$

Further, we note that certain terms in $W_{\sigma,s}$ are identically zero, namely, those involving $H_{SL,1} = H_{SS,1} = H_{SS,2} = H_{p,\ell>0} = H_{D,\ell>0} = 0$. Here $\mathcal{E}_{\sigma,0}^{(1)}$ is the energy of the isolated molecules corresponding to the σ-th relativistic correction. Comparing Eq. (1.4-5) with Eqs. (1.4-7) and (1.4-11) gives $\mathcal{E}_0^{(1)}$ and the coefficients W_s of $\mathcal{E}_{ab}^{(1)} = \sum_s W_s/R^s$;

$$\mathcal{E}_0^{(1)} = \sum_\sigma \mathcal{E}_{\sigma,0}^{(1)} \quad ; \quad W_s = \sum_\sigma W_{\sigma,s} \tag{1.4-14}$$

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 α^2/R^6, has the form

$$\mathcal{E}_{ab} = \alpha^2 \frac{W_4}{R^4} + \frac{C_6}{R^6} + \alpha^2 \frac{W_6}{R^6} + \cdots \qquad (1.4\text{-}15)$$

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,[31] but they have not been studied systematically. Three of the orbital-magnetic interaction terms were obtained by Mavroyannis and Stephen.[2] Using field theoretic techniques they obtained the interaction energies:[32]

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[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 ($R \gg \lambda_0$) where retardation becomes important.

$$U_2 = \frac{\alpha^2}{3R^6} \sum_{A,B}{}' \frac{\langle A'|\underline{\mu}(a)|A\rangle \langle A|\underline{L}(a)|A'\rangle \langle B'|\underline{\mu}(b)|B\rangle \langle B|\underline{L}(b)|B'\rangle}{\left(E_e^{(0)} - \epsilon(A,B)\right)} \tag{1.4-16}$$

$$U_3 = \frac{-\alpha^4}{18R^4} \sum_{A,B}{}' \frac{[\epsilon(A')-\epsilon(A)][\epsilon(B')-\epsilon(B)]}{\left(E_e^{(0)} - \epsilon(A,B)\right)} \times \left\{ |\langle A'|\underline{\mu}(a)|A\rangle|^2 |\langle B'|\underline{L}(b)|B\rangle|^2 + |\langle A'|\underline{L}(a)|A\rangle|^2 |\langle B'|\underline{\mu}(b)|B\rangle|^2 \right\} \tag{1.4-17}$$

$$U_4 = \frac{\alpha^4}{24R^6} \sum_{A,B}{}' \frac{|\langle A'|\underline{L}(a)|A\rangle|^2 |\langle B'|\underline{L}(b)|B\rangle|^2}{\left(E_e^{(0)} - \epsilon(A,B)\right)} \tag{1.4-18}$$

Here $\underline{\mu}(a)$ and $\underline{L}(a)$ 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 α^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 α^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 α^2. However, it is clear that many interesting new interaction energies arise from our treatment. Indeed, these lower order (in α) terms should dominate in problems of chemical interest.

Appendix 1.A: Expansion of H_{rel} and V_e in Inverse Powers of the Intermolecular Separation.

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 $R > R_a + R_b$.[33] 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[34] and A. R. Edmonds.[35]

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.[36] The expansion coefficients for V_e are well known and have been discussed by several authors[27,28,37] (see Sec. 1.A-e).

Expansion Coefficients of H_{rel}

The relativistic Hamiltonians H_σ, for σ = LL, SS, SL, p, D can be expanded in powers of 1/R;

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[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.

[34] M. E. Rose, "Elementary Theory of Angular Momentum" (John Wiley and Sons, Inc., New York, 1957).

[35] A. R. Edmonds, "Angular Momentum in Quantum Mechanics" (Princeton University Press, Princeton, New Jersey, 1957).

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

[37] M. E. Rose, J. Math. and Phys. 37, 215 (1958).

$$H_{\sigma} = H_{\sigma,0} + \sum_{m=1}^{\infty} \frac{H_{\sigma,m}}{R^{m}} \quad , \qquad (1.4\text{-}8)$$

where

$$H_{SL,1} = H_{SS,1} = H_{SS,2} = 0$$

$$H_{P,m} = H_{D,m} = 0 \quad , \quad m > 0 \, , \qquad (1.4\text{-}9)$$

and

$$H_{\sigma,0} = H_{\sigma,0}^{(a)} + H_{\sigma,0}^{(b)} \qquad (1.4\text{-}10)$$

Here $H_{\sigma,0}^{(a)}$ is the Hamiltonian for the isolated molecule a, corresponding to the relativistic correction σ . 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. <u>Expansion Coefficients of the Orbit-Orbit Hamiltonian, H_{LL}</u>

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

$$H_{LL,0}^{(a)} = -\frac{1}{2} \sum_{k>j}^{n_a} \frac{1}{r_{jk}^{3}} \left[r_{jk}^{2} \underline{p}_j \cdot \underline{p}_k + \underline{r}_{jk} \cdot (\underline{r}_{jk} \cdot \underline{p}_j) \underline{p}_k \right] \quad , \qquad (1.A\text{-}1)$$

with an analogous equation for molecule b. For many purposes it is more convenient to write $H_{LL,0}(a)$ as contractions of irreducible spherical tensors. We write

$$\underline{\rho}_j \cdot \underline{\rho}_k = \sum_{\omega} (-1)^{\omega}\, T_1^{\omega}(\underline{\rho}_j)\, T_1^{-\omega}(\underline{\rho}_k) \tag{1.A-2}$$

$$\underline{r}_{jk} \cdot \underline{\rho}_j = \left(\frac{4\pi}{3}\right)^{1/2} \sum_{\omega} (-1)^{\omega}\, \mathcal{Y}_1^{\omega}(\underline{r}_{jk})\, T_1^{-\omega}(\underline{\rho}_j) \quad , \tag{1.A-3}$$

where the solid spherical harmonic, $\mathcal{Y}_l^m(\underline{r})$, is defined by[38]

$$\mathcal{Y}_l^m(\underline{r}) = r^l\, Y_l^m(\theta,\phi) \quad . \tag{1.A-4}$$

Here $\omega = 0, \pm 1$ and the spherical components, $T_1^{\omega}(\underline{A})$, of a vector $\underline{A}$ are defined in terms of the ordinary Cartesian components by[39]

$$T_1^{\pm 1}(\underline{A}) = \mp \frac{1}{(2)^{1/2}}(A_x \pm iA_y)$$

$$T_1^{0}(\underline{A}) = A_z \quad . \tag{1.A-5}$$

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[38] The phase convention we use for the spherical harmonics, $Y_l^m(\theta,\phi)$, 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 $Y_l^m(\theta,\phi)$; see ref. 38.

Using Eq. (1.A-3) we write

$$\mathbf{r}_{jk}\cdot(\mathbf{r}_{jk}\cdot\boldsymbol{\rho}_j)\boldsymbol{\rho}_k = \frac{4\pi}{3}\sum_{\omega}\sum_{\kappa}(-1)^{\omega+\kappa}\mathcal{Y}_1^{\omega}(\mathbf{r}_{jk})\,\mathcal{Y}_1^{\kappa}(\mathbf{r}_{jk})\,T_1^{-\omega}(\boldsymbol{\rho}_j)\,T_1^{-\kappa}(\boldsymbol{\rho}_k). \tag{1.A-6}$$

The coupling rule for spherical harmonics gives

$$\mathcal{Y}_1^{\omega}(\mathbf{r}_{jk})\,\mathcal{Y}_1^{\kappa}(\mathbf{r}_{jk}) = r_{jk}^2\sum_{\ell}\frac{3}{[4\pi(2\ell+1)]^{1/2}}\,C(11\ell;\omega\kappa)\,C(11\ell;00) \times Y_{\ell}^{\omega+\kappa}(\theta_{jk},\phi_{jk}) \quad . \tag{1.A-7}$$

In Eq. (1.A-7), $C(\ell_1\ell_2\ell_3;m_1m_2)$, is a Clebsch-Gordon coefficient[40] and $\ell = 0,2$. It should be noted that

$$C(\ell_1\ell_2\ell_3;m_1m_2) \equiv C(\ell_1\ell_2\ell_3;m_1,m_2,m_1+m_2) = 0 \tag{1.A-8}$$

unless

$$\ell_3 = \ell_1+\ell_2,\ \ell_1+\ell_2-1,\ \cdots\ |\ell_1-\ell_2| \tag{1.A-9}$$

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[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, 1959).

and

$$|m_1| \le l_1 \quad , \quad |m_2| \le l_2 \quad , \quad |m_1 + m_2| \le l_3 \tag{1.A-10}$$

Equations (1.A-1), (1.A-2), (1.A-6) and (1.A-7) yield

$$H_{LL,0}^{(a)} = -\left(\frac{\pi}{3}\right)^{1/2} \sum_{k>j} \frac{1}{r_{jk}} \left[\begin{array}{l} 4 \sum_{\omega} (-1)^{\omega} Y_0^0(\vartheta_{jk},\phi_{jk})\, T_1^{\omega}(\rho_j)\, T_1^{-\omega}(\rho_k) \\ + \left(\frac{6}{5}\right)^{1/2} \sum_{\omega,\kappa} (-1)^{\omega+\kappa} C(112;\omega\kappa) \\ \qquad \times Y_2^{\omega+\kappa}(\vartheta_{jk},\phi_{jk})\, T_1^{-\omega}(\rho_j)\, T_1^{-\kappa}(\rho_k) \end{array} \right] \tag{1.A-11}$$

where

$$C(112,\omega\kappa) = \frac{1}{(6)^{1/2}} \left[\frac{(2+\omega+\kappa)!\,(2-\omega-\kappa)!}{(1+\omega)!\,(1-\omega)!\,(1+\kappa)!\,(1-\kappa)!} \right]^{1/2} . \tag{1.A-12}$$

From the form of Eq. (1.A-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

$$\begin{aligned} T_0^0(\rho_j\rho_k) &= \sum_{\omega} C(110;\omega,-\omega)\, T_1^{\omega}(\rho_j)\, T_1^{-\omega}(\rho_k) \\ &= -\frac{1}{(3)^{1/2}} \sum_{\omega} (-1)^{\omega}\, T_1^{\omega}(\rho_j)\, T_1^{-\omega}(\rho_k) \end{aligned} \tag{1.A-13}$$

and the second rank tensor

$$T_2^{-\kappa}(\rho_j\rho_k) = \sum_{\omega} C(112;-\omega,-\kappa+\omega)\, T_1^{-\omega}(\rho_j)\, T_1^{-\kappa+\omega}(\rho_k) . \qquad (1.A\text{-}14)$$

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

$$H_{LL,0}^{(a)} = \sum_{k>j} \frac{1}{r_{jk}} \left\{ \frac{2}{(3)^{1/2}} T_0^0(\rho_j\rho_k) - \left(\frac{2\pi}{15}\right)^{1/2} \sum_{\kappa} (-1)^{\kappa} Y_2^{\kappa}(\theta_{jk},\phi_{jk})\, T_2^{-\kappa}(\rho_j\rho_k) \right\} .$$
(1.A-15)

Constructing the invariant

$$W_0^0(\mathbf{r}_{jk}^2\rho_j\rho_k) = \sum_{\kappa} C(220;\kappa,-\kappa)\, Y_2^{\kappa}(\mathbf{r}_{jk})\, T_2^{-\kappa}(\rho_j\rho_k)$$

$$= \frac{1}{(5)^{1/2}} \sum_{\kappa} (-1)^{\kappa}\, Y_2^{\kappa}(\mathbf{r}_{jk})\, T_2^{-\kappa}(\rho_j\rho_k) \qquad (1.A\text{-}16)$$

we obtain

$$H_{LL,0}^{(a)} = \frac{2}{(3)^{1/2}} \sum_{k>j} \frac{1}{r_{jk}^3} \left\{ r_{jk}^2\, T_0^0(\rho_j\rho_k) - \left(\frac{\pi}{2}\right)^{1/2} W_0^0(\mathbf{r}_{jk}^2\rho_j\rho_k) \right\} . \qquad (1.A\text{-}17)$$

Equation (1.A-17) shows explicitly that $H_{LL,0}^{(a)}$ is a scalar invariant.

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

$$\sum_{m=1}^{\infty} \frac{H_{LL,m}}{R^m} = -\frac{1}{2} \sum_{k}^{n_a} \sum_{t}^{n_b} \frac{1}{r_{kt}^3} \left[r_{kt}^2\, \rho_k \cdot \rho_t + \mathbf{r}_{kt} \cdot (\mathbf{r}_{kt} \cdot \rho_k) \rho_t \right] . \qquad (1.A\text{-}18)$$

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

$$\sum_{m=1}^{\infty} \frac{H_{LL,m}}{R^m} = \sum_{k,t} \left\{ H_{LL}^{(1)}(k,t) + H_{LL}^{(2)}(k,t) \right\} \qquad (1.A\text{-}19)$$

where

$$H_{LL}^{(1)}(k,t) = -\frac{2}{3}\frac{1}{r_{kt}} \sum_{\omega} (-1)^{\omega}\, T_1^{\omega}(\rho_k)\, T_1^{-\omega}(\rho_t) \qquad (1.A\text{-}20)$$

$$H_{LL}^{(2)}(k,t) = \left(\frac{2\pi}{15}\right)^{1/2} \frac{1}{r_{kt}} \sum_{\omega,\kappa} (-1)^{\omega+\kappa}\, C(112,\omega\kappa)\, Y_2^{\omega+\kappa}(\vartheta_{kt},\phi_{kt}) \times T_1^{-\omega}(\rho_k)\, T_1^{-\kappa}(\rho_t) \qquad (1.A\text{-}21)$$

Clearly

$$H_{LL,m} = \sum_{k,t} \left\{ H_{LL,m}^{(1)}(k,t) + H_{LL,m}^{(2)}(k,t) \right\} \qquad (1.A\text{-}22)$$

To expand $H_{LL}^{(2)}(k,t)$ in powers of $1/R$ we must first expand $Y_2^{\omega+\kappa}(\vartheta_{kt},\phi_{kt})$ in spherical harmonics of (ϑ_k,ϕ_k) and (ϑ_t,ϕ_t). This is easily done by generalizing the corresponding one center result of Rose[37] and one obtains

$$Y_{\lambda}^{\mu}(\vartheta_{kt},\phi_{kt}) = \frac{1}{r_{kt}^{\lambda}} \sum_{\sigma=0}^{\lambda} \sum_{\tau=0}^{\lambda-\sigma} \sum_{\rho=-\sigma}^{\sigma} A(\lambda,\mu,\sigma,\tau,\rho; r_k, r_t) \times R^{\lambda-\sigma-\tau}\, Y_{\sigma}^{\rho}(\vartheta_k,\phi_k)\, Y_{\tau}^{\mu-\rho}(\vartheta_t,\phi_t) \qquad (1.A\text{-}23)$$

where

$$A(\lambda,\mu;\sigma,\tau,\rho;r_k,r_t) = (-1)^{\lambda-\sigma} r_k^{\sigma} r_t^{\tau}$$

$$\times\left[\frac{4\pi(2\lambda+1)(\lambda+\mu)!(\lambda-\mu)!}{(2\sigma+1)(2\tau+1)\{(\lambda-\sigma-\tau)!\}^2(\sigma+\rho)!(\sigma-\rho)!(\tau-\mu+\rho)!(\tau+\mu-\rho)!}\right]^{1/2} \qquad (1.A\text{-}24)$$

Also needed is the two center expansion of $\frac{1}{r_{kt}^n}$ for $n>0$. Sack[41] has recently shown that[42]

$$\frac{1}{r_{kt}^n} = \sum_{\substack{\ell_1,\ell_2,\ell_3=0\\ \ell_1+\ell_2+\ell_3\ \text{even}}}^{\infty} \sum_{m_1=-\ell_1}^{\ell_1} \sum_{s,g=0}^{\infty} \frac{G(n,\ell_1,\ell_2,\ell_3;m_1;s,g;r_k,r_t)}{R^{n+\ell_1+\ell_2+2s+2g}}$$

$$\times\, Y_{\ell_1}^{m_1}(\theta_k,\phi_k)\, Y_{\ell_2}^{-m_1}(\theta_t,\phi_t) \qquad (1.A\text{-}25)$$

where

$$G(n;\ell_1,\ell_2,\ell_3;m_1;s,g;r_k,r_t) = 4\pi(-1)^{\ell_1}(-1)^{\frac{1}{2}(\ell_1+\ell_2+\ell_3)}K(\ell_1,\ell_2;\ell_3;m_1)$$

$$\times\, N(n,\ell_1,\ell_2,\ell_3;s,g;r_k,r_t) \qquad (1.A\text{-}26)$$

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41. R. A. Sack, J. Math. Phys. **5**, 245 (1964); **5**, 252 (1964); **5**, 260 (1964); see also P. R. Fontana, J. Math. Phys. **2**, 825 (1961); Y. N. Chiu, J. Math. Phys. **2**, 283 (1964).

42. This expression (for n=1) agrees with the earlier work of refs. 27, 28 and 37.

$$K(l_1,l_2,l_3,m_1) = \frac{[\frac{1}{2}(l_1+l_2+l_3)]!}{[\frac{1}{2}(l_1+l_2-l_3)]!\,[\frac{1}{2}(l_1+l_3-l_2)]!\,[\frac{1}{2}(l_2+l_3-l_1)]!}$$

$$\times\left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)(l_1+l_2-l_3)!\,(l_1+l_3-l_2)!\,(l_2+l_3-l_1)!}{(l_1+l_2+l_3+1)!}\right]^{1/2}$$

$$\times\, C(l_1 l_2 l_3;-m_1,m_1) \qquad (1.A-27)$$

$$N(n;l_1,l_2,l_3;s,g;r_k,r_t) = \frac{2^{l_1+l_2-s-g}\,\Gamma[\frac{1}{2}(n+l_1+l_2+l_3)+s+g]}{\Gamma(\frac{n}{2})\,\Gamma[\frac{1}{2}(n-1)]\,(2l_1+2s+1)!!\,(2l_2+2g+1)!!\,s!\,g!}$$

$$\times\,\Gamma[\tfrac{1}{2}(n+l_1+l_2-l_3-1)+s+g]\; r_k^{2s+l_1}\, r_t^{2g+l_2}$$

(1.A-28)

Here $\Gamma(x)$ is the Gamma function and $(2k)!! = 2\cdot4\cdots 2k = 2^k k!$; $(2k+1)!! = 1\cdot3\cdots(2k+1) = 2^{k+1}\,\Gamma(k+3/2)/\Gamma(1/2)$, where k is an integer. For n=1 Eq. (1.A-25) simplifies greatly.

$$\frac{1}{r_{kt}} = \sum_{l_1,l_2=0}^{\infty}\ \sum_{m_1=-l_1}^{l_1} \frac{G(1;l_1,l_2,l_1+l_2;m_1;0,0;r_k,r_t)}{R^{1+l_1+l_2}}$$

$$\times\, Y_{l_1}^{m_1}(\theta_k,\phi_k)\; Y_{l_2}^{-m_1}(\theta_t,\phi_t) \qquad (1.A-29)$$

$$G(1;l_1,l_2,l_1+l_2;m_1;0,0,r_k,r_t) = \frac{4\pi(-1)^{l_2}(l_1+l_2)!\, r_k^{l_1}\, r_t^{l_2}}{\left[(2l_1+1)(2l_2+1)(l_1-m_1)!(l_1+m_1)!(l_2-m_1)!(l_2+m_1)!\right]^{1/2}} \tag{1.A-30}$$

The results of Eqs. (1.A-23) and (1.A-25) now enable us to expand $H_{LL}^{(1)}(k,t)$ and $H_{LL}^{(2)}(k,t)$ in powers of $1/R$.

Using Eqs. (1.A-20) and (1.A-29)

$$H_{LL}^{(1)}(k,t) = -\frac{2}{3}\sum_{l_1,l_2}\sum_{m_1}\sum_{\omega}(-1)^{\omega}G(1,l_1,l_2,l_1+l_2;m_1;0,0;r_k,r_t)/R^{1+l_1+l_2}$$
$$\times Y_{l_1}^{m_1}(\theta_k,\phi_k)\,Y_{l_2}^{-m_1}(\theta_t,\phi_t)\,T_1^{\omega}(\rho_k)\,T_1^{-\omega}(\rho_t) \tag{1.A-31}$$

Next define a tensor operator, $\Omega_u^{\nu}(\underline{r}^l\rho)$, of rank u;

$$\Omega_u^{\nu}(\underline{r}^l\rho) = \sum_m C(l1u;m,\nu-m)\,Y_l^m(\underline{r})\,T_1^{\nu-m}(\rho) \tag{1.A-32}$$

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

$$Y_l^m(\underline{r})\,T_1^{\nu-m}(\rho) = \sum C(l1u;m,\nu-m)\,\Omega_u^{\nu}(\underline{r}^l\rho) \tag{1.A-33}$$

Thus

$$H^{(1)(k,t)}_{LL,m_1} = -\frac{2}{3}\sum_{\{\eta\}} (-1)^{\omega} G(1; l_1, l_2, l_1+l_2; m_1; 0, 0; r_k, r_t)$$

$$\times C(l_1, 1, u; m_1, \omega)\, C(l_2, 1, q; -m_1, -\omega)\, r_k^{-l_1} r_t^{-l_2}$$

$$\times \Omega_u^{m_1+\omega}(\underline{r}_k^{l_1} \rho_k)\, \Omega_q^{-m_1-\omega}(\underline{r}_t^{l_2} \rho_t) \qquad (1.A\text{-}34)$$

In general the summation is over the set of indices $\{\eta\}$, given by[43]

$$l_1, l_2 = 0, 1, \cdots, \infty\,;\; m_1 = -l_1, -l_1+1, \cdots, l_1\,;\; \omega = 0, \pm 1\,;$$

$$u = l_1+1, l_1, \cdots, |l_1-1| \;;\; q = l_2+1, l_2, \cdots, |l_2-1|$$

with

$$l_1 + l_2 + 1 = m \qquad (1.A\text{-}35)$$

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

$$H^{(2)(k,t)}_{LL} = -\left(\frac{2\pi}{15}\right)^{1/2} \sum_{l_1, l_2, l_3}\; \sum_{m_1, s, g}\; \sum_{\sigma=0}^{2}\; \sum_{\tau=0}^{2-\sigma}\; \sum_{\varrho, \omega, \kappa} (-1)^{\omega+\kappa}$$

$$\times G(3; l_1, l_2, l_3; m_1; s, g; r_k, r_t)\, A(2, \omega+\kappa; \sigma, \tau, \varrho; r_k, r_t)$$

$$\times C(112; \omega\kappa)\, Y_{l_1}^{m_1}(\vartheta_k, \phi_k)\, Y_{\sigma}^{\varrho}(\vartheta_k, \phi_k)\, T_1^{-\omega}(\rho_k)$$

$$\times Y_{l_2}^{-m_1}(\vartheta_t, \phi_t)\, Y_{\tau}^{\omega+\kappa-\varrho}(\vartheta_t, \phi_t)\, T_1^{-\kappa}(\rho_t) / R^{1+l_1+l_2+2s+2g+\sigma+\tau}$$

$$(1.A\text{-}36)$$

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[43] Usually the summation will be restricted further by the conditions given by Eqs. (1.A-10).

Let us define

$$D(n,\{\chi\}) = (-1)^{\omega+\kappa} G(n;l_1,l_2,l_3;m_1;s,g,r_k,r_t) A(2,\omega+\kappa,\sigma,\tau,\rho;r_k,r_t)$$

$$\times C(112;\omega\kappa)\left[\frac{(2l_1+1)(2\sigma+1)}{4\pi(2q+1)}\right]^{1/2} C(l_1,\sigma,q;m_1,\rho)$$

$$\times C(l_1,\sigma,q;0,0)\left[\frac{(2l_2+1)(2\tau+1)}{4\pi(2f+1)}\right]^{1/2} C(l_2,\tau,f;-m_1,\omega+\kappa-\rho)$$

$$\times C(l_2,\tau,f;0,0) \qquad (1.A\text{-}37)$$

where $\{\chi\}$ 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

$$H^{(2)}_{LL,m}(\hat{k},t) = -\left(\frac{2\pi}{15}\right)^{1/2}\sum_{\{\chi\},u,v} D(3,\{\chi\})\, r_k^{-q} r_t^{-f}\, C(q1u;m_1+\rho,-\omega)$$

$$\times C(f1v,\omega+\kappa-m_1-\rho,-\kappa)\,\Omega_u^{m_1+\rho-\omega}(r_k^{q}\rho_k)\,\Omega_v^{-m_1-\rho+\omega}(r_t^{f}\rho_t)\,. \qquad (1.A\text{-}38)$$

In general the summation in Eq. (1.A-38) is over the set of indices, $\{\chi\}$, and u and v ;[43]

$$\{\chi\}:\ l_1,l_2,s,g=0,1,\cdots,\infty\ ;\quad l_3=l_1+l_2,\, l_1+l_2-1,\cdots,|l_1-l_2|,$$

$$l_1+l_2+l_3 \text{ even}\ ;\ m_1=-l_1,-l_1+1,\cdots,l_1\ ;\ \sigma=0,1,2\ ;\ \tau=0,1,\cdots,(2-\sigma);$$

$$\rho=-\sigma,-\sigma+1,\cdots,\sigma;\ \omega,\kappa=0,\pm1\ ;\ q=l_1+\sigma,\, l_1+\sigma-1,\cdots,|l_1-\sigma|,$$

$$q+l_1+\sigma \text{ even}\ ;\ f=l_2+\tau,\, l_2+\tau-1,\cdots,|l_2-\tau|,\ f+l_2+\tau \text{ even}\ ,$$

(1.A-39)

with

$$1 + l_1 + l_2 + 2s + 2q + \sigma + \tau = m \quad , \qquad (1.A\text{-}40)$$

$$u = q+1,\ q,\ \cdots,\ |q-1| \quad ; \quad v = f+1,\ f,\ \cdots,\ |f-1| \qquad (1.A\text{-}41)$$

Using Eqs. (1.A-22), (1.A-34) and (1.A-38) it is relatively easy to obtain the $H_{LL,m}$, particularly for small m. $H_{LL,m}$, for m=1,2,3, is given explicitly in Appendix 1.B both 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

$$H^{(a)}_{SS,0} = \sum_{k>j}^{n_a} \left\{ -\frac{8\pi}{3} (\underline{S}_j \cdot \underline{S}_k)\, \delta^{(3)}(\underline{r}_{jk}) + \frac{1}{r^5_{jk}} \left[r^2_{jk}\, \underline{S}_j \cdot \underline{S}_k - 3(\underline{S}_j \cdot \underline{r}_{jk})(\underline{S}_k \cdot \underline{r}_{jk}) \right] \right\} \qquad (1.A\text{-}42)$$

Analogous to the derivation of Eq. (1.A-11) it is easy to show that[8,44]

$$H^{(a)}_{SS,0} \sum_{k>j} \left[\begin{array}{l} -\frac{8\pi}{3}\, \delta^{(3)}(\underline{r}_{jk}) \sum_{\omega} (-1)^{\omega}\, T_1^{-\omega}(\underline{S}_j)\, T_1^{\omega}(\underline{S}_k) \\ -\left(\frac{24\pi}{5}\right)^{1/2} \frac{1}{r^3_{jk}} \sum_{\omega,\kappa} (-1)^{\omega+\kappa}\, C(112;\omega\kappa)\, Y_2^{\omega+\kappa}(\theta_{jk},\phi_{jk}) \\ \qquad \times\, T_1^{-\omega}(\underline{S}_j)\, T_1^{-\kappa}(\underline{S}_k) \end{array} \right] \qquad (1.A\text{-}43)$$

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44. P. R. Fontana, Phys. Rev. 125, 220 (1962).

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

$$H_{SS,0}^{(a)} = \sum_{k>j} \left[\begin{array}{l} +\frac{8\pi}{(3)^{1/2}} \delta^{(3)}(\underline{r}_{jk}) \, T_0^0(\underline{S}_j \underline{S}_k) \\ -\left(\frac{24\pi}{5}\right)^{1/2} \frac{1}{r_{jk}^3} \sum_{\kappa} (-1)^{\kappa} Y_2^{\kappa}(\theta_{jk}, \phi_{jk}) \, T_2^{-\kappa}(\underline{S}_j \underline{S}_k) \end{array} \right] . \qquad (1.A\text{-}44)$$

The tensors $T_0^0(\underline{S}_j \underline{S}_k)$ and $T_2^{-\kappa}(\underline{S}_j \underline{S}_k)$ are defined by Eqs. (1.A-13) and (1.A-14), respectively, and $\delta^{(3)}(\underline{r}_{jk})$ is a scalar.

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

$$\sum_{m=3}^{\infty} \frac{H_{SS,m}}{R^m} = \sum_{k}^{m_a} \sum_{t}^{m_b} \frac{1}{r_{kt}^5} \left[r_{kt}^2 \, \underline{S}_k \cdot \underline{S}_t - 3(\underline{S}_k \cdot \underline{r}_{kt})(\underline{S}_t \cdot \underline{r}_{kt}) \right] . \qquad (1.A\text{-}45)$$

Expressed in irreducible tensorial form we obtain

$$\sum_{m=3}^{\infty} \frac{H_{SS,m}}{R^m} = \sum_{k,t} H_{SS}(k,t) = \sum_{k,t} \sum_{m=3}^{\infty} \frac{H_{SS,m}^{(kt)}}{R^m} \qquad (1.A\text{-}46)$$

where

$$H_{SS}(k,t) = -\left(\frac{24\pi}{5}\right)^{1/2} \frac{1}{r_{kt}^3} \sum_{\omega,\kappa} (-)^{\omega+\kappa} C(112;\omega\kappa) \, Y_2^{\omega+\kappa}(\theta_{kt},\phi_{kt}) \, T_1^{-\omega}(\underline{S}_k) \, T_1^{-\kappa}(\underline{S}_t) . \qquad (1.A\text{-}47)$$

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

$$H_{SS,m}^{(k,t)} = -\left(\frac{24\pi}{5}\right)^{1/2} \sum_{\{\chi\}} D(5,\{\chi\}) \, Y_g^{m_1+\rho}(\theta_k,\phi_k) \, T_1^{-\omega}(\underline{S}_k)$$

$$\times \, Y_f^{-m_1-\rho+\omega+\kappa}(\theta_t,\phi_t) \, T_1^{-\kappa}(\underline{S}_t) . \qquad (1.A\text{-}48)$$

Here the summation is over the set of indices, $\{\chi\}$, given by Eq. (1.A-39) with[43]

$$3+l_1+l_2+2s+2\gamma+\sigma+\tau=m \qquad (1.A-49)$$

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 $\Omega_u^{\nu}(r^{g}s)$ of rank u (see Eq. (1.A-32)) and proceeding as in the derivation of Eq. (1.A-38) we obtain

$$H_{SS,m}(k,t) = -\left(\frac{24\pi}{5}\right)^{1/2}\sum_{\{\chi\},u,v} D(s,\{\chi\})\, r_k^{-g}\, r_t^{-f}\, C(g1u;m_1+\rho,-\omega)$$
$$\times C(f1v;\omega+\kappa-m_1-\rho,-\kappa)\,\Omega_u^{m_1+\rho-\omega}(\underline{r}_k^{g}\underline{S}_k)\,\Omega_v^{-m_1-\rho+\omega}(\underline{r}_t^{f}\underline{S}_t)\,. \qquad (1.A-50)$$

The restriction on the summation indices u and v 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, is given by

$$H_{SL,0}^{(a)} = \frac{1}{2}\sum_{\alpha}^{N_a}\sum_{j}^{n_a}\frac{Z_\alpha}{r_{j\alpha}^3}(\underline{r}_{j\alpha}\times\underline{p}_j)\cdot\underline{S}_j$$
$$-\frac{1}{2}\sum_{k\neq j}^{n_a}\frac{1}{r_{jk}^3}\left[(\underline{r}_{jk}\times\underline{p}_j)\cdot\underline{S}_j-2(\underline{r}_{jk}\times\underline{p}_k)\cdot\underline{S}_j\right] \qquad (1.A-51)$$

The irreducible tensor components of the vector $\underline{r}\times\underline{p}$ are given by

$$T_1^{\omega}(\underline{r}\times\underline{p}) = \left(\frac{8\pi}{3}\right)\frac{1}{i}\,\Omega_1^{\omega}(\underline{r}\,\underline{p}) \tag{1.A-52}$$

where $\Omega_1^{\omega}(\underline{r}\,\underline{p})$ is defined by Eq. (1.A-32). Hence

$$\begin{aligned} H^{1(a)}_{SL,0} = {} & \frac{1}{2}\sum_{\alpha}\sum_{j}\frac{Z_\alpha}{r_{j\alpha}^3}\sum_{\omega}(-1)^{\omega}\,T_1^{\omega}(\underline{r}_{j\alpha}\times\underline{p}_j)\,T_1^{-\omega}(\underline{s}_j) \\ & -\frac{1}{2}\sum_{k\neq j}\frac{1}{r_{jk}^3}\sum_{\omega}(-1)^{\omega}\left[T_1^{\omega}(\underline{r}_{jk}\times\underline{p}_j)-2\,T_1^{\omega}(\underline{r}_{jk}\times\underline{p}_k)\right]T_1^{-\omega}(\underline{s}_j) \end{aligned} \tag{1.A-53}$$

From Eqs. (1.A-[illegible]), (1.A-8) and (1.A-10) we obtain

$$\begin{aligned} \sum_{m=2}^{\infty}\frac{H_{SL,m}}{R^m} = {} & \sum_{\gamma}^{\gamma_b}\sum_{k}^{n_a} H^{(1)}_{SL,m}(k,\gamma) + \sum_{\alpha}^{\gamma_a}\sum_{t}^{n_b} H^{(2)}_{SL,m}(\alpha,t) \\ & + \sum_{k}^{n_a}\sum_{t}^{n_b}\left\{H^{(3)}_{SL,m}(k,t) + H^{(4)}_{SL,m}(k,t)\right\} \end{aligned} \tag{1.A-54}$$

where

$$H^{(1)}_{SL}(k,\gamma) = \frac{Z_\gamma}{2r_{k\gamma}^3}(\underline{r}_{k\gamma}\times\underline{p}_k)\cdot\underline{s}_k \tag{1.A-55}$$

$$H^{(2)}_{SL}(\alpha,t) = \frac{Z_\alpha}{2r_{t\alpha}^3}(\underline{r}_{t\alpha}\times\underline{p}_t)\cdot\underline{s}_t \tag{1.A-56}$$

$$H^{(3)}_{SL}(k,t) = -\frac{1}{2r_{kt}^3}\left[(\underline{r}_{kt}\times\underline{p}_k)\cdot\underline{s}_k - 2(\underline{r}_{kt}\times\underline{p}_t)\cdot\underline{s}_k\right] \tag{1.A-57}$$

$$H^{(4)}_{SL}(k,t) = -\frac{1}{2r_{kt}^3}\left[(\underline{r}_{tk}\times\underline{p}_t)\cdot\underline{s}_t - 2(\underline{r}_{tk}\times\underline{p}_k)\cdot\underline{s}_t\right] \tag{1.A-58}$$

Analogous to the derivation of Eq. (1 A-53) it is clear that

$$H_{SL}^{(1)}(k,\gamma) = \frac{Z_\gamma}{2 r_{k\gamma}^3} \sum_{\omega}^{1} (-1)^{\omega} T_1^{\omega}(\underline{r}_{k\gamma} \times \underline{p}_k)\, T_1^{-\omega}(\underline{s}_k) \quad \text{(1.A-59)}$$

Let us define

$$\begin{aligned}\tilde{K}(k,\gamma,\{\epsilon\}) &= (-1)^{\omega} G(3;\ell_1,\ell_2,\ell_3;m_1;s,g;r_k,r_\gamma)\, A(1,\kappa;\sigma,\tau,\rho;r_k,r_\gamma)\\ &\times C(111;\kappa,\omega-\kappa)\left[\frac{(2\ell_1+1)(2\sigma+1)}{4\pi(2q+1)}\right]^{1/2} C(\ell_1,\sigma,q;m_1,\rho)\\ &\times C(\ell_1,\sigma,q;00)\left[\frac{(2\ell_2+1)(2\tau+1)}{4\pi(2f+1)}\right]^{1/2} C(\ell_2,\tau,f;-m_1,\kappa-\rho)\\ &\times C(\ell_2,\tau,f;00)\end{aligned} \quad \text{(1.A-60)}$$

where $\{\epsilon\}$ is the set of summation indices on which K depends (see Eq. (1.A-65)). Then using Eqs. (1.A-32), (1.A-52), (1.A-59) and proceeding as in the derivation of $H_{LL,m}$, it is easy to show that

$$\begin{aligned}H_{SL,m}^{(1)}(k,\gamma) &= \frac{Z_\gamma}{i}\left(\frac{2\pi}{3}\right)^{1/2} \sum_{\{\epsilon\}}^{1} \tilde{K}(k,\gamma,\{\epsilon\})\, r_k^{-q}\\ &\times \sum_{u=|q-1|}^{q+1} C(q1u;m_1+\rho,\omega-\kappa)\, \Omega_u^{m_1+\rho+\omega-\kappa}(\underline{r}_k^{q}\underline{p}_k)\, T_1^{-\omega}(\underline{s}_k)\, Y_f^{-m_1-\rho+\kappa}(\theta_\gamma,\phi_\gamma)\end{aligned} \quad \text{(1.A-61)}$$

Similarly one can readily show that

$$H^{(2)}_{SL,m}(\alpha,t) = -\frac{Z_\alpha}{i}\left(\frac{2\pi}{3}\right)^{1/2}\sum_{\{\epsilon\}}\tilde{K}(\alpha,t,\{\epsilon\})\, r_t^{-f}$$

$$\times\sum_{u=|f-1|}^{f+1} C(f1u,-m_1-\rho+\kappa,\omega-\kappa)\, Y_g^{m_1+\rho}(\theta_\alpha,\phi_\alpha)\,\Omega_u^{-m_1-\rho+\omega}(\underline{r}_t^f\rho_t)\,\overline{T}_1^{-\omega}(\underline{s}_t)\;;$$

(1.A-62)

$$H^{(3)}_{SL,m}(k,t) = -\frac{1}{i}\left(\frac{2\pi}{3}\right)^{1/2}\sum_{\{\epsilon\}}\tilde{K}(k,t,\{\epsilon\})$$

$$\times\left[\begin{array}{l} r_k^{-g}\displaystyle\sum_{u=|g-1|}^{g+1} C(g1u;m_1-\rho,\omega-\kappa)\,\Omega_u^{m_1+\rho+\omega-\kappa}(\underline{r}_k^g\rho_k)\,\overline{T}_1^{-\omega}(\underline{s}_k)\,Y_f^{-m_1-\rho+\kappa}(\theta_t,\phi_t) \\ -2r_t^{-f}\displaystyle\sum_{u=|f-1|}^{f+1} C(f1u,-m_1-\rho+\kappa,\omega-\kappa)\,Y_g^{m_1+\rho}(\theta_k,\phi_k)\,\overline{T}_1^{-\omega}(\underline{s}_k)\,\Omega_u^{-m_1-\rho+\omega}(\underline{r}_t^f\rho_t) \end{array}\right]$$

(1.A-63)

$$H^{(4)}_{SL,m}(k,t) = +\frac{1}{i}\left(\frac{2\pi}{3}\right)^{1/2}\sum_{\{\epsilon\}}\tilde{K}(k,t,\{\epsilon\})$$

$$\times\left[\begin{array}{l} r_t^{-f}\displaystyle\sum_{u=|f-1|}^{f+1} C(f1u,-m_1-\rho+\kappa,\omega-\kappa)\,Y_g^{m_1+\rho}(\theta_k,\phi_k)\,\Omega_u^{-m_1-\rho+\omega}(\underline{r}_t^f\rho_t)\,\overline{T}_1^{-\omega}(\underline{s}_t) \\ -2r_k^{-g}\displaystyle\sum_{u=|g-1|}^{g+1} C(g1u,m_1+\rho,\omega-\kappa)\,\Omega_u^{m_1+\rho+\omega-\kappa}(\underline{r}_k^g\rho_k)\,Y_f^{-m_1-\rho+\kappa}(\theta_t,\phi_t)\,\overline{T}_1^{-\omega}(\underline{s}_t) \end{array}\right]$$

(1.A-64)

The first summation in Eqs. (1.A-61)-(1.A-64) is over the set of indices, $\{\varepsilon\}$, given by[43]

$$l_1, l_2, s, g = 0, 1, \cdot\cdot, \infty ; \quad l_3 = l_1 + l_2, l_1 + l_2 - 1, \quad , |l_1 - l_2| ,$$

$$l_1 + l_2 + l_3 \text{ even} \quad ; m_1 = -l_1, -l_1 + 1, \cdots, l_1 ; \sigma = 0, 1 ; \tau = 0, 1, (1-\sigma) ;$$

$$\rho = -\sigma, -\sigma + 1, \cdots, \sigma ; \omega, \kappa = 0, \pm 1 ; q = l_1 + \sigma, l_1 + \sigma - 1, \cdots, |l_1 - \sigma| ,$$

$$l_1 + \sigma + q \text{ even} \quad ; f = l_2 + \tau, l_2 + \tau - 1, \cdots, |l_2 - \tau| , l_2 + \tau + f \text{ even},$$

$$(1.A\text{-}65)$$

with

$$2 + l_1 + l_2 + 2s + 2g + \sigma + \tau = m \quad . \qquad (1.A\text{-}66)$$

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

$$H_{0,0}^{(a)} = H_p^{(a)} = -\frac{1}{8} \sum_{k}^{n_a} p_k^4 \qquad (1.A\text{-}67)$$

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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.

$$H_{p,m} = 0 \quad , m > 0 \tag{1.A-68}$$

$$H_{D,0}^{(a)} = \frac{\pi}{2}\left\{ \sum_{k}^{n_a} \sum_{\alpha}^{N_a} Z_\alpha \, \delta^{(3)}(\underline{r}_{k\alpha}) - 2 \sum_{k>j}^{n_a} \delta^{(3)}(\underline{r}_{kj}) \right\} \tag{1.A-69}$$

$$H_{D,m} = 0 \quad , m > 0 \tag{1.A-70}$$

$H_p^{(a)}$ 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

$$V_e = \sum_{i,q} \frac{e_i e_q}{r_{iq}} \tag{1.A-71}$$

Here $\frac{e_i e_q}{r_{iq}}$ is the Coulombic interaction between a particle (nuclei or electron) of charge e_i in molecule a and another particle of charge e_q in molecule b. Then for $R > R_a + R_b$ we may write

$$V_e = \sum_{m=1}^{\infty} \frac{V_m}{R^m} \tag{1.A-72}$$

where

$$V_m = \sum_{i,q} e_i e_q \sum_{l_1,l_2} \sum_{m_1} G(1; l_1, l_2, l_1+l_2; m_1; 0, 0; r_i, r_q) \times Y_{l_1}^{m_1}(\theta_i, \phi_i)\, Y_{l_2}^{-m_1}(\theta_q, \phi_q) \quad , \tag{1.A-73}$$

$$l_1, l_2 = 0, 1, \ldots, \infty \;,\quad m_1 = -l_1, -l_1+1, \ldots, l_1$$

$$1 + l_1 + l_2 = n \qquad (1.A\text{-}34)$$

and $G(1; l_1, l_2, l_1+l_2; m_1, 0, 0, r_k, r_t)$ is given by Eq. (1.A-30). The significance of the expansion coefficients, V_n, is well known.[1,21,37] They represent the interaction of the various electrostatic multipoles of molecule a with those of molecule b.

Appendix 1.B: Summary of the Expansion Coefficients of H_{rel} through $O(1/R^3)$.

The expansion coefficients of H_{rel} are derived in general in Appendix 1.A. Here the $H_{\sigma,m}$ are given explicitly for σ = LL,SS,SL and $m \neq 0$, through $O(1/R^3)$, both in irreducible tensorial form and in terms of Cartesian coordinates. The coefficients $H_{\sigma,0}$ are given explicitly in Appendix 1.A.

1. Expansion Coefficients of H_{rel} in Irreducible Tensorial Form

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

$$S_1^m(a) = \sum_k^{n_a} T_1^m(\underline{s}_k) \; ; \quad P_1^m(a) = \sum_k^{n_a} T_1^m(\underline{p}_k) \; , \quad r_1^m(a) = \sum_k^{n_a} T_1^m(\underline{r}_k) \tag{1.B-1}$$

$$D_2^m(a) = \left(\frac{4\pi}{3}\right)^{1/2} \sum_k^{n_a} \Omega_2^m(\underline{r}_k \underline{p}_k) = \sum_k^{n_a} T_2^m(\underline{r}_k \underline{p}_k) \tag{1.B-2}$$

$$L_1^m(a) = \sum_k^{n_a} T_1^m(\underline{r}_k \times \underline{p}_k) = \sum_k T_1^m(\underline{l}_k) = \frac{\sqrt{2}}{i} D_1^m(a) \; ; \tag{1.B-3}$$

$$\gamma_1^m(a) = \sum_k^{n_a} \left\{ T_1^m(\underline{r}_k^2 \underline{p}_k) + \left(\frac{5}{3}\right)^{1/2} r_k^2 \, T_1^m(\underline{p}_k) \right\} \; ; \tag{1.B-4}$$

$$\gamma_2^m(a) = \sum_k^{n_a} T_2^m(\underline{r}_k^2 \underline{p}_k) \; ; \quad \gamma_3^m(a) = \sum_k^{n_a} T_3^m(\underline{r}_k^2 \underline{p}_k) \tag{1.B-5}$$

where

$$T_l^m(r_k^2 p_k) = \left(\frac{8\pi}{15}\right)^{1/2} \Omega_l^m(r_k^2 p_k) \quad ; \qquad (1.B\text{-}6)$$

$$\left[T_l^m(k)\, T_{l'}^{m'}(k)\right]_a = \sum_{k}^{n_a} T_l^m(k)\, T_{l'}^{m'}(k) \quad , \qquad (1.B\text{-}7)$$

with analogous definitions for molecule b. In Eq. (1.B-7) the tensor $T_l^m(k)$ is a function of the coordinates of electron k. The tensors Ω_l^m are defined by Eq. (1.A-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;

$$P_{ab}\, f(a,b) = f(b,a) \quad . \qquad (1.B\text{-}8)$$

Expansion Coefficients of the Orbit-Orbit Hamiltonian, H_{LL}

$$H_{LL,1} = -\frac{1}{2}\left[1 + P_{ab}\right]\left[\mathcal{P}_1^0(a)\mathcal{P}_1^0(b) - \mathcal{P}_1^{-1}(a)\mathcal{P}_1^1(b)\right] \qquad (1.B\text{-}9)$$

$$H_{LL,2} = +\frac{1}{2}\left[1 - P_{ab}\right]\left[i\, L_1^{-1}(a)\mathcal{P}_1^1(b) - i\, L_1^1(a)\mathcal{P}_1^{-1}(b) - (6)^{1/2} D_2^0(a)\mathcal{P}_1^0(b)\right] \qquad (1.B\text{-}10)$$

$$H_{LL,3} = C_{LL,3} + F_{LL,3} + G_{LL,3} \qquad (1.B\text{-}11)$$

where

$$C_{LL,3} = -\tfrac{1}{4}\left[1+P_{ab}\right]\left[L_1^0(a)\,L_1^0(b) + L_1^{-1}(a)\,L_1^1(b)\right] \qquad (1.B\text{-}12)$$

$$F_{LL,3} = +\tfrac{3}{2}\left[1+P_{ab}\right]\left[\begin{array}{l}\dfrac{i}{(2)^{1/2}}\left\{D_2^{-1}(a)\,L_1^1(b) - D_2^1(a)\,L_1^{-1}(b)\right\} \\ + D_2^{-1}(a)\,D_2^1(b) + D_2^0(a)\,D_2^0(b)\end{array}\right] \qquad (1.B\text{-}13)$$

$$G_{LL,3} = \frac{1}{2(15)^{1/2}}\left[1+P_{ab}\right]\left[\begin{array}{l}2\left\{\mathcal{T}_1^0(a) - 3(6)^{1/2}\,\mathcal{T}_3^0(a)\right\}\ell_1^0(b) \\ +\left\{\mathcal{T}_1^1(a) - 3(5)^{1/2}\,\mathcal{T}_2^1(a) - 3\,\mathcal{T}_3^1(a)\right\}\ell_1^{-1}(b) \\ +\left\{\mathcal{T}_1^{-1}(a) + 3(5)^{1/2}\,\mathcal{T}_2^{-1}(a) - 3\,\mathcal{T}_3^{-1}(a)\right\}\ell_1^1(b)\end{array}\right]$$

(1.B-14)

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

$$H_{SS,1} = 0 \qquad , \qquad H_{SS,2} = 0 \qquad (1.B\text{-}15)$$

$$H_{SS,3} = -\left[1+P_{ab}\right]\left[S_1^0(a)\,S_1^0(b) + S_1^{-1}(a)\,S_1^1(b)\right] \qquad (1.B\text{-}16)$$

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

$$H_{SL,1} = 0 \qquad (1.B\text{-}17)$$

$$H_{SL,2} = \frac{\left[1-P_{ab}\right]}{i}\left[\begin{array}{l}\tfrac{1}{2}(Z_a - n_a)\left[T_1^1(\underline{p}_t)\,T_1^{-1}(\underline{s}_t) - T_1^{-1}(\underline{p}_t)\,T_1^1(\underline{s}_t)\right]_b \\ + \ell_1^1(a)\,S_1^{-1}(b) - \ell_1^{-1}(a)\,S_1^1(b)\end{array}\right]$$

(1.B-18)

where

$$Z_a = \sum_{\alpha}^{\nu_a} Z_\alpha \quad ; \quad Z_b = \sum_{\gamma}^{\nu_b} Z_\gamma \qquad (1.B-19)$$

$$H_{SL,3} = C_{SL,3} + F_{SL,3} + G_{SL,3} \qquad (1.B-20)$$

where

$$C_{SL,3} = -\frac{1}{2}[1+P_{ab}]\left[2L^{0}_{1}(a)S^{0}_{1}(b) + L^{-1}_{1}(a)S^{1}_{1}(b) + L^{1}_{1}(a)S^{-1}_{1}(b)\right] \qquad (1.B-21)$$

$$F_{SL,3} = [1+P_{ab}]\left[\begin{array}{l} \frac{(Z_a - n_a)}{4}\left[\begin{array}{l} T^{-1}_{1}(\underline{r}_t)\,T^{1}_{1}(\underline{s}_t) + T^{1}_{1}(\underline{r}_t)\,T^{-1}_{1}(\underline{s}_t) + 2\,T^{0}_{1}(\underline{r}_t)\,T^{0}_{1}(\underline{s}_t) \\ -\frac{6i}{(2)^{1/2}}\left\{T^{-1}_{2}(\underline{r}_t\underline{\rho}_t)\,T^{1}_{1}(\underline{s}_t) - T^{1}_{2}(\underline{r}_t\underline{\rho}_t)\,T^{-1}_{1}(\underline{s}_t)\right\} \end{array}\right] \\ +\frac{3i}{(2)^{1/2}}\left\{D^{-1}_{2}(a)S^{1}_{1}(b) - D^{1}_{2}(a)S^{-1}_{1}(b)\right\} \end{array}\right] \qquad (1.B-22)$$

$$G_{SL,3} = \frac{i}{2}[1+P_{ab}]\left[\begin{array}{l} r^{-1}_{1}(a)\left[T^{1}_{1}(\underline{\rho}_t)\,T^{0}_{1}(\underline{s}_t) - T^{0}_{1}(\underline{\rho}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b - r^{1}_{1}(a)\left[T^{-1}_{1}(\underline{\rho}_t)\,T^{0}_{1}(\underline{s}_t) - T^{0}_{1}(\underline{\rho}_t)\,T^{-1}_{1}(\underline{s}_t)\right]_b \\ +2r^{0}_{1}(a)\left[T^{1}_{1}(\underline{\rho}_t)\,T^{-1}_{1}(\underline{s}_t) - T^{-1}_{1}(\underline{\rho}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b - 2\rho^{-1}_{1}(a)\left[T^{1}_{1}(\underline{r}_t)\,T^{0}_{1}(\underline{s}_t) + 2\,T^{0}_{1}(\underline{r}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b \\ +2\rho^{1}_{1}(a)\left[T^{-1}_{1}(\underline{r}_t)\,T^{0}_{1}(\underline{s}_t) + 2\,T^{0}_{1}(\underline{r}_t)\,T^{-1}_{1}(\underline{s}_t)\right]_b + 2\rho^{0}_{1}(a)\left[T^{1}_{1}(\underline{r}_t)\,T^{-1}_{1}(\underline{s}_t) - T^{-1}_{1}(\underline{r}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b \end{array}\right]$$

$$-\frac{i}{2}[1+P_{ab}]\sum_{\alpha}^{\nu_a} Z_\alpha \left[\begin{array}{l} T^{-1}_{1}(\underline{r}_\alpha)\left[T^{1}_{1}(\underline{\rho}_t)\,T^{0}_{1}(\underline{s}_t) - T^{0}_{1}(\underline{\rho}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b \\ -T^{1}_{1}(\underline{r}_\alpha)\left[T^{-1}_{1}(\underline{\rho}_t)\,T^{0}_{1}(\underline{s}_t) - T^{0}_{1}(\underline{\rho}_t)\,T^{-1}_{1}(\underline{s}_t)\right]_b \\ +2\,T^{0}_{1}(\underline{r}_\alpha)\left[T^{1}_{1}(\underline{\rho}_t)\,T^{-1}_{1}(\underline{s}_t) - T^{-1}_{1}(\underline{\rho}_t)\,T^{1}_{1}(\underline{s}_t)\right]_b \end{array}\right]$$

(1.B-23)

The $H_{\sigma,m}$, σ = LL, SS, SL and $m \neq 0$, represent the interaction of various orbital and spin magnetic multipoles[47] of molecule a with those of molecule b. We have written the $H_{\sigma,3}$ in the form $H_{\sigma,3} = C_{\sigma,3} + F_{\sigma,3} + G_{\sigma,3}$. Here $C_{\sigma,3}$ is the coefficient of the $1/R^3$ term that one would expect from the usual magnetic dipole-dipole interaction:[6]

$$H^{(int)} = \frac{\alpha^2}{4R^3}\left[\underline{M}(a)\cdot\underline{M}(b) - 3\,M_z(a)\,M_z(b)\right] \tag{1.B-24}$$

$$\underline{M}(a) = \underline{L}(a) + 2\,\underline{S}(a) \quad , \tag{1.B-25}$$

where $\underline{L}(a)$ and $\underline{S}(a)$ are, respectively, the electronic orbital and spin angular momentum operators for molecule a. Thus $F_{\sigma,3}$ and $G_{\sigma,3}$ may be regarded as correction terms to the semi-classical result of Eq. (1.B-24). It should be noted that $F_{SS,3} = G_{SS,3} = 0$.

b. Expansion Coefficients of H_{rel} in Cartesian Coordinate Form

To simplify the results we use the following notation:

$$\underline{S}(a) = \sum_{k}^{n_a} \underline{s}_k \;;\quad \underline{P}(a) = \sum_{k}^{n_a} \underline{p}_k \;;\quad \underline{r}(a) = \sum_{k}^{n_a} \underline{r}_k \tag{1.B-26}$$

$$\underline{L}(a) = \sum_{k}^{n_a} \underline{l}_k = \sum_{k}^{n_a} \underline{r}_k \times \underline{p}_k \;;\quad [cdf]_a = \sum_{k}^{n_a} c_k d_k f_k \;, \tag{1.B-27}$$

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

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[47] Magnetic multipole moments have recently been discussed by M. Mizushima, Phys. Rev. 134, A883 (1964).

$$H_{LL,1} = -\frac{1}{2}\left[\underline{\ell}(a)\cdot\underline{\ell}(b) + \ell_z^{(a)}\ell_z^{(b)}\right] \qquad (1.B\text{-}28)$$

$$H_{LL,2} = \frac{1}{2}\left[1-P_{ab}\right]\left[L_x^{(a)}\ell_y^{(b)} - L_y^{(a)}\ell_x^{(b)} + \left[\underline{r}\cdot\underline{\rho} - 3z\rho_z\right]_a \ell_z^{(b)}\right] \qquad (1.B\text{-}29)$$

$$H_{LL,3} = C_{LL,3} + F_{LL,3} + G_{LL,3} \qquad (1.B\text{-}29)$$

where

$$C_{LL,3} = \frac{1}{4}\left[\underline{L}^{(a)}\underline{L}^{(b)} - 3L_z^{(a)}L_z^{(b)}\right] \qquad (1.B\text{-}30)$$

$$F_{LL,3} = \left[1+P_{ab}\right]\left[\begin{array}{l} \frac{1}{2}[x\rho_x]_a[y\rho_y]_b - [x\rho_x + y\rho_y - z\rho_z]_a[z\rho_z]_b \\ +\frac{1}{4}\left\{[x\rho_x]_a[x\rho_x]_b + [y\rho_y]_a[y\rho_y]_b\right\} \\ +\frac{3}{4}\left\{[z\rho_x + x\rho_z]_a L_y^{(b)} - [y\rho_z + z\rho_y]_a L_x^{(b)}\right\} \\ -\frac{3}{8}\left\{[y\rho_z + z\rho_y]_a[y\rho_z + z\rho_y]_b + [z\rho_x + x\rho_z]_a[z\rho_x + x\rho_z]_b\right\} \end{array}\right]$$

(1.B-31)

$$G_{LL,3} = \left[1+P_{ab}\right]\left[\begin{array}{l} \frac{1}{4}\left[y^2\rho_x - x^2\rho_x - 2z^2\rho_x - 2xy\rho_y + 4xz\rho_z\right]_a \ell_x^{(b)} \\ +\frac{1}{4}\left[x^2\rho_y - y^2\rho_y - 2z^2\rho_y - 2xy\rho_x + 4yz\rho_z\right]_a \ell_y^{(b)} \\ +\left[r^2\rho_z - 2z^2\rho_z + xz\rho_x + yz\rho_y\right]_a \ell_z^{(b)} \end{array}\right]$$

(1.B-32)

$$H_{SS,3} = \underline{S}(a)\cdot\underline{S}(b) - 3\,S_z(a)\,S_z(b) \qquad (1.B\text{-}33)$$

$$H_{SL,2} = \left[1-P_{ab}\right]\left[\tfrac{1}{2}\left(Z_a - n_a\right)\left[p_x S_y - p_y S_x\right]_b + \ell_x(a)\,S_y(b) - \ell_y(a)\,S_x(b)\right] \qquad (1.B\text{-}34)$$

$$H_{SL,3} = C_{SL,3} + F_{SL,3} + G_{SL,3} \qquad (1.B\text{-}35)$$

where

$$C_{SL,3} = \tfrac{1}{2}\left[1+P_{ab}\right]\left[\underline{L}(a)\;\underline{S}(b) - 3\,L_z(a)\,S_z(b)\right] \qquad (1.B\text{-}36)$$

$$F_{SL,3} = \tfrac{1}{2}\left[1+P_{ab}\right]\left[\begin{array}{l}\left(Z_a - n_a\right)\left[\underline{\ell}\cdot\underline{S} - 3z p_x S_y + 3z p_y S_x\right]_b \\ 6\left[z p_x\right]_a S_y(b) - 6\left[z p_y\right]_a S_x(b) - 3\,\underline{L}(a)\cdot\underline{S}(b) + 3\,L_z(a)\,S_z(b)\end{array}\right] \qquad (1.B\text{-}37)$$

$$G_{SL,3} = \tfrac{1}{2}\left[1+P_{ab}\right]\left[\begin{array}{l}X(a)\left[p_y S_z - p_z S_y\right]_b + Y(a)\left[p_z S_x - p_x S_z\right]_b - 2Z(a)\left[p_x S_y - p_y S_x\right]_b \\ -2\,\ell_x(a)\left[2zS_y + yS_z\right]_b + 2\,\ell_y(a)\left[2zS_x + xS_z\right]_b - 2\,\ell_z(a)\left[yS_x - xS_y\right]_b\end{array}\right]$$

$$-\tfrac{1}{2}\left[1+P_{ab}\right]\sum_{\alpha}^{N_a} Z_\alpha\left[\begin{array}{c}X_\alpha\left[p_y S_z - p_z S_y\right]_b + Y_\alpha\left[p_z S_x - p_x S_z\right]_b \\ -2\,Z_\alpha\left[p_x S_y - p_y S_x\right]_b\end{array}\right] \qquad (1.B\text{-}38)$$

Appendix 1.C: Some Useful Irreducible Spherical Tensors.

In Appendix 1.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[48] of rank ℓ has $(2\ell+1)$ components, T_ℓ^m, with $m = -\ell, -\ell+1, \cdots, \ell$, which satisfy the commutator relations[49]

$$[J_x \pm iJ_y , T_\ell^m] = [(\ell \mp m)(\ell \pm m+1)]^{1/2} T_\ell^{m\pm 1} \qquad (1.C\text{-}1)$$

$$[J_z , T_\ell^m] = m T_\ell^m \qquad (1.C\text{-}2)$$

Here $\underline{J}$ is an angular momentum operator, $\underline{J} = \sum_k \underline{j}_k$, and we are primarily concerned with $\underline{J} = \underline{L}$ and $\underline{J} = \underline{S}$. For a tensor operator of rank one, $\underline{A}$, the irreducible spherical components are given by Eq. (1.A-5).

Now let $T_{\ell_1}^{m_1}(R_1)$ and $T_{\ell_2}^{m_2}(R_2)$ 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[34,35]

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

[49] This definition of irreducible tensors is due to G. Racah, Phys. Rev. <u>61</u>, 186 (1942); <u>62</u>, 438 (1942); <u>63</u>, 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.

$$T_{l}^{m}(R_1 R_2) = \sum_{m_1} C(l_1 l_2 l; m_1, m-m_1)\, T_{l_1}^{m_1}(R_1)\, T_{l_2}^{m-m_1}(R_2) \tag{1.C-3}$$

Using Eq. (1.C-3) one can construct irreducible tensor operators of any desired rank. Equations (1.C-1) and (1.C-2) provide a convenient check on the tensors so obtained.

The irreducible tensors relevant to the results of Appendix 1.B can be written down by comparison with the following tensors.[50]

$$T_0^0(\underline{A}\underline{B}) = -\frac{1}{(3)^{1/2}}\, \underline{A}\cdot\underline{B} \tag{1.C-4}$$

$$T_1^1(\underline{A}\underline{B}) = \frac{1}{2}(A_z B_x - A_x B_z + iA_z B_y - iA_y B_z) \tag{1.C-5}$$

$$T_1^0(\underline{A}\underline{B}) = \frac{i}{(2)^{1/2}}(A_x B_y - A_y B_x) \tag{1.C-6}$$

$$T_1^{-1}(\underline{A}\underline{B}) = \frac{1}{2}(A_z B_x - A_x B_z - iA_z B_y + iA_y B_z) \tag{1.C-7}$$

$$T_2^2(\underline{A}\underline{B}) = \frac{1}{2}(A_x B_x - A_y B_y + iA_x B_y + iA_y B_x) \tag{1.C-8}$$

$$T_2^1(\underline{A}\underline{B}) = -\frac{1}{2}(A_z B_x + A_x B_z + iA_z B_y + iA_y B_z) \tag{1.C-9}$$

$$T_2^0(\underline{A}\underline{B}) = \frac{1}{(6)^{1/2}}(-\underline{A}\cdot\underline{B} + 3A_z B_z) \tag{1.C-10}$$

---

[50] Here $T_l^m(\underline{A}\underline{B}\cdots)$ is the irreducible spherical tensor of rank l formed by coupling the components of the first rank tensors $T_1^m(\underline{A}), T_1^m(\underline{B}), \cdots$. The tensors $T_l^m(\underline{A}\underline{B})$ were taken from ref. 8 (see also C. 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).

$$T_2^{-1}(\underline{A}\,\underline{B}) = \frac{1}{2}\left(A_zB_x + A_xB_z - iA_zB_y - iA_yB_z\right) \tag{1.C-11}$$

$$T_2^{-2}(\underline{A}\,\underline{B}) = \frac{1}{2}\left(A_xB_x - A_yB_y - iA_xB_y - iA_yB_x\right) \tag{1.C-12}$$

$$T_1^{1}(\underline{A}^2\underline{B}) = -\frac{3}{(30)^{1/2}}\left[\begin{array}{l}\frac{1}{3}A^2B_x - A_x^2B_x - A_xA_yB_y - A_xA_zB_z \\ +i\left(\frac{1}{3}A^2B_y - A_y^2B_y - A_xA_yB_x - A_yA_zB_z\right)\end{array}\right] \tag{1.C-13}$$

$$T_1^{0}(\underline{A}^2\underline{B}) = -\frac{3}{(15)^{1/2}}\left(A_xA_zB_x + A_yA_zB_y + A_z^2B_z - \frac{1}{3}A^2B_z\right) \tag{1.C-14}$$

$$T_1^{-1}(\underline{A}^2\underline{B}) = \frac{3}{(30)^{1/2}}\left[\begin{array}{l}\frac{1}{3}A^2B_x - A_x^2B_x - A_xA_yB_y - A_xA_zB_z \\ -i\left(\frac{1}{3}A^2B_y - A_y^2B_y - A_xA_yB_x - A_yA_zB_z\right)\end{array}\right] \tag{1.C-15}$$

$$T_2^{1}(\underline{A}^2\underline{B}) = \frac{1}{(6)^{1/2}}\left[\begin{array}{l}A_z^2B_x - A_y^2B_x + A_xA_yB_y - A_xA_zB_z \\ +i\left(A_z^2B_y - A_x^2B_y + A_xA_yB_x - A_yA_zB_z\right)\end{array}\right] \tag{1.C-16}$$

$$T_2^{-1}(\underline{A}^2\underline{B}) = \frac{1}{(6)^{1/2}}\left[\begin{array}{l}A_z^2B_x - A_y^2B_x + A_xA_yB_y - A_xA_zB_z \\ -i\left(A_z^2B_y - A_x^2B_y + A_xA_yB_x - A_yA_zB_z\right)\end{array}\right] \tag{1.C-17}$$

$$T_3^{1}(\underline{A}^2\underline{B}) = \frac{1}{(30)^{1/2}}\left[\begin{array}{l}\frac{3}{2}A_x^2B_x + \frac{1}{2}A_y^2B_x - 2A_z^2B_x + A_xA_yB_y - 4A_xA_zB_z \\ +i\left(\frac{3}{2}A_y^2B_y + \frac{1}{2}A_x^2B_y - 2A_z^2B_y + A_xA_yB_x - 4A_yA_zB_z\right)\end{array}\right] \tag{1.C-18}$$

$$T_3^0(\underline{A}^2\underline{B}) = -\frac{1}{(10)^{1/2}}\left[A^2B_z - 3A_z^2B_z + 2A_xA_zB_x + 2A_yA_zB_y\right] \tag{1.C-19}$$

$$T_3^{-1}(\underline{A}^2\underline{B}) = -\frac{i}{(30)^{1/2}}\left[\begin{array}{l}\frac{3}{2}A_x^2B_x + \frac{1}{2}A_y^2B_x - 2A_z^2B_x + A_xA_yB_y - 4A_xA_zB_z \\ -i\left(\frac{3}{2}A_y^2B_y + \frac{1}{2}A_x^2B_y - 2A_z^2B_y + A_xA_yB_x - 4A_yA_zB_z\right)\end{array}\right] \tag{1.C-20}$$

Appendix 1.D: The Breit-Pauli Hamiltonian with External Fields

If the molecule under consideration is acted upon by external fields the results of Sec. 1.2 must be modified[11] in the following manner. Let $\varphi_j^{(e)}$ be the external electrostatic potential, $\underline{\mathcal{E}}_j^{(e)}$ be the external electric field strength, $\underline{\mathcal{H}}_j^{(e)}$ the external magnetic field strength, and $\underline{\mathcal{A}}_j^{(e)}$ the external vector potential - all at the position of electron j. Then the non-relativistic Hamiltonian, H_e, of Sec. 1.2 must be replaced by $\tilde{H}_e$:

$$\tilde{H}_e = H_e - \sum_j \varphi_j^{(e)} \qquad (1.\overset{D}{\cancel{B}}-1)$$

Furthermore, the following terms of order α^2 should be added to H_{rel}:

$$H_1 = \frac{1}{2}\sum_j \left(\underline{\mathcal{E}}_j^{(e)} \times \underline{p}_j\right)\cdot\underline{s}_j + \frac{i}{4}\sum_j \underline{p}_j\cdot\underline{\mathcal{E}}_j^{(e)} \qquad (1.\overset{D}{\cancel{B}}-2)$$

$$H_2 = \sum_j \underline{\mathcal{H}}_j^{(e)}\cdot\underline{s}_j + \sum_j \underline{\mathcal{A}}_j^{(e)}\cdot\underline{p}_j \qquad (1.\overset{D}{\cancel{B}}-3)$$

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-Pauli 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. $(1.\overset{D}{\cancel{B}}-1)$.

Equations $(1.\overset{D}{\cancel{B}}-2)$ and $(1.\overset{D}{\cancel{B}}-3)$ are straight forward generalizations of the corresponding terms in ref. 11, p. 181, and have been discussed by Hirschfelder, Curtiss and Bird.[6] We give them here for completeness and clarity.

II

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

$$\begin{aligned}\mathcal{E}_{ab} &= E_{ab} + \alpha^2 \mathcal{E}^{(1)}_{ab} \\ &= \alpha^2 W_4/R^4 + C_6/R^6 + \alpha^2 W_6/R^6 + \cdots .\end{aligned} \tag{2.1-1}$$

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;

$$\langle A',B'|T|A,B\rangle = \int \varphi^{*}(A')\,\varphi^{*}(B')\,T\,\varphi(A)\,\varphi(B)\,d\tau_a\,d\tau_b \,. \tag{2.1-2}$$

Here $\varphi(A)$ is a non-relativistic eigenfunction of the isolated molecule a, say, characterized by a set of quantum numbers A, and 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 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;

$$T = \sum T_{l_1}^{m_1}(a)\,T_{l_2}^{m_2}(b) \tag{2.1-3}$$

Thus the matrix element of Eq. (2.1-2) factorizes into a sum over products of integrals involving the isolated molecules a and b;

$$\langle A', B' | T | A, B \rangle = \sum \langle A' | T_{\ell_1}^{m_1}(a) | A \rangle \langle B' | T_{\ell_2}^{m_2}(b) | B \rangle . \qquad (2.1\text{-}4)$$

For the interaction of two atoms a and b (i.e. the problem at hand) the non-relativistic eigenfunctions $\varphi(A)$ and $\varphi(B)$ 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.

<u>Notation</u>: 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 <u>interatomic</u> separation, R, is defined as the distance between the two nuclei, a and b. The geometry[1] of the problem is given in Fig. 1.1. Again all results are in atomic units; energy $\sim e^2/a_0$, length $\sim a_0$.

Let $\underline{L}(a)$ and $\underline{S}(a)$ 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

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[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

$$A = k_a\,,\, L_a,\, M_a,\, S_a\,,\, \sigma_a \tag{2.1-5}$$

where

$$\begin{aligned} \mathbf{L}^2(a)\,\varphi(A) &= L_a(L_a+1)\,\varphi(A) \;;\; L_z(a)\,\varphi(A) = M_a\,\varphi(A) \\ \mathbf{S}^2(a)\,\varphi(A) &= S_a(S_a+1)\,\varphi(A) \;;\; S_z(a)\,\varphi(A) = \sigma_a\,\varphi(A)\,. \end{aligned} \tag{2.1-6}$$

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

$$\Delta\epsilon(A) = \Delta\epsilon_a(k,L,S) = \epsilon(A') - \epsilon(k_a,L_a,S_a) \quad , \tag{2.1-7}$$

and it should be noted that the non-relativistic energy $\epsilon(A)$ is independent of the quantum numbers M_a and σ_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 $O(1/R^8)$ (see Sec. 1.3 for the general treatment). The results, which are well known,[2,3] 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

$$V_e = \sum_{m=3}^{\infty} \frac{V_m}{R^m} \tag{2.2-1}$$

$$V_m = \sum_{k}^{m_a} \sum_{t}^{m_b} \sum_{l_1=1}^{m-2} \sum_{m_1=-l_<}^{l_<} G(1; l_1, m-l_1-1, m-1; m_1; 0,0; r_k, r_t) \times Y_{l_1}^{m_1}(\vartheta_k, \phi_k)\, Y_{m-l_1-1}^{-m_1}(\vartheta_t, \phi_t) \,, \tag{2.2-2}$$

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

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2. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "The Molecular Theory of Gases and Liquids" (John Wiley and Sons Inc., New York, 1954), p. 916 et seq.

3. H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

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;

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

Thus, since $V_1 = V_2 = 0$, the formalism of Sec. 1.3 gives[4] the following result for the non-relativistic interaction energy through $O(1/R^8)$.

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

$\underline{C_6}$ The lead term in the $1/R$ expansion of the interaction energy is the usual London dispersion energy.[2,3,5] The coefficient, C_6, is given by

$$C_6 = \langle \Psi^{(0)} | V_3 | \Psi_3^{(1)} \rangle \qquad (2.2\text{-}5)$$

where in general

$$\langle \Psi^{(0)} | V_m | \Psi_q^{(1)} \rangle = \sum_{A,B}{}' \frac{\langle A', B' | V_m | A, B \rangle \langle A, B | V_q | A', B' \rangle}{(\Delta E(A) + \Delta E(B))} \qquad (2.2\text{-}6)$$

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[4] The coefficient C_7 is easily shown to be identically zero by symmetry considerations.

[5] F. London, Zeits f. physik. Chemie B11, 222 (1930); Trans. Faraday Soc. 33, 8 (1937).

The coefficient V_3 of the $1/R^3$ term in the expansion of V_e is

$$V_3 = \left[\underline{r}(a)\cdot\underline{r}(b) - 3\,z(a)\,z(b) \right]$$

$$= -\left[r_1^{-1}(a)\, r_1^{1}(b) + r_1^{1}(a)\, r_1^{-1}(b) + 2\, r_1^{0}(a)\, r_1^{0}(b) \right] . \qquad (2.2\text{-}7)$$

Here $-\underline{r}(a)$ 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.A-5)). From symmetry considerations the expression for C_6 may be written in the form[6]

$$C_6 = 6 \sum_{k_a}{}' \sum_{k_b}{}' \frac{|\langle 0|r_1^0|k,1,0\rangle_a|^2 \, |\langle 0|r_1^0|k,1,0\rangle_b|^2}{(\Delta E_a(k,1) + \Delta E_b(k,1))} \qquad (2.2\text{-}8)$$

where

$$\langle k',L',M'|r_1^0|k,L,M\rangle_a = \langle k_a',L_a',M_a'|r_1^0(a)|k_a,L_a,M_a\rangle . \qquad (2.2\text{-}9)$$

Let us define the mean oscillator strength $f(k,1)$ for the transition ($k = 1$, $L = 0$) ⟷ (k, $L = 1$) ;

$$f(k,1) = -\frac{2}{3}\,\Delta E(k,1) \sum_{M=-1}^{1} |\langle 0|\underline{r}|k,1,M\rangle|^2$$

$$= -2\,\Delta E(k,1)\, |\langle 0|r_1^0|k,1,0\rangle|^2 . \qquad (2.2\text{-}10)$$

---

[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

$$C_6 = \frac{3}{2} \sum_{k_a}{}' \sum_{k_b}{}' \frac{f^{(a)}_{(k,1)} f^{(b)}_{(k,1)}}{(\Delta\epsilon_a(k,1) + \Delta\epsilon_b(k,1))\,\Delta\epsilon_a(k,1)\,\Delta\epsilon_b(k,1)} \tag{2.2-11}$$

From Eq. (2.2-8) it follows that C_6 has the same sign as ($\Delta\epsilon_a(k,1) + \Delta\epsilon_b(k,1)$). Hence for the interaction of two ground state atoms C_6 is negative and the London dispersion energy is attractive.

<u>C_8</u> The energy C_8/R^8 is the usual dipole-quadrapole dispersion energy.[2,3] The coefficient C_8 is given by

$$C_8 = \langle \Psi^{(0)} | V_4 | \Psi^{(1)}_4 \rangle + \langle \Psi^{(0)} | V_3 | \Psi^{(1)}_5 \rangle + \langle \Psi^{(0)} | V_5 | \Psi^{(1)}_3 \rangle \tag{2.2-12}$$

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

$$V_4 = \frac{3}{(2)^{1/2}} \{1 - P_{ab}\} \{ r_1^{-1}(a) Q_2^{1}(b) + r_1^{1}(a) Q_2^{-1}(b) + (3)^{1/2} r_1^{0}(a) Q_2^{0}(b) \} \tag{2.2-13}$$

where

$$Q_2^m(b) = \sum_t^{n_b} T_2^m(\underline{r}_t^2) \quad ; \quad P_{ab}\, g(a,b) = g(b,a) \;, \tag{2.2-14}$$

and the second rank tensor, $T_2^m(r_t^2)$, 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[6]

$$C_8 = \frac{45}{2}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}' \frac{|\langle 0|r_1^0|k,1,0\rangle_a|^2 |\langle 0|Q_2^0|k,2,0\rangle_b|^2}{(\Delta E_a(k,1)+\Delta E_b(k,2))}$$

$$= -\frac{45}{4}\{1+P_{ab}]\sum_{k_a}{}'\sum_{k_b}{}' \frac{f^{(a)}_{(k,1)}\,|\langle 0|Q_2^0|k,2,0\rangle_b|^2}{\Delta E_a(k,1)(\Delta E_a(k,1)+\Delta E_b(k,2))}\ .$$

(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 $O(\alpha^2)$, is discussed in Sec. 1.4. Here we derive an expression for the relativistic interaction energy $\mathcal{E}_{ab}^{(1)}$, 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));

$$\mathcal{E}_{ab}^{(1)} = \sum_{\sigma} \mathcal{E}_{ab}^{(1)}(\sigma) \qquad , \quad \sigma = \text{LL, SS, SL, p, D} \qquad \text{(2.2-}$$

where

$$\mathcal{E}_{ab}^{(1)}(\sigma) = \sum_{n=1}^{\infty} \frac{W_{\sigma,n}}{R^n} \qquad \text{(2.3-}$$

and

$$W_{\sigma,n} = \sum_{\ell=0}^{n} \sum_{m=0}^{n-\ell} \langle \psi_m | H_{\sigma,\ell} | \psi_{n-\ell-m} \rangle \qquad \text{(2.3-}$$

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

$$H_{SS,1} = H_{SS,2} = H_{SL,1} = H_{p,\ell>0} = H_{D,\ell>0} = 0 \quad . \qquad \text{(2.3-}$$

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

$$\Psi_0 = \Psi^{(0)} \ , \ \Psi_1 = \Psi_2 = 0 \tag{2.3-5}$$

$$\Psi_m = \Psi_m^{(1)} \ , \ \text{for } m = 3,4,5 \ , \ \Psi_6 = \Psi_6^{(1)} + \Psi_6^{(2)} . \tag{2.3-6}$$

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

$$\langle \Psi_0 | H_{\sigma,l} | \Psi_0 \rangle \equiv 0 \ , \ \text{for } l>0, \text{ all } \sigma . \tag{2.3-7}$$

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

$$W_{\sigma,n} = \sum_{l=0}^{n-3} \sum_{\substack{m=0 \\ m \neq 1,2,n-l-1,n-l-2}}^{n-l} \langle \Psi_m | H_{\sigma,l} | \Psi_{n-l-m} \rangle \quad , n > 2 , \tag{2.3-8}$$

$$W_{\sigma,1} = W_{\sigma,2} = 0 \tag{2.3-9}$$

The natural perturbation parameter, α^2 , which is used to order the relativistic corrections in a perturbation sense, is suppressed in the equations given here. In actual fact $\mathcal{E}_{ab}^{(1)}$, *being of* $O(\alpha^2)$, *is multiplied by* α^2 *in the final results* (see Eqs. (2.1-1)).

a. Contribution of the Orbit-Orbit Hamiltonian, H_{LL}

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

$$\mathcal{E}_{ab}^{(1)}(LL) = \sum_{m=3}^{6} \frac{W_{LL,m}}{R^m} \qquad (2.3\text{-}10)$$

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

$\underline{W_{LL,3}}$ From Eq. (2.3-8), making use of the Hermitian character of $H_{LL,o}$, we find[7]

$$W_{LL,3} = 2\langle \Psi_3^{(1)} | H_{LL,o} | \Psi^{(0)} \rangle \qquad (2.3\text{-}11)$$

where in general

$$\langle \Psi_m^{(1)} | H_{\sigma,q} | \Psi^{(0)} \rangle = \sum_{A,B}{}' \frac{\langle A',B' | V_m | A,B \rangle \langle A,B | H_{\sigma,q} | A',B' \rangle}{(\Delta E(A) + \Delta E(B))} . \qquad (2.3\text{-}12)$$

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

$$W_{LL,3} = 0 . \qquad (2.3\text{-}13)$$

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[7] In this work, as mentioned in part I, we assume all the $\Psi^{(n)}$ are real.

$\underline{W_{LL,4}}$. From Eq. (2.3-8), omitting terms of the type given by Eq. (2.3-11) which are zero,

$$W_{LL,4} = 2\langle \Psi_3^{(1)} | H_{LL,1} | \Psi^{(0)} \rangle \quad (2.3\text{-}14)$$

Equations (1.B-9), (2.2-7), and (2.3-12) then yield

$$W_{LL,4} = \sum_{A,B}{}' \frac{\begin{bmatrix} \langle A'|r_1^{-1}(a)|A\rangle\langle B'|r_1^{1}(b)|B\rangle \\ +\langle A'|r_1^{1}(a)|A\rangle\langle B'|r_1^{-1}(b)|B\rangle \\ +2\langle A'|r_1^{0}(a)|A\rangle\langle B'|r_1^{0}(b)|B\rangle \end{bmatrix}\begin{bmatrix} 2\langle A|\ell_1^{0}(a)|A'\rangle\langle B|\ell_1^{0}(b)|B'\rangle \\ -\langle A|\ell_1^{-1}(a)|A'\rangle\langle B|\ell_1^{1}(b)|B'\rangle \\ -\langle A|\ell_1^{1}(a)|A'\rangle\langle B|\ell_1^{-1}(b)|B'\rangle \end{bmatrix}}{(\Delta\epsilon(A) + \Delta\epsilon(B))} . \quad (2.3\text{-}15)$$

Here $\ell_1^m(b)$ are the irreducible tensorial components of the current operator $\underline{\ell}(b)$; $\underline{\ell}(b) = \sum_t^{m_b} p_t$. The interaction energy $W_{LL,4}/R^4$ is an (orbital-current)-(electrostatic-dipole) dispersion energy. From symmetry considerations it follows that[6]

$$W_{LL,4} = 2\sum_{k_a}{}'\sum_{k_b}{}' \frac{\langle 0|r_1^{0}|k,1,0\rangle_a \langle k,1,0|\ell_1^{0}|0\rangle_a \langle 0|r_1^{0}|k,1,0\rangle_b \langle k,1,0|\ell_1^{0}|0\rangle_b}{(\Delta\epsilon_a(k,1) + \Delta\epsilon_b(k,1))} . \quad (2.3\text{-}16)$$

Making use of the commutator relation

$$i\,[H_0(a), r_1^0(a)] = \ell_1^0(a) \quad (2.3\text{-}17)$$

it is easy to show that

$$W_{LL,4} = -2 \sum_{k_a}{}' \sum_{k_b}{}' \frac{\Delta\epsilon_a(k,1)\,\Delta\epsilon_b(k,1)}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))} \left|\langle 0|r_1^0|k,1,0\rangle_a\right|^2 \left|\langle 0|r_1^0|k,1,0\rangle_b\right|^2 . \qquad (2.3\text{-}18)$$

The coefficient $W_{LL,4}$ may be expressed in terms of the average oscillator strengths, $f(k,1)$, of Eq. (2.2-10):

$$W_{LL,4} = -\frac{1}{2} \sum_{k_a}{}' \sum_{k_b}{}' \frac{f^{(a)}(k,1)\, f^{(b)}(k,1)}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))} \qquad (2.3\text{-}19)$$

From Eq. (2.3-18) it is apparent that $W_{LL,4}$ 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, <u>which is of $O(\alpha^2)$</u>, 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_4 should be noted (compare Eqs. (2.2-11) and (2.3-19)).

<u>$W_{LL,5}$</u> From Eq. (2.3-9), omitting terms of the type given by Eq. (2.3-11) which vanish,

$$W_{LL,5} = 2\langle \Psi_4^{(1)}|H_{LL,1}|\Psi^{(0)}\rangle + 2\langle \Psi_3^{(1)}|H_{LL,2}|\Psi^{(0)}\rangle . \qquad (2.3\text{-}20)$$

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

$$W_{LL,5} = 0 \tag{2.3-21}$$

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

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

where

$$W_{LL,4;2} = 2\langle \Psi_4^{(1)} | H_{LL,2} | \Psi^{(0)} \rangle \tag{2.3-23}$$

$$W_{LL,3,3} = 2\langle \Psi_3^{(1)} | H_{LL,3} | \Psi^{(0)} \rangle \tag{2.3-24}$$

$$W_{LL,6;0} = 2\langle \Psi_6^{(2)} | H_{LL,0} | \Psi^{(0)} \rangle + \langle \Psi_3^{(1)} | H_{LL,0} | \Psi_3^{(1)} \rangle \tag{2.3-25}$$

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

<u>$W_{LL,4;2}$</u> Using Eqs. (1.B-10), (2.2-13) and (2.3-12) yields

$$W_{LL,4,2} = \frac{3}{(2)^{1/2}} {\sum_{A,B}}' \begin{bmatrix} \langle A'|r_1^{-1}(a)|A\rangle\langle B'|Q_2^{1}(b)|B\rangle + \langle A'|r_1^{1}(a)|A\rangle\langle B'|Q_2^{-1}(b)|B\rangle \\ +(3)^{1/2}\langle A'|r_1^{0}(a)|A\rangle\langle B'|Q_2^{0}(b)|B\rangle - \langle A'|Q_2^{1}(a)|A\rangle\langle B'|r_1^{-1}(b)|B\rangle \\ -\langle A'|Q_2^{-1}(a)|A\rangle\langle B'|r_1^{1}(b)|B\rangle - (3)^{1/2}\langle A'|Q_2^{0}(a)|A\rangle\langle B'|r_1^{0}(b)|B\rangle \end{bmatrix}$$

$$\frac{\times \begin{bmatrix} i\langle A|L_1^{-1}(a)|A'\rangle\langle B|Q_1^{1}(b)|B'\rangle - i\langle A|L_1^{1}(a)|A'\rangle\langle B|Q_1^{-1}(b)|B'\rangle \\ -(6)^{1/2}\langle A|D_1^{0}(a)|A'\rangle\langle B|Q_1^{0}(b)|B'\rangle - i\langle A|Q_1^{1}(a)|A'\rangle\langle B|L_1^{-1}(b)|B'\rangle \\ +i\langle A|Q_1^{-1}(a)|A'\rangle\langle B|L_1^{1}(b)|B'\rangle + (6)^{1/2}\langle A|Q_1^{0}(a)|A'\rangle\langle B|D_2^{0}(b)|B'\rangle \end{bmatrix}}{\left(\Delta\epsilon(A) + \Delta\epsilon(B)\right)}$$

(2.3-26)

Applying the selection rules (see Appendix 2 A) for the tensor operators involved in the expression for $W_{LL,4;2}$ gives[6]

$$W_{LL,4;2} = 9\{1 + P_{ab}\} {\sum_{k_a}}' {\sum_{k_b}}' \frac{\langle 0|r_1^{0}|k,1,0\rangle_a \langle k,1,0|Q_1^{0}|0\rangle_a \langle 0|Q_2^{0}|k,2,0\rangle_b \langle k,2,0|D_2^{0}|0\rangle_b}{\left(\Delta\epsilon_a(k,1) + \Delta\epsilon_b(k,2)\right)}.$$

(2.3-27)

It is easy to show that

$$+\frac{i}{2}\left[H_0(a), Q_2^{0}(a)\right] = D_2^{0}(a) \qquad (2.3\text{-}28)$$

and similarly for atom b . Equations (2.3-17), (2.3-27) and (2.3-28) give

$$W_{LL,4;2} = -\frac{9}{2}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}' \frac{\Delta\epsilon_a(k,1)\Delta\epsilon_b(k,2)}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,2))} |\langle 0|r_1^0|k,1,0\rangle_a|^2 |\langle 0|Q_2^0|k,2,0\rangle_b|^2$$

$$= \frac{9}{4}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}' \frac{\Delta\epsilon_b(k,2)}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,2))} f^{(a)}(k,1) |\langle 0|Q_2^0|k,2,0\rangle_b|^2.$$

(2.3-29)

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_8 and $W_{LL,4;2}$ (compare Eqs. (2.2-15) and (2.3-29)).

<u>$W_{LL,3;3}$</u> From Eqs. (1.B-11) and (2.3-24)

$$W_{LL,3;3} = 2\langle\Psi_3^{(1)}|C_{LL,3}|\Psi^{(0)}\rangle + 2\langle\Psi_3^{(1)}|F_{LL,3}|\Psi^{(0)}\rangle + 2\langle\Psi_3^{(1)}|G_{LL,3}|\Psi^{(0)}\rangle$$

(2.3-30)

where $C_{LL,3}$, $F_{LL,3}$ and $G_{LL,3}$ are given by Eqs. (1.B-12) - (1.B-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[6]

$$W_{LL,3;3} = \frac{-6}{(15)^{1/2}}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}' \frac{\langle 0|r_1^0|k,1,0\rangle_a\langle k,1,0|\mathcal{Y}_1^0|0\rangle_a\langle 0|r_1^0|k,1,0\rangle_b\langle k,1,0|\rho_1^0|0\rangle_b}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))} .$$

(2.3-31)

Here $\mathcal{Y}_1^0(a)$ is the first rank tensor defined by

$$\mathcal{Y}_1^0(a) = \frac{-3}{(15)^{1/2}}\sum_j^{n_a}\left\{T_1^0(\underline{r}_j)(\underline{r}_j\cdot\underline{\rho}_j) - 2r_j^2\,T_1^0(\underline{\rho}_j)\right\} . \quad (2.3\text{-}32)$$

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

$$W_{LL,3;3} = \frac{+6i}{(15)^{1/2}}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}'\Delta\epsilon_b(k,1)\frac{\langle 0|r_1^0|k,1,0\rangle_a\langle k,1,0|\mathcal{Y}_1^0|0\rangle_a|\langle 0|r_1^0|k,1,0\rangle_b|^2}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))}$$

$$= \frac{-3i}{(15)^{1/2}}\{1+P_{ab}\}\sum_{k_a}{}'\sum_{k_b}{}'\frac{\langle 0|r_1^0|k,1,0\rangle_a\langle k,1,0|\mathcal{Y}_1^0|0\rangle_a f^{(b)}(k,1)}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))} .$$

(2.3-33)

$\underline{W_{LL,6;0}}$ Let us define the following quantity:[6]

$$W(H_{\sigma,0}) = \left\{1 + P_{ab}\right\} \left[-\frac{3}{2}\langle 0|H_{\sigma,0}|0\rangle_a \sum_{k_a,k_b}{}' \frac{f^{(a)}_{(k,1)}\, f^{(b)}_{(k,1)}}{(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))^2\,\Delta\epsilon_a(k,1)\,\Delta\epsilon_b(k,1)} \right.$$

$$-6\sum_{k''_a,k''_b}{}'\sum_{k_a}{}' \frac{\langle 0|r_1^0|k'',1,0\rangle_a \langle k'',1,0|r_1^0|k,0,0\rangle_a \langle k,0,0|H_{\sigma,0}|0\rangle_a\, f^{(b)}(k'',1)}{(\Delta\epsilon_a(k'',1)+\Delta\epsilon_b(k'',1))\,\Delta\epsilon_a(k,0)\,\Delta\epsilon_b(k'',1)}$$

$$\left. -3\sum_{k_a,k_b}{}'\sum_{k''_a}{}' \frac{\langle 0|r_1^0|k'',1,0\rangle_a \langle k'',1,0|H_{\sigma,0}|k,1,0\rangle_a \langle k,1,0|r_1^0|0\rangle_a\, f^{(b)}(k,1)}{(\Delta\epsilon_a(k'',1)+\Delta\epsilon_b(k,1))(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1))\,\Delta\epsilon_b(k,1)} \right].$$

(2.3-34)

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

$$W_{LL,6;0} = W(H_{LL,0}) \tag{2.3-35}$$

The interaction energy, $W_{LL,6;0}/R^6$, 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 $W_{LL,4;2}$, $W_{LL,3;3}$ and $W_{LL,6;0}$, 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 $O(1/R^6)$, to $\mathcal{E}_{ab}^{(1)}$ from the spin-spin Hamiltonian, H_{SS} , is given by

$$\mathcal{E}_{ab}^{(1)}(SS) = \sum_{n=3}^{6} \frac{W_{SS,n}}{R^n} , \tag{2.3-36}$$

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

$$W_{SS,n} = \sum_{\substack{l=0 \\ l \neq 1,2}}^{n-3} \sum_{\substack{m=0 \\ m \neq 1,2,\, n-l-1,\, n-l-2}}^{n-l} \langle \Psi_m | H_{SS,l} | \Psi_{n-l-m} \rangle . \tag{2.3-37}$$

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

$$\langle \Psi_m^{(1)} | H_{SS,q} | \Psi^{(0)} \rangle = 0 . \tag{2.3-38}$$

This integral vanishes for $q = 0$ since $H_{SS,0} = H_{SS,0}^{(a)} + H_{SS,0}^{(b)}$. For $q \neq 0$, $H_{SS,q}$ is given symbolically (see Eq. (1.A-48)) by

$$H_{SS,q} = \sum_{k}^{n_a} \sum_{t}^{n_b} \sum_{\omega,\kappa} f(k,t,\omega,\kappa)\, T_1^{-\omega}(\underline{S}_k)\, T_1^{-\kappa}(\underline{S}_t) \tag{2.3-39}$$

and thus is not diagonal in the spin quantum numbers. Since the operator V_m 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 $W_{SS,n}$; $n \leq 6$, is given by

$$W_{SS,6} = 2\langle \Psi_6^{(2)} | H_{SS,0} | \Psi^{(0)} \rangle + \langle \Psi_3^{(1)} | H_{SS,0} | \Psi_3^{(1)} \rangle \; . \tag{2.3-40}$$

It should be noted that $H_{SS,0}^{(a)}$, say, is comprised of two terms (see Eq. (1.A-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

$$W_{SS,6} = W(\Delta_{SS,0}) \equiv W_{SS,6;0} \tag{2.3-41}$$

where

$$\Delta_{SS,0}^{(a)} = -\frac{8\pi}{3} \sum_{k>j}^{n_a} (\underline{S}_j \cdot \underline{S}_k)\, \delta^{(3)}(\underline{r}_{jk}) \quad , \tag{2.3-42}$$

and $W(\Delta_{SS,0})$ is defined by Eq. (2.3-34). The energy $W_{SS,6}/R^6$ 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 .

c. Contribution of the Relativistic Hamiltonians, H_p and H_D.

The contribution, through $O(1/R^6)$, to $\mathcal{E}_{ab}^{(1)}$ from the Hamiltonian's H_σ, for $\sigma = p$ and D, is given by

$$\mathcal{E}_{ab}^{(1)}(\sigma) = \sum_{n=3}^{6} \frac{W_{\sigma,n}}{R^n} \quad , \sigma = p, D, \tag{2.3-43}$$

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

$$W_{\sigma,n} = \sum_{\substack{m=0 \\ m \neq 1,2,n-1,n-2}}^{n} \langle \Psi_m | H_{\sigma,0} | \Psi_{n-m} \rangle \tag{2.3-44}$$

It is easy to show that the only non-vanishing $W_{\sigma,n}$, $n \leq 6$, 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 $\Theta(\alpha^2/R^6)$, is given by

$$\mathcal{E}_{ab} = \alpha^2 \frac{W_4}{R^4} + \frac{C_6}{R^6} + \alpha^2 \frac{W_6}{R^6} \tag{2.4-1}$$

where

$$W_4 = W_{LL,4} \tag{2.4-2}$$

$$W_6 = W_{LL,4;2} + W_{LL,3;3} + W_{6;0} \tag{2.4-3}$$

and

$$W_{6;0} = \sum_{\sigma} W_{\sigma,6;0} \quad . \tag{2.4-4}$$

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

$$\alpha_d(a) = \sum_{k_a}{}' \frac{f^{(a)}(k,1)}{\left[\Delta E_a(k,1)\right]^2} \tag{2.4-5}$$

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[8] For the polarizabilities of the rare gas atoms, see for example A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. A259, 424 (1960).

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

$$C_6 = 3/2 \sum_{k_a}{}' \sum_{k_b}{}' \frac{f^{(a)}_{(k,1)} f^{(b)}_{(k,1)} \Delta\epsilon_a(k,1)\, \Delta\epsilon_b(k,1)}{\left(\Delta\epsilon_a(k,1)+\Delta\epsilon_b(k,1)\right)\left\{\Delta\epsilon_a(k,1)\Delta\epsilon_b(k,1)\right\}^2} \qquad (2.4\text{-}6)$$

Applying Unsöld's approximation[9] to Eq. (2.4-6, and using Eq. (2.4-5) yields F. London's[5] formula for C_6;

$$C_6 = -3/2 \frac{\Delta_a \Delta_b}{\Delta_a + \Delta_b} \alpha_d(a) \alpha_d(b) \qquad (2.4\text{-}7)$$

In a similar manner one obtains the following approximation for W_4;

$$W_4 = 1/2 \frac{\Delta_a^2 \Delta_b^2}{\Delta_a + \Delta_b} \alpha_d(a) \alpha_d(b) \qquad (2.4\text{-}8)$$

The results[10] 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[2,3] that choosing the average energies, Δ, 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.[11] The estimates for C_6 agree (to within 10-30 per cent) with the accurate theoretical values of the van der Waals coefficient, C_6^K,

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[9] A. Unsöld, Z. Physik 43, 563 (1927).

[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. I, 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 ($\alpha_d(a)$, C_6^K and I_a from refs. 8, 12 and 11, respectively).

	Accurate theoretical values		Oscillator with $\Delta = I$ Eqs. (2.4-7), (2.4-8)				Oscillator with Δ^K Eqs. (2.4-7), (2.4-8)			Unsöld with $\bar{\Delta}^K$ Eqs. (2.4-9), (2.4-10)		
Interaction a-b	$\alpha_d(a)$	$-C_6^K$	Δ_a	$-C_6$	W_4	$-\frac{W_4}{C_6}$	Δ_a^K	W_4	$-\frac{W_4}{C_6}$	$\bar{\Delta}_a^K$	W_4	$-\frac{W_4}{C_6}$
He-He	1.384	1.456	0.9033	1.298	0.353	0.272	1.014	0.499	0.342	1.273	0.786	0.540
He-Ne		3.01		2.33	0.557	0.239		1.21	0.401		2.81	0.967
He-A		9.63		8.12	1.42	0.174		2.31	0.240		6.38	0.657
Ne-Ne	2.663	6.31	0.7923	4.21	0.882	0.209	1.19	2.96	0.469	2.28	11.0	1.74
Ne-A		19.7		14.8	2.27	0.153		5.52	0.280		23.5	1.18
A-A	11.080	65.4	0.5790	53.3	5.96	0.112	0.710	11.0	0.168	1.55	52.3	0.800

determined by A. E. Kingston[12]. Values for W_4 are also listed in Table I, for $\Delta = \Delta^K$, the value of Δ 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 to Eq. (2.3-19) and using the Reiche-Thomas-Kuhn sum rule[13], $\sum_{k_a}' f^{(a)}(k,1) = n_a$ yields

$$W_4 = \tfrac{1}{2} \frac{n_a n_b}{\Delta_a + \Delta_b} \qquad (2.4\text{-}9)$$

Here n_a is the number of electrons in atom a. The corresponding approximation for C_6 is given by

$$C_6 = -3/2 \frac{n_a n_b}{(\Delta_a + \Delta_b)\Delta_a \Delta_b} \qquad (2.4\text{-}10)$$

If the average energies, Δ, 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 $\Delta = \bar{\Delta}^K$, the value of Δ 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 $\Delta = \bar{\Delta}^K$ are given in Table I.

$\underline{W_6}$ Approximations for the coefficients $W_{LL,4;2}$ and $W_{LL,3;3}$

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[12] A. E. Kingston, Phys. Rev. A135, 1018 (1964).

[13] An excellent discussion of the various sum rules is given in the review article by J. O. Hirschfelder, W. Byers Brown and S. T. Epstein, in "Advances in Quantum Chemistry" (edited by P. O. Löwdin, Academic Press, New York, 1964), p. 225 et seq.

are easily obtained from the frequently used harmonic oscillator model.[14] In this approximation each electron in atom a , say, is represented by a 3-dimensional harmonic oscillator of fundamental frequency ν_a . The energy $h\nu_a = \Delta_a$ 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 Δ and the polarizabilities, α_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

$$W_{LL,4;2} = 9/4\left\{1+P_{ab}\right\}\frac{\Delta_a^2\Delta_b}{(\Delta_a+2\Delta_b)}\alpha_d(a)\alpha_d(b) \qquad (2.4\text{-}11)$$

$$W_{LL,3;3} = -3/4\left\{1+P_{ab}\right\}\frac{\Delta_a^2\Delta_b}{\Delta_a+\Delta_b}\alpha_d(a)\alpha_d(b) . \qquad (2.4\text{-}12)$$

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

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

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[14] See for example H. Margenau, J. Chem. Phys. 9, 896 (1938); refs. 2 and 3; J. F. Hornig and J. O. Hirschfelder, J. Chem. Phys. 20, 1812 (1952); P. R. Fontana, Phys. Rev. 123, 1865 (1961).

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 $\Delta = I$.

Interaction a-b	$-C_6$	$W_{LL,4;2}$	$-W_{LL,3;3}$	$W_{LL,4;2} + W_{LL,3;3}$
He-He	1.298	2.345	1.172	1.173
He-Ne	2.33	3.96	1.98	1.99
He-A	8.12	12.3	6.02	6.27
Ne-Ne	4.21	6.68	3.34	3.34
Ne-A	14.8	20.5	10.2	10.4
A-A	53.3	61.7	30.9	30.9

$$W_{\sigma,6;0}=\{1+P_{ab}\}\left[-6\frac{\langle 0|H_{\sigma,0}|0\rangle_a\langle 0|r_1^0(a)\,r_1^0(a)|0\rangle_a\langle 0|r_1^0(b)\,r_1^0(b)|0\rangle_b}{(\Delta\epsilon_a(2,1)+\Delta\epsilon_b(2,1))^2}\right.$$
$$+12\frac{\langle 0|r_1^0(a)\,r_1^0(a)\,H_{\sigma,0}^{(a)}|0\rangle\langle 0|r_1^0(b)\,r_1^0(b)|0\rangle_b}{(\Delta\epsilon_a(2,1)+\Delta\epsilon_b(2,1))\,\Delta\epsilon_a(2,0)}$$
$$-12\frac{\langle 0|H_{\sigma,0}|0\rangle_a\langle 0|r_1^0(a)\,r_1^0(a)|0\rangle_a\langle 0|r_1^0(b)\,r_1^0(b)|0\rangle_b}{(\Delta\epsilon_a(2,1)+\Delta\epsilon_b(2,1))\,\Delta\epsilon_a(2,0)}$$
$$\left.+6\frac{\langle 0|r_1^0(a)\,H_{\sigma,0}^{(a)}\,r_1^0(a)|0\rangle_a\langle 0|r_1^0(b)\,r_1^0(b)|0\rangle_b}{(\Delta\epsilon_a(2,1)+\Delta\epsilon_b(2,1))^2}\right]. \tag{2.4-13}$$

The choice of the average energies made in Eq. (2.4-13) tends to overestimate each term in $W_{\sigma,6;0}$. We have evaluated these coefficients for the He-He interaction using the simple approximate ground state helium wave function

$$\Psi(1,2) = \frac{Z_a^3}{\pi}\, e^{-Z_a(r_1+r_2)}\,\frac{(\alpha_1\beta_2-\beta_1\alpha_2)}{\sqrt{2}} \ . \tag{2.4-14}$$

The integrals for σ = SS, SL, p, and D are easily done.[15] 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

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[15] The integrals, $\langle 0|H_{\sigma 0}|0\rangle$, for all σ 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 $Z = 2$)

$$W_{LL,6;0} = 3.204 \quad ; \quad W_{SS,6;0} = -6.312$$

$$W_{SL,6;0} = 0 \quad ; \quad W_{p,6;0} = 67.523$$

$$W_{D,6;0} = -47.342 \quad ; \quad W_{6;0} = 17.073 \quad . \qquad (2.4\text{-}15)$$

For the rare gas interactions considered here, the relativistic interaction energy, $\alpha^2(W_{LL,4;2} + W_{LL,3;3})/R^6$, 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.[16] 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 $\mathcal{O}(\alpha^2/R^6)$ by

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[16] As mentioned previously the Unsöld's approximation for $W_{6;0}$ probably overestimates the magnitude of this coefficient. One would expect $W_{6;0}$ 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 $O(\alpha^2/R^6)$.

$$\mathcal{E}_{ab} = \alpha^2 \frac{W_4}{R^4} + \frac{C_6}{R^6} + \cdots$$

$$= \frac{C_6}{R^6}\left[1 - \beta\alpha^2 R^2\right] + \cdots \qquad (2.4\text{-}16)$$

where

$$\beta = -W_4/C_6 \qquad (2.4\text{-}17)$$

For the interaction of the rare gas atoms considered[17] in Table I $\beta \sim 1$. The ratio of the (orbital-current)-(electrostatic-dipole) dispersion energy, E_4, to the van der Waals energy, E_6, given by

$$E_4/E_6 = -\beta\alpha^2 R^2 \qquad (2.4\text{-}18)$$

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.[18]

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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. A237, 383 (1956)).

TABLE III

Values of $E_4/E_6 = -\beta\alpha^2R^2$ 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.

R	$-E_4/E_6$	R	$-E_4/E_6$
10	0.00533	60	0.192
20	0.0213	70	0.261
30	0.0479	80	0.341
40	0.0852	90	0.431
50	0.133	100	0.533

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[19,20] 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_ℓ^m be a component of an irreducible spherical tensor operator of rank ℓ, $m = -\ell, -\ell+1, \ldots, \ell$, which is defined with respect to the angular momentum operator $\underline{J}$. (see Appendix 1.C) Let us consider the matrix elements of T_ℓ^m with respect to the eigenfunctions, $\varphi(J,\omega)$, of J^2 and J_z;

$$J^2\varphi(J,\omega) = J(J+1)\varphi(J,\omega) \tag{2.A-1}$$

$$J_z\varphi(J,\omega) = \omega\varphi(J,\omega) \tag{2.A-2}$$

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 $\underline{J} = \underline{L}, \underline{S}$.

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

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19. E. P. Wigner, Z. Phys. 43, 624 (1927); C. Eckart, Rev. Mod. Phys. 2, 305 (1930).

20. M. E. Rose, "Elementary Theory of Angular Momentum" (John Wiley and Sons, Inc., New York, 1957), A. R. Edmonds, "Angular Momentum in Quantum Mechanics" (Princeton University Press, Princeton, New Jersey, 1957).

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

$$\langle k',J',\omega'|T_{\ell}^{m}|k,J,\omega\rangle = C(J\,\ell\,J',\omega\,m\,\omega')\langle k',J'\|T_{\ell}\|k,J\rangle . \qquad (2.A-3)$$

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

$$\langle k',J',\omega'|T_{\ell}^{m}|k,J,\omega\rangle = (-1)^{\ell+m}\left(\frac{2J'+1}{2J+1}\right)^{1/2} C(J'\,\ell\,J;-\omega',m,-\omega$$

$$\times\langle k',J'\|T_{\ell}\|k,J\rangle . \qquad (2.A-4)$$

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

$$\omega' = \omega + m \qquad (2.A-5)$$

$$J' = J+\ell,\ J+\ell-1,\ \cdots,\ |J-\ell| \qquad (2.A-6)$$

$$|\omega| \leq J\ ;\ |m| \leq \ell\ ;\ |\omega'| \leq J' . \qquad (2.A-7)$$

Also the following relations are useful

$$C(J\ell J';000)=0 \quad \text{, unless } J+\ell+J' \text{ even,} \tag{2.A-8}$$

$$C(J0J';\omega 0\omega')=\delta_{J,J'}\,\delta_{\omega,\omega'} \; . \tag{2.A-9}$$

The selection rules for J_1^m , with $m = 1,0,-1$, are[20]

$$\langle k,J',\omega'|J_1^m|k,J,\omega\rangle=\delta_{J,J'}\,\delta_{\omega',\omega+m}(-1)^m[J(J+1)]^{1/2}$$
$$\times\, C(J1J;\omega+m,-m)\; . \tag{2.A-10}$$

The Wigner-Eckart theorem permits a further simplification over that afforded by the selection rules for the Γ_ℓ^m . Namely, all non-zero matrix elements of the type given by Eq. (2.A-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.A-3) once only, for some convenient choice of ω , m and ω' .

Appendix 2.B: On the Vanishing of $\langle \Psi^{(0)} | H_{\sigma,\ell} | \Psi^{(0)} \rangle$, for $\ell > 0$.

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

$$\langle \Psi^{(0)} | H_{\sigma,\ell} | \Psi^{(0)} \rangle \equiv 0 \quad ; \text{for all } \sigma,\ \ell > 0 \tag{2.B-1}$$

where $\Psi^{(0)}$ is given by

$$\Psi^{(0)} = \varphi(A')\varphi(B') \tag{2.B-2}$$

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

$$\sum_{m=1}^{\infty} \frac{H_{LL,m}}{R^m} = -\frac{1}{2i} \sum_{k}^{n_a} \sum_{t}^{n_b} \underline{B}(k,t) \cdot \underline{p}_t \ , \tag{2.B-3}$$

$$\underline{B}(k,t) = \frac{1}{r_{kt}^3} \left[\underline{r}_{kt}^2 \underline{\nabla}_k + \underline{r}_{kt} (\underline{r}_{kt} \cdot \underline{\nabla}_k) \right] \tag{2.B-4}$$

where

$$(\underline{p}_t \cdot \underline{B}(k,t)) = 0 \tag{2.B-5}$$

Consider the integral

$$I = \langle \Psi^{(0)} | \underline{B}(k,t) \cdot \underline{p}_t | \Psi^{(0)} \rangle$$

$$= \tfrac{1}{2} \langle \varphi(A')\varphi(B') | \underline{p}_t \cdot \underline{B}(k,t) + \underline{B}(k,t) \cdot \underline{p}_t | \varphi(A')\varphi(B') \rangle . \qquad (2.B\text{-}6)$$

Integrating over the electronic coordinates of atom a gives

$$I = \tfrac{1}{2} \langle \varphi(B') | \underline{p}_t \cdot \underline{F}(t) + \underline{F}(t) \cdot \underline{p}_t | \varphi(B') \rangle \qquad (2.B\text{-}7)$$

where

$$\underline{F}(t) = \langle \varphi(A') | \underline{B}(k,t) | \varphi(A') \rangle . \qquad (2.B\text{-}8)$$

Since $\underline{F}(t)$ is a function of the position coordinates of electron t, the operator $(\underline{p}_t \cdot \underline{F}(t) + \underline{F}(t) \cdot \underline{p}_t)$ is a purely imaginary Hermitian operator of atom b. Since $\varphi(B')$ is chosen to be real, the integral I vanishes. Thus from Eq. (2.B-3) we obtain[21]

$$\sum_{m=1}^{\infty} \frac{\langle \Psi^{(0)} | H_{LL,m} | \Psi^{(0)} \rangle}{R^m} = 0 . \qquad (2.B\text{-}9)$$

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[21] It is well known that for a real atomic wave function Ψ_a, of the orbital form, the expectation value of $H^{(a)}_{LL,0}$ 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. Fröman, 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 $(S_a = S_b = \sigma_a = \sigma_b = 0)$ 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 $W_{LL,6,0}$.[22] 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

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

where

$$Q_1 = \frac{1}{r_{12}}\underline{\nabla}_1 \cdot \underline{\nabla}_2 \tag{2.C-2}$$

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

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[22] The methods used are similar to those used in the derivation of the one-center expansion of the spin-orbit Hamiltonian by M. Blume and R. E. Watson, Proc. Roy. Soc. A270, 127 (1962).

The one-center expansion for $1/r_{12}$ is given by[23]

$$\frac{1}{r_{12}} = \sum_{k,q} \frac{4\pi}{(2k+1)}\, Y_k^{q*}(1)\, Y_k^{q}(2)\, \frac{r_<^{k}}{r_>^{k+1}} , \tag{2.C-4}$$

where $Y_k^q(i)$ is the spherical harmonic $Y_k^q(\theta_i,\phi_i)$. The corresponding one-center expansion for the operator Q_1 is given in spherical tensor form by

$$Q_1 = \frac{(4\pi)^2}{3} \sum_{k,q,\omega} \frac{(-1)^{\omega}}{(2k+1)}\, Y_k^{q*}(1)\, Y_k^{q}(2)\, \frac{r_<^{k}}{r_>^{k+1}}\, \mathcal{Y}_1^{\omega}(\underline{\nabla}_1)\, \mathcal{Y}_1^{-\omega}(\underline{\nabla}_2) . \tag{2.C-5}$$

Here $\mathcal{Y}_\ell^{\omega}(\underline{\nabla})$ is the solid harmonic operator obtained by replacing the components of $\underline{r}$ in $\mathcal{Y}_\ell^{\omega}(\underline{r}) = r^{\ell}\, Y_\ell^{\omega}(\theta,\phi)$ by the components of the gradient operator in $\underline{r}$-space.

Using the gradient formula[20], the κ-th component of the first rank tensor $\left(\underline{\nabla}_1 \frac{1}{r_{12}}\right)$ is given by[22]

$$\left(\underline{\nabla}_1^{\kappa} \frac{1}{r_{12}}\right) = -4\pi \sum_{k,k',q} (-1)^{q}\, C(k1k';00)\, C(k1k';q,-\kappa)\, Y_{k'}^{\kappa-q}(1)\, Y_{k}^{q}(2)\, A_{k,k'} \tag{2.C-6}$$

where

$$A_{k,k+1} = +\left(\frac{2k+1}{2k+3}\right)^{1/2} r_2^{k}/r_1^{k+2}\, \epsilon(r_1-r_2)$$

$$A_{k,k-1} = -\left(\frac{2k+1}{2k-1}\right)^{1/2} r_1^{k-1}/r_2^{k+1}\, \epsilon(r_2-r_1) \tag{2.C-7}$$

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[23] See for example E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra" (Cambridge University Press, London, 1935).

and $\epsilon(x-y) = 1$ for $x > y$; $= 0$ for $y > x$. The κ-th spherical component of the vector $(\underline{r}_{12}\cdot\underline{\nabla}_1)\underline{\nabla}_2$ is

$$(\underline{r}_{12}\cdot\underline{\nabla}_1)\underline{\nabla}_2^{\kappa} = \left(\frac{4\pi}{3}\right)^{3/2}\sum_{\omega}(-1)^{\omega}\,\mathcal{Y}_1^{\omega}(\underline{r}_{12})\,\mathcal{Y}_1^{-\omega}(\underline{\nabla}_1)\,\mathcal{Y}_1^{\kappa}(\underline{\nabla}_2) \qquad (2.C\text{-}8)$$

Finally, we require the one-center expansion of $\mathcal{Y}_1^{\omega}(\underline{r}_{12})$, which has been derived by Rose[24];

$$\mathcal{Y}_1^{\omega}(\underline{r}_{12}) = (24\pi)^{1/2}\sum_{L=0}^{1}\sum_{M}(-1)^{L}\frac{C(L,1-L,1;M,\omega-M)}{[(2L+1)!\,(3-2L)!\,]^{1/2}}\,r_2^{L}\,r_1^{1-L}$$
$$\times\, Y_L^{M}(2)\,Y_{1-L}^{\omega-M}(1) \qquad (2.C\text{-}9)$$

Combining the results of Eqs. (2.C-6) - (2.C-9) we obtain the one-center expansion for the operator Q_2[25]

$$Q_2 = \frac{(4\pi)^3}{3}(2)^{1/2}\sum_{k,k',q}\sum_{L=0}^{1}\sum_{M,\omega,\kappa}(-1)^{q+L+\omega+\kappa}\frac{C(L,1-L,1;M,\omega-M)}{[(2L+1)!\,(3-2L)!\,]^{1/2}}$$
$$\times\, C(k1k';00)\,C(k1k';q,-\kappa)\,r_2^{L}\,r_1^{1-L}A_{k,k'}$$
$$\times\, Y_{k'}^{\kappa-q}(1)\,Y_{1-L}^{\omega-M}(1)\,\mathcal{Y}_1^{-\omega}(\underline{\nabla}_1)\,Y_k^{q}(2)\,Y_L^{M}(2)\,\mathcal{Y}_1^{-\kappa}(\underline{\nabla}_2).$$

(2.C-10)

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[24] M. E. Rose, J. Math. and Phys. 37, 215 (1958).

[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_{LL} 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.A-13), contains the following integrals:[21]

$$\langle 0 | r_1^0 H_{LL} r_1^0 | 0 \rangle = I_1 + I_2 \qquad (2.C\text{-}11)$$

$$\langle 0 | r_1^0 r_1^0 H_{LL} | 0 \rangle = I_3 + I_4 + I_5 + I_6 \qquad (2.C\text{-}12)$$

where

$$I_1 = \langle 0 | z_1 Q_1 z_2 | 0 \rangle \quad ; \quad I_2 = \langle 0 | z_1 Q_2 z_2 | 0 \rangle$$

$$I_3 = \langle 0 | z_1^2 Q_1 | 0 \rangle \quad ; \quad I_4 = \langle 0 | z_1^2 Q_2 | 0 \rangle$$

$$I_5 = \langle 0 | z_1 z_2 Q_1 | 0 \rangle \quad ; \quad I_6 = \langle 0 | z_1 z_2 Q_2 | 0 \rangle \qquad (2.C\text{-}13)$$

$$|0\rangle = \psi(1,2) = \frac{Z_\alpha^3}{\pi} e^{-Z_\alpha (r_1 + r_2)} \qquad (2.C\text{-}14)$$

Here we evaluate the integral I_2 explicitly. The other integrals are easier and can be treated in an analogous manner. The following properties[20,26] 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;

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26. A. Simon, J. H. Vander Sluis and L. C. Biedenharn, Tables of the Racah Coefficients, Technical Report ORNL-1679, Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

$$\sum_{\alpha} C(abc;\alpha,\gamma-\alpha)\, C(abd,\alpha,\gamma-\alpha) = \delta_{cd} \qquad (2.C\text{-}15)$$

$$[(2e+1)(2f+1)]^{1/2} W(abcd;ef) = \sum_{\alpha,\beta} C(abe;\alpha,\beta)\, C(edc;\alpha+\beta,\gamma-\alpha-\beta) \times C(bdf;\beta,\gamma-\alpha-\beta)\, C(afc;\alpha,\gamma-\alpha) \qquad (2.C\text{-}16)$$

$$C(abe;\alpha\beta)\, C(edc;\alpha+\beta,\delta) = \sum_{f} [(2e+1)(2f+1)]^{1/2} W(abcd;ef) \times C(bdf;\beta\delta)\, C(afc;\alpha,\beta+\delta) \qquad (2.C\text{-}17)$$

$$\sum_{e} (2e+1)(2f+1)\, W(abcd;ef)\, W(abcd;eg) = \delta_{fg}. \qquad (2.C\text{-}18)$$

Letting Q_2 operate on the product $(z_2 \psi(1,2))$, the integral I_2 may be written as

$$I_2 = I_2^{(1)} + I_2^{(2)} \qquad (2.C\text{-}19)$$

where

$$I_2^{(1)} = -Z_a \frac{(4\pi)^3}{3} (2)^{1/2} \sum_{k,k',q} \sum_{L=0}^{1} \sum_{M,\omega} (-1)^{q+L+\omega} \frac{C(L,1-L,1;M,\omega-M)}{[(2L+1)!\,(3-2L)!]^{1/2}}$$

$$\times C(k1k';00)\, C(k1k';q,0)$$

$$\times \int Y_1^0(1)\, Y_1^{-\omega}(1)\, Y_{k'}^{-q}(1)\, Y_{1-L}^{\omega-M}(1)\, Y_k^{q}(2)\, Y_L^{M}(2)\, r_2^{L} r_1^{2-L} A_{k,k'} \Psi$$

(2.C-20)

and

$$I_2^{(2)} = Z_a^2 \frac{(4\pi)^4}{9} (2)^{1/2} \sum_{k,k',q} \sum_{L=0}^{1} \sum_{M,\omega,\kappa} (-1)^{q+L+\omega+\kappa} \frac{C(L,1-L,1;M,\omega-M)}{[(2L+1)!\,(3-2L)!]^{1/2}}$$

$$\times C(k1k';00)\, C(k1k';q,-\kappa)$$

$$\times \int Y_1^0(1)\, Y_1^{-\omega}(1)\, Y_{k'}^{\kappa-q}(1)\, Y_{1-L}^{\omega-M}(1)\, Y_1^0(2)\, Y_k^{q}(2)\, Y_L^{M}(2)\, Y_1^{-\kappa}(2)\, r_2^{L+1} r_1^{2-L} A_{k,k'} \Psi$$

(2.C-21)

Integrating over the angles in Eq. (2.C-20) yields[27]

$$I_2^{(1)} = Z_a \frac{(4\pi)^2}{3} (2)^{1/2} \sum_{\substack{k,k',q \\ k=0,1}} \sum_{\omega,l} (-1)^k C(1,1-k,k;-\omega,\omega+q)\, C(1,1-k,l;-\omega,\omega+q$$

$$\times C(kk'1;q,-q)\, C(lk'1;q,-q)\, C(1,1-k,l;00)\, C(k1k';00)$$

$$\times C(lk'1;00) \left[\frac{(2k'+1)^2}{(2k+1)!\,(2-2k)!\,(2k+1)}\right]^{1/2} \Theta(k,k')$$

(2.C-22)

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[27] We have made use of the symmetry relations for the Clebsch-Gordon coefficients, see for example refs. 20 and 26.

where

$$\Theta(k,k') = \int_0^\infty \int_0^\infty r_2^{k+2} r_1^{4-k} A_{k,k'} \Psi^2(1,2)\, dr_1 dr_2 \quad . \qquad (2.C\text{-}23)$$

Using Eq. (2.C-15) and summing over ω and q gives

$$I_2^{(1)} = Z_a \left(\frac{4\pi}{3}\right)^2 (6)^{1/2} \sum_{k=0}^{1} \sum_{k'} \left[\frac{(2k'+1)}{(2k+1)!(2-2k)!(2k+1)}\right]^{1/2}$$

$$\times\, C(1,1-k,k;00)\{C(k1k';00)\}^2\, \Theta(k,k') \quad .$$

(2.C-24)

Integrating over the angles in Eq. (2.C-21)[27] ;

$$I_2^{(2)} = -Z_a^2 \left(\frac{4\pi}{9}\right)^2 (6)^{1/2} \sum_{k,k'} \sum_{L=0}^{1} \sum_{M,\omega,K} \sum_{l,p} C(1,1-L,L;-\omega,\omega-M)$$

$$\times\, C(1,1-L,l;-\omega,\omega-M)\, C(L1p;M,-K)\, C(pk1;M-K,K-M)$$

$$\times\, C(lk'1;M,-M)\, C(k1k';00)\, C(1,1-L,l;00)\, C(1Lp;00)$$

$$\times\, C(lk'1;00)\, C(pk1;00) \left[\frac{(2k'+1)(2k+1)}{(2L+1)!(2-2L)!}\right]^{1/2} C(1kk';-K,K-M)$$

$$\times\, N(L,k,k')$$

(2.C-25)

where

$$N(L,k,k') = \int_0^\infty \int_0^\infty r_2^{L+3} r_1^{4-L} A_{kk'} \Psi^2(1,2)\, dr_1 dr_2 \quad . \qquad (2.C\text{-}26)$$

Summing over ω, K, M and using Eqs. (2.C-15) and (2.C-16) yields

$$I_2^{(2)} = -Z_a^2 \frac{(4\pi)^2}{9} (6)^{1/2} \sum_{k,k'} \sum_{L=0}^{1} \sum_{p} W(L11k;pk')\, C(kk';00)$$

$$\times C(1,1-L,L;00)\, C(L1p;00)\, C(Lk'1;00)\, C(pk1;00)$$

$$\times (2k'+1) \left[\frac{(2k+1)(2p+1)}{(2L+1)!\,(2-2L)!}\right]^{1/2} N(L,k,k') \tag{2.C-27}$$

Applying Eq. (2.C-17) one can express the product $\{C(L1p;00)\, C(pk1;00)\}$ in terms of the Racah coefficient $W(L11k;pk')$. Then summing over p and using Eq. (2.C-18) one obtains finally

$$I_2^{(2)} = -Z_a^2 \frac{(4\pi)^2}{9} (6)^{1/2} \sum_{k,k'} \sum_{L=0}^{1} C(1,1-L,L;00) \left\{C(1kk';00)\, C(Lk'1;00)\right\}^2$$

$$\times \left[\frac{(2k'+1)(2k+1)}{(2L+1)!\,(2-2L)!}\right]^{1/2} N(L,k,k') \,. \tag{2.C-28}$$

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:

$$I_1 = -Z_a \frac{(4\pi)^2}{3} \int_0^\infty \int_0^\infty \frac{r_1^3 r_2^2}{r_>} \Psi^2_{(1,2)}\, dr_1\, dr_2$$

$$+ Z_a^2 \left(\frac{4\pi}{3}\right)^2 \sum_k \left\{C(1k1;00)\right\}^2 M(k) \tag{2.C-29}$$

where

$$M(k) \equiv \int_0^\infty\int_0^\infty r_1^3 r_2^3 \frac{r_<^k}{r_>^{k+1}} \Psi^2(1,2)\, dr_1\, dr_2 \quad ; \qquad (2.C\text{-}30)$$

$$I_3 = \frac{(4\pi)^2}{9} Z_a^2 \int_0^\infty\int_0^\infty r_1^4 r_2^2 \frac{r_<}{r_>^2} \Psi^2(1,2)\, dr_1\, dr_2 \quad ; \qquad (2.C\text{-}31)$$

$$I_4 = -Z_a^2 \frac{(4\pi)^2}{3}\left(\frac{2}{3}\right)^{1/2} \sum_k \sum_{L=0}^{1} C(1-L,1,L;00)\left\{C(Lk1;00)\right\}^2 \times \left[\frac{2k+1}{(2L)!(2-2L)!}\right]^{1/2} S(k,L) \qquad (2.C\text{-}32)$$

$$S(k,L) = \int_0^\infty\int_0^\infty r_1^{5-L} r_2^{L+2} A_{k,L} \Psi^2(1,2)\, dr_1\, dr_2 \quad ; \qquad (2.C\text{-}33)$$

$$I_5 = Z_a^2 \left(\frac{4\pi}{3}\right)^2 \sum_k \left\{C(1k1;00)\right\}^2 M(k) \quad ; \qquad (2.C\text{-}34)$$

$$I_6 = I_2^{(2)} \qquad (2.C\text{-}35)$$

The values of the radial integrals appearing in $I_1, \cdots, I_6$ are:

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

$$\Theta(1,2) = \left(\frac{3}{5}\right)^{1/2}\frac{3}{(4)^4\pi^2} \quad ;$$

$$N(0,0,1) = \frac{33}{(3)^{1/2}(4)^5\pi^2 Z_a} \quad ; \quad N(1,1,0) = -3N(0,0,1)$$

$$N(0,2,1) = -\left(\frac{5}{3}\right)^{1/2}\frac{15}{(4)^5\pi^2 Z_a} \quad ; \quad N(1,1,2) = \frac{-3}{5}N(0,2,1)$$

$$N(1,3,2) = \frac{(21)^{1/2}}{5}N(0,2,1) \quad ;$$

$$\int_0^\infty\!\!\int_0^\infty \frac{r_1^3 r_2^2}{r_>}\psi^2_{(1,2)}\,dr_1\,dr_2 = \frac{25}{2(4)^4\pi^2} \quad ;$$

$$M(0) = \frac{33}{2(4)^4\pi^2 Z_a} \quad ; \quad M(2) = \frac{15}{2(4)^4\pi^2 Z_a} \quad ;$$

$$\int_0^\infty\!\!\int_0^\infty r_1^4 r_2^2 \frac{r_<}{r_>^2}\psi^2_{(1,2)}\,dr_1\,dr_2 = \frac{3}{(4)^3\pi^2 Z_a} \quad ;$$

$$S(1,0) = \frac{3}{(5)^{1/2}}N(0,2,1) \quad ; \quad S(2,1) = N(0,2,1)$$

$$S(0,1) = N(0,0,1) .$$

Finally, evaluating the Clebsch-Gordon coefficients in the expressions for the integrals $I_1, \ldots, I_6$ we obtain;

$$I_1 = -Z_a/8 \quad ; \quad I_2 = -Z_a/12$$

$$I_3 = Z_a/12 \quad ; \quad I_4 = -Z_a/12$$

$$I_5 = 13Z_a/6(4)^2 \quad ; \quad I_6 = 7Z_a/6(4)^2 . \qquad (2.C-36)$$