ONE- AND TWO CENTER EXPANSIONS OF THE BREIT-PAULI HAMILTONIAN*

by

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ABSTRACT

The orbit-orbit, spin-spin and spin-orbit Hamiltonians of the Breit-Pauli approximation are expressed in terms of irreducible tensors. One- and two-center expansions are given in a form in which the coordinate variables of the interacting particles are separated. In the one-center expansions of the orbit-orbit and spin-orbit Hamiltonians the Author

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use of the gradient formula reduces some of the infinite sums to finite ones. Two center expansions are discussed in detail for the case of non-overlapping charge distributions. The angular parts of the matrix elements of these Hamiltonians are evaluated for product wave functions.

1. Introduction

Relativistic effects cause energy splittings and energy shifts in atoms and molecules. They are responsible for certain "forbidden transitions" which are often significant in spectroscopy. These effects also modify the interaction between atoms and molecules at large separations.

The lowest order relativistic corrections to the energy of a system can be calculated by using the Breit-Pauli Hamiltonian. Corrections of order higher than α^2 (where α is the fine structure constant) cannot be obtained consistently in this approximation. This Hamiltonian is limited to systems containing nuclei with $Z \ll 137$. However, this does not seem to be a practical limitation for many problems since the valence electrons are shielded by the inner shell electrons and thus are not appreciably affected by the bare nuclear charges. In long range force calculations the Breit-Pauli approximation is valid for intermolecular separations less than the wavelength of the characteristic transition in the molecules.[1,2] At larger separations retardation effects become more important and quantum electrodynamics must be used to calculate the higher order corrections.[3]

In this paper one-and two-center expansions for the orbit-orbit, spin-spin and spin-orbit Hamiltonians are derived using the algebra of irreducible tensors.[4,5] This

technique makes it possible to separate the coordinate variables of the interacting particles. If product wave functions are used, then the matrix elements can be evaluated in a straightforward manner.

In the one-center expansions the coefficient involving the radial variables contains an infinite sum. In the case of the orbit-orbit and spin-orbit Hamiltonians, the use of the gradient formula results in a finite sum. This technique has also been used by Blume and Watson[6] for the spin-orbit Hamiltonian.

In the two-center expansions only the expressions for non-overlapping charge distributions are discussed in detail. The general case, however, can be treated using the same techniques.

For other expansions and integrations of the spin-spin Hamiltonian see Ref. 7.

2. The Breit-Pauli Hamiltonian

The following Breit-Pauli Hamiltonian[8] describes the interactions of electrons moving in a nuclear Coulomb field. The operators for the spin and linear momentum of the j-th electron are denoted by $\underset{\sim}{s}_j$ and $\underset{\sim}{p}_j = (1/i)\underset{\sim}{\nabla}_j$, respectively. All the results are in atomic units (energy in e^2/a_o units, length in a_o units where a_o is the Bohr radius). The vector going from electron k to electron j is $\underset{\sim}{r}_{jk} = \underset{\sim}{r}_j - \underset{\sim}{r}_k$. We use Greek indices to designate nuclei and Roman indices to represent electrons.

The derivation of the Breit-Pauli Hamiltonian is discussed for a 2-electron atom by Bethe and Salpeter.[9,10] The generalization to a molecular system is given by Hirschfelder, Curtiss and Bird.[11] The grouping of the terms is similar to the one used by Bethe and Salpeter:[9]

$$H = H_e + \alpha^2 H_{rel} \tag{2-1}$$

where $\alpha = e^2/\hbar c$ is the fine structure constant;

$$H_e = -\frac{1}{2}\sum_j \nabla_j^2 - \sum_{j,\beta} \frac{Z_\beta}{r_{j\beta}} + \sum_{k>j} \frac{1}{r_{jk}} + \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \tag{2-2}$$

and

$$H_{rel} = H_{LL} + H_{SS} + H_{SL} + H_P + H_D \tag{2-3}$$

with

$$H_{LL} = -\frac{1}{2}\sum_{k>j}\frac{1}{r_{jk}^3}\left[r_{jk}^2\,\underline{p}_j\cdot\underline{p}_k + \underline{r}_{jk}\cdot(\underline{r}_{jk}\cdot\underline{p}_j)\underline{p}_k\right] \tag{2-4}$$

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

$$H_{SL} = \frac{1}{2}\sum_{\beta,j}\frac{Z_\beta}{r_{j\beta}^3}(\underline{r}_{j\beta}\times\underline{p}_j)\cdot\underline{s}_j - \frac{1}{2}\sum_{k\neq j}\frac{1}{r_{jk}^3}\left[(\underline{r}_{jk}\times\underline{p}_j)\cdot\underline{s}_j - 2(\underline{r}_{jk}\times\underline{p}_k)\cdot\underline{s}_j\right] \tag{2-6}$$

$$H_P = -\frac{1}{8}\sum_j p_j^4 \tag{2-7}$$

$$H_D = \frac{\pi}{2}\left[\sum_{\beta,j} Z_\beta\,\delta^{(3)}(\underline{r}_{j\beta}) - 2\sum_{k>j}\delta^{(3)}(\underline{r}_{jk})\right] \tag{2-8}$$

Eq. (2-2) is the usual non-relativistic Hamiltonian for the system. Z_α is the nuclear charge of the α-th nucleus.

The first term in the relativistic Hamiltonian, H_{rel}, gives the orbit-orbit interaction corresponding to the classical electromagnetic coupling of the electrons.

The coupling of the spin magnetic moments is given by H_{SS}. The Fermi contact term involving the delta function gives the behaviour of this Hamiltonian when $r_{jk} = 0$. The second term is only applicable when $r_{jk} \neq 0$.

H_{SL} represents the spin-orbit magnetic coupling between electrons.

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.

In the above equations the nuclei are considered fixed (Born-Oppenheimer approximation) and we assume no external electric or magnetic fields.

In order to derive the one-and two-center expansions of the Breit-Pauli Hamiltonian, it is convenient to use the algebra of irreducible spherical tensors.[4,5] This method allows the separation of the variables into product form and permits the application of the Wigner-Eckart theorem[12] in the calculation of matrix elements. The first step in this procedure is to write the various terms in the Breit-

Pauli Hamiltonian as contractions of irreducible tensors. To illustrate the method of contraction, we consider H_{LL} specifically and then state the results for the other relativistic Hamiltonians without derivation.

In the first term of H_{LL} one has to contract $\underset{\sim}{p}_j \cdot \underset{\sim}{p}_k$. This can be done by introducing the following spherical tensor of the aribitrary vector $\underset{\sim}{A}$;

$$T_1^{\pm 1}(\underset{\sim}{A}) = \mp \frac{1}{\sqrt{2}}\left(A_x \pm i A_y\right) \quad ; \quad T_1^0 = A_z \qquad (2\text{-}9)$$

Then

$$\underset{\sim}{\rho}_j \cdot \underset{\sim}{\rho}_k = \sum_{\omega=-1}^{1} (-1)^{\omega} T_1^{\omega}(\underset{\sim}{\rho}_j)\, T_1^{-\omega}(\underset{\sim}{\rho}_k) \qquad (2\text{-}10)$$

The second term of H_{LL} can be written as a double contraction. The first contraction is as follows

$$\underset{\sim}{r}_{jk} \cdot \underset{\sim}{\rho}_j = \left(\frac{4\pi}{3}\right)^{1/2} \sum_{\omega} (-1)^{\omega} \mathcal{Y}_1^{\omega}(\underset{\sim}{r}_{jk})\, T_1^{-\omega}(\underset{\sim}{\rho}_j) \qquad (2\text{-}11)$$

where $\mathcal{Y}_1^{\omega}(\underset{\sim}{r}_{jk})$ is a solid spherical harmonic which in general is defined as[13]

$$\mathcal{Y}_\ell^m(\underset{\sim}{r}) = r^\ell Y_\ell^m(\theta, \varphi) \qquad (2\text{-}12)$$

Then

$$\underline{r}_{jk}\cdot(\underline{r}_{jk}\cdot\underline{\rho}_j)\underline{\rho}_k = \frac{4\pi}{3}\sum_{\omega=-1}^{1}\sum_{\eta=-1}^{1}(-1)^{\omega+\eta}Y_1^{\omega}(\underline{r}_{jk})Y_1^{\eta}(\underline{r}_{jk})T_1^{-\omega}(\underline{\rho}_j)T_1^{-\eta}(\underline{\rho}_k) \quad (2\text{-}13)$$

The two solid spherical harmonics can now be coupled together;[14]

$$Y_1^{\omega}(\underline{r}_{jk})Y_1^{\eta}(\underline{r}_{jk}) = r_{jk}^2\sum_{\ell}\frac{3}{[4\pi(2\ell+1)]^{1/2}}C(11\ell;\omega,\eta) \times C(11\ell;00)Y_{\ell}^{\omega+\eta}(\theta_{jk},\varphi_{jk}) \quad . \quad (2\text{-}14)$$

The Clebsch-Gordan coefficient C(1,1,ℓ;00) vanishes unless (1 + 1 +ℓ) is even and ℓ is in the range 0 to 2.

Using Eqs. (2-10) - (2-14), one obtains:

$$H_{LL} = \sum_{k>j}\frac{1}{r_{jk}}\left[\begin{array}{l} -\frac{2}{3}\sum_{\omega}(-1)^{\omega}T_1^{\omega}(\underline{\rho}_j)T_1^{-\omega}(\underline{\rho}_k) \\ -\left(\frac{2\pi}{15}\right)^{1/2}\sum_{\omega,\eta}(-1)^{\omega+\eta}C(112;\omega,\eta) \\ \times Y_2^{\omega+\eta}(\theta_{jk},\varphi_{jk})T_1^{-\omega}(\underline{\rho}_j)T_1^{-\eta}(\underline{\rho}_k) \end{array}\right] \quad (2\text{-}15)$$

The first part of Eq. (2-15) contains a contribution from the $\ell = 0$ term of Eq. (2-14). The Clebsch-Gordan coefficient in Eq. (2-15) can be given in closed form.

$$C(112;\omega\eta) = \left[\frac{(2+\omega+\eta)!(2-\omega-\eta)!}{6(1+\omega)!(1-\omega)!(1+\eta)!(1-\eta)!}\right]^{1/2} . \qquad (2\text{-}16)$$

In a similar fashion the spin-spin Hamiltonian can be contracted to yield.[16]

$$H_{SS} = \sum_{k>j} \left[\begin{array}{l} -\frac{8\pi}{3}\delta^{(3)}(\underset{\sim}{r}_{jk}) \sum_{\omega} (-1)^{\omega} T_1^{\omega}(\underset{\sim}{S}_j) T_1^{-\omega}(\underset{\sim}{S}_k) \\ -\left(\frac{24\pi}{5}\right)^{1/2} \frac{1}{r_{jk}^3} \sum_{\omega,\eta} (-1)^{\omega+\eta} C(112;\omega\eta) \\ \quad \times Y_2^{\omega+\eta}(\theta_{jk},\phi_{jk}) T_1^{-\omega}(\underset{\sim}{S}_j) T_1^{-\eta}(\underset{\sim}{S}_k) \end{array} \right] . \qquad (2\text{-}17)$$

It is sometimes convenient to couple the spins together to form a total spin tensor defined by[4,5]

$$T_\ell^{-\nu}(\underset{\sim}{S}_j,\underset{\sim}{S}_k) = \sum_{\kappa} C(11\ell;-\kappa,-\nu+\kappa) T_1^{-\kappa}(\underset{\sim}{S}_j) T_1^{-\nu+\kappa}(\underset{\sim}{S}_k) . \qquad (2\text{-}18)$$

Then the Fermi contact term contracts to a scalar and in the spin dipole-dipole term the spin transforms like a second rank tensor;

$$H_{SS} = \sum_{k>j} \left[\begin{array}{l} \frac{8\pi}{\sqrt{3}} \delta^{(3)}(r_{jk}) \, T_0^0(S_j, S_k) \\ -\left(\frac{24\pi}{5}\right)^{1/2} \frac{1}{r_{jk}^3} \sum_{\nu} (-1)^{\nu} Y_2^{\nu}(\theta_{jk}, \phi_{jk}) \, T_2^{-\nu}(S_j, S_k) \end{array} \right] . \qquad (2\text{-}19)$$

In the spin-orbit Hamiltonian, H_{SL}, one can first introduce a tensor $T_1^{\omega}(rxp)$ to give

$$\begin{aligned} H_{SL} = & \frac{1}{2} \sum_{\beta} \sum_{j} \frac{Z_\beta}{r_{j\beta}^3} \sum_{\omega} (-1)^{\omega} T_1^{\omega}(r_{j\beta} \times p_j) \, T_1^{-\omega}(S_j) \\ & - \frac{1}{2} \sum_{k \neq j} \frac{1}{r_{jk}^3} \sum_{\omega} (-1)^{\omega} \left[T_1^{\omega}(r_{jk} \times p_j) \right. \\ & \left. - 2 T_1^{\omega}(r_{jk} \times p_k) \right] T_1^{-\omega}(S_j) . \end{aligned} \qquad (2\text{-}20)$$

In the first term of Eq. (2-20), $(r_{j\beta} x p_j)$ is the orbital angular momentum operator of electron j with respect to nucleus β. The vectors $(r_{jk} x p_k)$, however, are not angular momentum operators about a fixed center. Here it is convenient to write them as a contraction which separates the position variables from the momentum operator;

$$T_1^{\omega}(r_{jk} \times p_j) = \frac{1}{i} \sqrt{\frac{8\pi}{3}} \sum_{\eta=-1}^{1} C(111; \eta, \omega-\eta) \, Y_1^{\eta}(r_{jk}) \, T_1^{\omega-\eta}(p_j) . \qquad (2\text{-}21)$$

The Clebsch-Gordan coefficient in Eq. (2-21) is given by

$$C(111;\eta,\omega-\eta)=\frac{1}{\sqrt{8}}\begin{bmatrix}\left[\dfrac{(1+\eta)!(1-\omega+\eta)!(1+\omega)!(1-\omega)!}{(1-\eta)!(1+\omega-\eta)![\eta!(\eta-\omega)!]^2}\right]^{1/2}\\ -\left[\dfrac{(1-\eta)!(1+\omega-\eta)!(1+\omega)!(1-\omega)!}{(1+\eta)!(1-\omega+\eta)![(1-\eta)!(\omega-\eta)!]^2}\right]^{1/2}\end{bmatrix} \qquad (2\text{-}22)$$

The remaining relativistic Hamiltonians, H_P and H_D, only involve scalars and thus need not be considered further.

3. One-Center Expansions

In general the origin of the coordinate system is arbitrary. The vectors $\underset{\sim}{r}_\beta$ and $\underset{\sim}{r}_j$ denote the position of a nucleus and an electron respectively.

The derivation of the one center expansion for H_{LL}, H_{SS} and H_{SL} respectively, consists of three steps. First one has to express the $Y_\ell^\mu(\theta_{jk}, \varphi_{jk})$ as a sum of products in the spherical harmonics of (θ_j, φ_j) and (θ_k, φ_k). Then $(1/r_{jk})^n$ is expanded in a similar manner. Finally the two expansions are coupled together.

The general addition theorem for the solid spherical harmonics is given by Rose;[17]

$$\mathcal{Y}_N^\mu(\underset{\sim}{r}_{jk}) = \left[4\pi(2N+1)!\right]^{1/2} \sum_{L=0}^{N} \sum_{\chi=-L}^{L} \frac{C(L,N-L,N;\chi,\mu-\chi)}{\left[(2L+1)!(2N-2L+1)!\right]^{1/2}} \times \mathcal{Y}_{N-L}^{\mu-\chi}(\underset{\sim}{r}_j)\,\mathcal{Y}_L^{\chi}(\underset{\sim}{r}_k) \qquad (3\text{-}1)$$

The one-center expansion for $(1/r_{jk})^n$ can always be written in the form[18]

$$\frac{1}{r_{jk}^n} = 4\pi \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \frac{R(-n,\ell)}{(2\ell+1)} (-1)^\nu Y_\ell^\nu(\theta_j,\varphi_j)\, Y_\ell^{-\nu}(\theta_k,\varphi_k) \qquad (3\text{-}2)$$

where $R(-n,\ell)$ is a function of r_j and r_k. Only the radial coefficients for n = 1,3 and 5 are required. If one uses the Laplace expansion then[18]

$$R(-1,\ell) = \frac{r_<^{\ell}}{r_>^{\ell+1}} \tag{3-3}$$

$$R(-3,\ell) = (2\ell+1)\sum_{n=0}^{\infty} \frac{r_<^{2n+\ell}}{r_>^{2n+\ell+3}} \tag{3-4}$$

$$R(-5,\ell) = \frac{(2\ell+1)}{3}\sum_{n=0}^{\infty} (n+1)(2\ell+2n+3)\frac{r_<^{2n+\ell}}{r_>^{2n+\ell+5}} \tag{3-5}$$

where $r_>$ and $r_<$ stand for the greater or lesser of r_j and r_k. The coefficients $R(-n,\ell)$ can also be written symmetrically with respect to r_j and r_k. There are two such expansions; they involve powers of $(r_j^2 + r_k^2)^{1/2}$ and $(r_j + r_k)$ respectively[18,19]

$$R(-1,\ell) = (2\ell+1)\sum_{n} \frac{(2n-1)!!\, r_j^n r_k^n}{(n+\ell+1)!!\,(n-\ell)!!\, r^{2n+1}} \tag{3-6}$$

$$R(-3,\ell) = (2\ell+1)\sum_{n} \frac{(2n+1)!!\, r_j^n\, r_k^n}{(n+\ell+1)!!(n-\ell)!!\, r^{2n+3}} \qquad (3\text{-}7)$$

$$R(-5,\ell) = \frac{(2\ell+1)}{3}\sum_{n} \frac{(2n+3)!!\, r_j^n\, r_k^n}{(n+\ell+1)!!(n-\ell)!!\, r^{2n+5}} \qquad (3\text{-}8)$$

where $r = (r_j^2 + r_k^2)^{1/2}$, $n = \ell, \ell+2, \ell+4, \cdots$, $(2k)!! = 2\cdot 4\cdots 2k$ and $(2k+1)!! = 1\cdot 3\cdots(2k+1)$;

$$R(-1,\ell) = 2(2\ell+1)\sum_{n=0}^{\infty} \frac{(2\ell+2n-1)!\,(\ell+n)\,(r_j r_k)^{\ell+n}}{(2\ell+n+1)!\, n!\,(r_j+r_k)^{2\ell+2n+1}} \qquad (3\text{-}9)$$

$$R(-3,\ell) = (2\ell+1)\sum_{n=0}^{\infty} \frac{(2\ell+2n+1)!\,(r_j r_k)^{\ell+n}}{(2\ell+n+1)!\, n!\,(r_j+r_k)^{2\ell+2n+3}} \qquad (3\text{-}10)$$

$$R(-5,\ell) = \frac{(2\ell+1)}{6}\sum_{n=0}^{\infty} \frac{(2\ell+2n+3)!\,(r_j r_k)^{\ell+n}}{(\ell+n+1)(2\ell+n+1)!\, n!\,(r_j+r_k)^{2\ell+2n+5}} \qquad (3\text{-}11)$$

Finally Eqs. (3-1) and (3-2) are combined using the coupling theorem for spherical harmonics.[14]

$$\frac{1}{r_{jk}^{n}} y_N^{\mu}(r_{jk}) = \left[4\pi(2N+1)!\right]^{1/2} \sum_{\ell,\nu} \sum_{L,\kappa} \sum_{q,t} \chi_N^{\mu}(\ell,\nu;L,\kappa;q;t)$$

(3-12)

$$\times r_j^{N-L} r_k^{L} R(-n,\ell) Y_q^{\mu+\nu-\kappa}(\theta_j,\varphi_j) Y_t^{\kappa-\nu}(\theta_k,\varphi_k)$$

where

$$\chi_N^{\mu}(\ell,\nu;L,\kappa;q;t) = (-1)^{L+\nu} \frac{C(L,N-L,N;\kappa,\mu-\kappa)C(N-L,\ell,q;\mu-\kappa,\nu)}{\left[(2q+1)(2t+1)(2L)!(2N-2L)!\right]^{1/2}}$$

(3-13)

$$\times C(N-L,\ell,q;00)C(L,\ell,t;\kappa,-\nu)C(L,\ell,t;00).$$

Here the sums over q and t are controlled by the Clebsch-Gordan coefficients.

One can now apply Eq. (3-12) to the tensorial representation of the relativistic Hamiltonians (Eqs. (2-15), (2-17) and (2-20)). The resulting one-center expansions are:

$$H_{LL} = -8\pi \sum_{k>j} \Bigg[+ \frac{1}{3} \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \sum_{\omega=-1}^{1} (-1)^{\nu+\omega} \frac{R(-1,\ell)}{(2\ell+1)} Y_\ell^{\nu}(\theta_j,\varphi_j) Y_\ell^{-\nu}(\theta_k,\varphi_k)$$
$$\times T_1^{\omega}(\underline{r}_j) T_1^{-\omega}(\underline{r}_k)$$
$$+ \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \sum_{L=0}^{2} \sum_{K=-L}^{L} \sum_{q,t} \sum_{\omega,\eta=-1}^{1} (-1)^{\omega+\eta} C(112;\omega,\eta)$$
$$\times \chi_2^{\omega+\eta}(\ell,\nu;L,K;q;t) r_j^{2-L} r_k^{L} \qquad (3\text{-}14)$$
$$\times R(-3,\ell) Y_q^{\omega+\eta+\nu-K}(\theta_j,\varphi_j) Y_t^{K-\nu}(\theta_k,\varphi_k)$$
$$\times T_1^{-\omega}(\underline{r}_j) T_1^{-\eta}(\underline{r}_k) \Bigg]$$

$$H_{SS} = -8\pi \sum_{k>j} \Bigg[+ \frac{1}{3} \delta^{(3)}(\underline{r}_{jk}) \sum_{\omega=-1}^{1} T_1^{\omega}(\underline{s}_j) T_1^{-\omega}(\underline{s}_k)$$
$$+ 6 \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \sum_{L=0}^{2} \sum_{K=-L}^{L} \sum_{q,t} \sum_{\omega,\eta=-1}^{1} (-1)^{\omega+\eta} C(112;\omega,\eta) \qquad (3\text{-}15)$$
$$\times \chi_2^{\omega+\eta}(\ell,\nu;L,K;q;t) r_j^{2-L} r_k^{L} R(-5,\ell)$$
$$\times Y_q^{\omega+\eta+\nu-K}(\theta_j,\varphi_j) Y_t^{K-\nu}(\theta_k,\varphi_k) T_1^{-\omega}(\underline{s}_j) T_1^{-\eta}(\underline{s}_k) \Bigg]$$

$$H_{SL} = \frac{1}{2}\sum_{\beta}\sum_{j}\frac{Z_\beta}{r_{j\beta}^3}\sum_{\omega=-1}^{1}(-1)^\omega T_1^{\omega}(\underline{r}_{j\beta}\times\underline{p}_j)\,T_1^{-\omega}(\underline{s}_j)$$

$$-\frac{4\pi}{i}\sum_{k\neq j}\sum_{\ell=0}^{\infty}\sum_{\nu=-\ell}^{\ell}\sum_{L=0}^{1}\sum_{K=-L}^{L}\sum_{q,t}\sum_{\omega,\eta=-1}^{1}(-1)^\omega C(111;\eta,\omega-\eta) \tag{3-16}$$

$$\times\chi_1^{\eta}(\ell,\nu;L,K;q;t)\,r_j^{L-L}\,r_k^{L}\,R(-3,\ell)$$

$$\times Y_q^{\eta+\nu-K}(\theta_j,\varphi_j)\,Y_t^{K-\nu}(\theta_k,\varphi_k)$$

$$\times\left[T_1^{\omega-\eta}(\underline{p}_j) - 2\,T_1^{\omega-\eta}(\underline{p}_k)\right]T_1^{-\omega}(\underline{s}_j)\ .$$

There is a striking similarity between the second terms of H_{LL} and H_{SS}, the difference being the radial coefficient R and the appearance of linear momentum operators in H_{LL} and spin in H_{SS}. It is interesting to note that the angular momentum operators do not appear in H_{LL}. It is indeed possible to rewrite this Hamiltonian in such a way that it contains angular momentum terms but the transformed Hamiltonian does not simplify appreciably.[20] In all these expansions, the variables associated with electron j and k are now separated. In this form the angular part of the matrix elements of these Hamiltonians can be carried out in a straightforward manner (see Sec. 5). A difficulty arises in the radial integrations since the coefficients $R(-n,\ell)$ for $n>1$ involve infinite sums.

In the case of H_{LL} and H_{SL} these infinite sums can be transformed into finite ones by applying the gradient formula to Eqs. (2-4) and (2-6) respectively. The procedure makes use of the fact that $\underset{\sim}{r}_{jk}/r_{jk}^3$ appears in these two Hamiltonians. By making use of the relationship

$$\frac{\underset{\sim}{r}_{jk}}{r_{jk}^3} = -\nabla_j \frac{1}{r_{jk}} \tag{3-17}$$

and the gradient formula[21]

$$T_1^{\mu}(\underset{\sim}{\nabla})\Phi(r)Y_{\ell}^{\nu}(\theta,\varphi) = \sqrt{\frac{\ell+1}{2\ell+3}}\,C(\ell,1,\ell+1;\nu,\mu)\,Y_{\ell+1}^{\nu+\mu}(\theta,\varphi)$$
$$\times\left(\frac{d\Phi}{dr} - \frac{\ell}{r}\Phi\right) - \sqrt{\frac{\ell}{2\ell-1}}\,C(\ell,1,\ell-1;\nu,\mu) \tag{3-18}$$
$$\times Y_{\ell-1}^{\nu+\mu}(\theta,\varphi)\left(\frac{d\Phi}{dr} + \frac{\ell+1}{r}\Phi\right)$$

the μ-th component of $\underset{\sim}{r}_{jk}/r_{jk}^3$ can be written as

$$T_1^{\mu}\left(-\nabla_j \frac{1}{r_{jk}}\right) = +4\pi \sum_{\ell,n,\nu} (-1)^{\nu} C(\ell 1 n; 00)$$
$$\times C(\ell 1 n;\nu,-\mu)\,Y_n^{\mu-\nu}(\theta_j,\varphi_j)\,Y_{\ell}^{\nu}(\theta_k,\varphi_k)\,A_{\ell,n} \tag{3-19}$$

where

$$A_{\ell,\ell+1} = \left(\frac{2\ell+1}{2\ell+3}\right)^{1/2} \frac{r_k^{\ell}}{r_j^{\ell+2}}\, \varepsilon(r_j - r_k)$$

$$A_{\ell,\ell-1} = -\left(\frac{2\ell+1}{2\ell-1}\right)^{1/2} \frac{r_j^{\ell-1}}{r_k^{\ell+1}}\, \varepsilon(r_k - r_j) \qquad (3\text{-}20)$$

and $\varepsilon(x-y) = 1$ for $x>y$; $\varepsilon = 0$ for $y>x$. With these equations one can rewrite H_{LL} and H_{SL} in the following way

$$H_{LL} = -\frac{(4\pi)^2}{6} \sum_{k>j} \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \sum_{\omega=-1}^{1} (-1)^{\nu+\omega} \frac{R(-1,\ell)}{(2\ell+1)}\, Y_{\ell}^{\nu}(\theta_j,\varphi_j)\, Y_{\ell}^{-\nu}(\theta_k,\varphi_k)$$

$$\times T_1^{\omega}(\rho_j)\, T_1^{-\omega}(\rho_k)$$

$$-\frac{(4\pi)^2\sqrt{2}}{6} \sum_{k>j} \sum_{\ell=0}^{\infty} \sum_{\nu=-\ell}^{\ell} \sum_{L=0}^{1} \sum_{\chi=-L}^{L} \sum_{\gamma\neq 0}^{1} \sum_{\omega,\eta=-1}^{1} G \qquad (3\text{-}21)$$

$$\times r_j^{1-L}\, r_k^{L}\, A_{\ell,n}\, Y_q^{\gamma+\omega-\nu-\chi}(\theta_j,\varphi_j)\, Y_{+}^{\nu+\chi}(\theta_k,\varphi_k)\, T_1^{-\omega}(\rho_j)\, T_1^{-\eta}(\rho_k)$$

where

$$G = (-1)^{L+\nu+\omega+\eta}\left[\frac{(2n+1)(2\ell+1)}{(2L)!(2-2L)!(2q+1)(2t+1)}\right]^{1/2}$$
$$\times C(L,1-L,1;\kappa,\omega-\kappa)C(\ell 1n;00)C(\ell 1n;\nu,-\eta)$$
$$\times C(n,1-L,q;\eta-\nu,\omega-\kappa)C(n,1-L,q;00) \qquad (3\text{-}22)$$
$$\times C(\ell Lt;\nu,\kappa)C(\ell Lt;00)$$

$$H_{SL} = \frac{1}{2}\sum_{\beta}\sum_{j}\frac{Z_\beta}{r_{j\beta}^3}\sum_{\omega=-1}^{1}(-1)^{\omega}T_1^{\omega}(\underline{r}_{j\beta}\times\underline{p}_j)T_1^{-\omega}(\underline{s}_j)$$
$$-\frac{2\pi\sqrt{2}}{i}\sum_{k\neq j}\sum_{\ell=0}^{\infty}\sum_{\nu=-\ell}^{\ell}\sum_{n}\sum_{\omega,\eta=-1}^{1}C(111;\eta,\omega-\eta) \qquad (3\text{-}23)$$
$$\times C(\ell 1n;\nu,-\eta)C(\ell 1n;00)Y_n^{\eta-\nu}(\theta_j,\phi_j)Y_\ell^{\nu}(\theta_k,\phi_k)$$
$$\times A_{\ell,n}\left[T_1^{\omega-\eta}(\underline{p}_j)-2T_1^{\omega-\eta}(\underline{p}_k)\right]T_1^{-\omega}(\underline{s}_j)\ .$$

In a calculation of matrix elements of H_{LL} the angular integration restricts the ranges of g and t and then $C(\ell,L,t;00)$, say, limits the sum over ℓ. For H_{SL} the angular integration directly limits the sum over ℓ.

4. Two-Center Expansion

One has to distinguish several regions in two-center expansions.[22] In longe range force calculations the distance, R, between the two centers is larger than the size of the charge distributions of the interacting molecules. In this case one can expand the Breit-Pauli Hamiltonian in a series in inverse powers of R. To obtain two-center expansions for the regions where the charge distributions overlap, one begins with the one-center result, transforms to the second center and re-expands the result.

The coordinate system used in the two-center expansion is given in Fig. 1. The x,y and z axes of the two coordinate systems are parallel. In general $\underset{\sim}{R}$ is not along the z axes. However, in most applications $\underset{\sim}{R}$ is chosen to lie along the z-axes. The vector $\underset{\sim}{r}_j$ specifies the position of electron j with respect to center A and $\underset{\sim}{r}'_k$ the position of electron k referred to center B. The position of the nuclei are designated by $\underset{\sim}{r}_\alpha$ and $\underset{\sim}{r}'_\beta$ respectively.

The quantities $Y_\ell^\mu(\theta_{jk}, \varphi_{jk})$ and r_{jk}^{-n} which occur in the tensor forms of the Breit-Pauli Hamiltonian must be expressed in terms of the variables of the two coordinate systems. To generalize Eq. (3-1) to two centers, one makes use of the relations $\underset{\sim}{r}_{jk} = \underset{\sim}{r}_j - \underset{\sim}{r}_k = \underset{\sim}{r}_j - \underset{\sim}{r}'_k - \underset{\sim}{R}$. Then

$$Y_N^{\mu}(\underset{\sim}{r}_{jk}) = \left[4\pi(2N+1)!\right]^{1/2} \sum_{L=0}^{N} \sum_{X=-L}^{L} (-1)^{N+L}$$

$$\times \frac{C(L, N-L, N; X, \mu-X)}{\left[(2L+1)!(2N-2L+1)!\right]^{1/2}} Y_{N-L}^{\mu-X}(\underset{\sim}{r}_k) Y_L^X(\underset{\sim}{r}_j) \qquad (4\text{-}1)$$

where on the right hand side we have permuted $\underset{\sim}{r}_k$ and $\underset{\sim}{r}_j$ which introduces the phase factor $(-1)^N$. Since $\underset{\sim}{r}_k = \underset{\sim}{r}_k' + \underset{\sim}{R}$, $Y_{N-L}^{\mu-X}(\underset{\sim}{r}_k)$ can be expanded using Eq. (3-1) to give

$$Y_N^{\mu}(\underset{\sim}{r}_{jk}) = 4\pi \sum_{L=0}^{N} \sum_{K=-L}^{L} \sum_{J=0}^{N-L} \sum_{\omega=-J}^{J} (-1)^{N+L} \left[(2N+1)!\right]^{1/2}$$

$$\times \frac{C(L, N-L, N; K, \mu-K) C(J, N-L-J, N-L; \omega, \mu-X-\omega)}{\left[(2L+1)!(2J+1)!(2N-2L-2J+1)!\right]^{1/2}}$$

$$\times Y_L^X(\underset{\sim}{\Omega}) Y_J^{\omega}(\underset{\sim}{r}_K') Y_{N-L-J}^{\mu-X-\omega}(\underset{\sim}{R}) \qquad (4\text{-}2)$$

If $\underset{\sim}{R}$ lies along the z-axes then[23]

$$Y_{N-L-J}^{\mu-X-\omega}(R_z) = R^{N-L-J} \left[\frac{2N-2L-2J+1}{4\pi}\right]^{1/2} \delta_{\mu-X-\omega, 0} \qquad (4\text{-}3)$$

and

$$Y_N^{\mu}(r_{jk}) = r_{jk}^{n}\, Y_N^{\mu}(\theta_{jk}, \varphi_{jk})$$

$$= \left[4\pi(2N+1)\right]^{1/2} \sum_{L=0}^{N} \sum_{J=0}^{N-L} \sum_{\chi=-L}^{L} \frac{(-1)^{N+L}}{(N-L-J)!}$$

$$\times \left[\frac{(N+\mu)!\,(N-\mu)!}{(2L+1)(2J+1)(L+\chi)!\,(L-\chi)!\,(J-\mu+\chi)!\,(J+\mu-\chi)!}\right]^{1/2} \qquad (4\text{-}4)$$

$$\times r_j^{L}\, r_k^{J}\, R^{N-L-J}\, Y_L^{\chi}(\theta_j, \varphi_j)\, Y_J^{\mu-\chi}(\theta_k', \varphi_k')$$

The two-center expansion of r_{jk}^{-n} for overlaping charge distributions is in general very complicated. For n = 1 the expansions have been done for the overlap regions.[22] A method[19] has been developed that can be used for the general expansion of r_{jk}^{-n}. For the non-overlapping region a useful expansion has recently been derived by Sack.[24] In this case electrons j and k are associated with centers A and B respectively. The following result is valid for R along the z-axes;[25]

$$\frac{1}{r_{jk}^{n}} = 4\pi \sum_{\substack{\ell_1,\ell_2,\ell_3 \\ \ell_1+\ell_2+\ell_3=\text{even}}} \sum_{\nu} \sum_{q,t} \frac{(-1)^{\ell_1}(-1)^{\frac{1}{2}(\ell_1+\ell_2+\ell_3)}}{R^{n+\ell_1+\ell_2+2q+2t}} K(\ell_1,\ell_2,\ell_3;\nu)$$

$$\times G(n;\ell_1,\ell_2,\ell_3;q,t;r_j,r_k') Y_{\ell_1}^{\nu}(\theta_j,\varphi_j) Y_{\ell_2}^{-\nu}(\theta_k',\varphi_k') \qquad (4\text{-}5)$$

where

$$K(\ell_1,\ell_2,\ell_3;\nu) = \frac{\left[\frac{1}{2}(\ell_1+\ell_2+\ell_3)\right]!}{\left[\frac{1}{2}(\ell_1+\ell_2-\ell_3)\right]!\left[\frac{1}{2}(\ell_1+\ell_3-\ell_2)\right]!\left[\frac{1}{2}(\ell_2+\ell_3-\ell_1)\right]!}$$

$$\times \left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)(\ell_1+\ell_2-\ell_3)!(\ell_1+\ell_3-\ell_2)!(\ell_2+\ell_3-\ell_1)!}{(\ell_1+\ell_2+\ell_3+1)!}\right]^{1/2} \qquad (4\text{-}6)$$

$$\times C(\ell_1\ell_2\ell_3;-\nu,\nu)$$

and

$$G(n;\ell_1,\ell_2,\ell_3;q,t;r_j,r_k') =$$

$$\frac{2^{\ell_1+\ell_2+q+t}\,\Gamma\left[\frac{1}{2}(n+\ell_1+\ell_2+\ell_3)+q+t\right]}{\Gamma\left(\frac{n}{2}\right)\Gamma\left[\frac{1}{2}(n-1)\right](2\ell_1+2q+1)!!(2\ell_2+2t+1)!!\,q!\,t!} \tag{4-7}$$

$$\times\,\Gamma\left[\frac{1}{2}(n+\ell_1+\ell_2-\ell_3-1)+q+t\right] r_j^{2q+\ell_1}\left(r_k'\right)^{2t+\ell_2}\ .$$

In Eq. (4-7) $\Gamma(x)$ is the Gamma function and the double factorials are defined in Sec. 3. The two center expansion for the orbit-orbit, spin-spin, and spin-orbit Hamiltonians can now be obtained by substituting Eqs. (4-4) and (4-5) in Eqs. (2-15), (2-17) and (2-20) respectively and coupling the various spherical harmonics. In the resulting equations[26] the variables associated with centers A and B are separated.

The Wigner-Eckart theorem[12] when applied to the angular parts of the matrix elements of H_{LL}, H_{SS}, and H_{SL} yields selection rules for these Hamiltonians.

5. Matrix Elements

The one-and two-center expansions of the Breit-Pauli Hamiltonians H_{LL}, H_{SS}, and H_{SL} are of the general form

$$H_{LL} \sim \sum \{\ \} Y_q^{\nu}(\theta_j,\varphi_j) Y_t^{\chi}(\theta_k,\varphi_k) T_1^{-\omega}(\underline{r}_j) T_1^{-\eta}(\underline{r}_k) \qquad (5\text{-}1)$$

$$H_{SS} \sim \sum \{\ \} Y_q^{\nu}(\theta_j,\varphi_j) Y_t^{\chi}(\theta_k,\varphi_k) T_1^{-\omega}(\underline{s}_j) T_1^{-\eta}(\underline{s}_k) \qquad (5\text{-}2)$$

$$H_{SL} \sim \sum \{\ \} Y_q^{\nu}(\theta_j,\varphi_j) Y_t^{\chi}(\theta_k,\varphi_k) T_1^{-\omega}(\underline{r}_j) T_1^{-\eta}(\underline{s}_k) . \qquad (5\text{-}3)$$

If the wave function Ψ is of the type

$$\Psi = \sum_n c_n \prod_i \{\psi_n(\underline{r}_i,\underline{s}_i) \qquad (5\text{-}4)$$

where

$$\Psi(\underline{r}_i, \underline{s}_i) = \Phi(r_i) Y_{\ell_i}^{m_i}(\theta_i, \varphi_i) \eta_{\mu_i}(\underline{s}_i) \qquad (5\text{-}5)$$

then the matrix elements of the Hamiltonians can be calculated in a straightforward manner. In Eq. (5-5) $\eta_{\mu_i}(\underline{s}_i)$ is a two component spinor ($\mu_i = \pm 1/2$).

In H_{LL} and H_{SL} one first has to operate with $T_1^{-\omega}(\underline{p}_j)$ on the wave function. Application of the gradient formula (Eq. (3-18)) yields

$$T_1^{-\omega}(\underline{p}_j) \Phi(r_j) Y_\ell^m(\theta_j, \varphi_j) = \frac{1}{i} \sum_u C(\ell 1 u; m, \omega) \qquad (5\text{-}6)$$

$$\times C(\ell 1 u; 00) Y_u^{m-\omega}(\theta_j \varphi_j) A_{\ell,u}(r_j)$$

where

$$A_{\ell,\ell+1} = \left(\frac{2\ell+1}{2\ell+3}\right)^{1/2} \left(\frac{d\Phi}{dr_j} - \frac{\ell}{r_j} \Phi\right) \qquad (5\text{-}7)$$

$$A_{\ell,\ell-1} = \left(\frac{2\ell+1}{2\ell-1}\right)^{1/2} \left(\frac{d\Phi}{dr_j} + \frac{\ell+1}{r_j} \Phi\right)$$

with all the other A's vanishing because of the triangular condition in $C(\ell,1,\mu;00)$. The angular integrations in H_{LL}, H_{SS}, and H_{SL} are now all of the same form, namely[27]

$$\langle Y_{\ell'}^{m'}(\theta_j,\varphi_j) \,|\, Y_q^{\nu}(\theta_j,\varphi_j) \,|\, Y_{\ell}^{m}(\theta_j,\varphi_j) \rangle$$

$$= \left[\frac{(2\ell+1)(2q+1)}{4\pi(2\ell'+1)}\right]^{1/2} C(\ell\, q\, \ell';\, m, \nu, m')\, C(\ell\, q\, \ell';\, 00)\,. \tag{5-8}$$

The selection rules for this angular integration can be directly obtained from the Clebsch-Gordan coefficients. The integral vanishes unless $\ell + \ell' \leq q \leq |\ell - \ell'|$ and the sum $\ell + \ell' + q$ is even. Also $m' = m + \nu$.

The integration over the spin variables is given by the expression[28]

$$\langle \eta_{\mu'}(s_j) | T_1^{-\omega}(\underline{s}_j) | \eta_{\mu}(s_j) \rangle$$

$$= \frac{\sqrt{3}}{2} C\left(\tfrac{1}{2}\, 1\, \tfrac{1}{2};\, \mu, -\omega, \mu'\right) \qquad (5\text{-}9)$$

$$= (-1)^{\frac{1}{2}-\mu} \tfrac{1}{2} \left[(1-\mu+\mu')!\,(1+\mu-\mu')!\right]^{1/2}.$$

The remaining radial integrals depend on the particular choice of $\underline{\Phi}(r_i)$ and cannot be done in a general manner.

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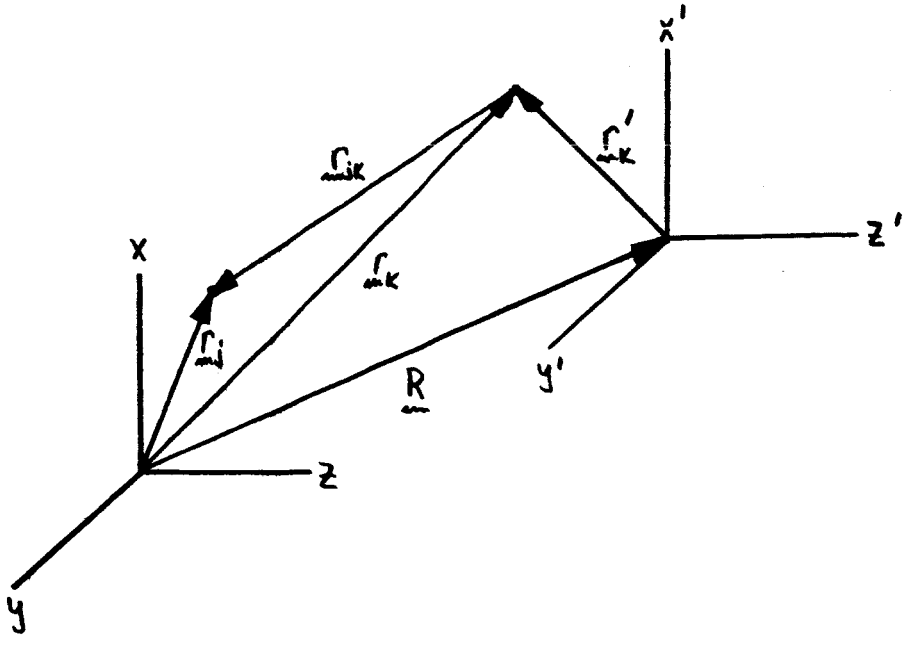
Fig. 1



Coordinate system for two-center expansions

REFERENCES

1. E. A. Power and S. Zienau, Jour. Franklin Inst. 263, 331 (1957).

2. W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. (to be published).

3. H. B. L. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).
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).
C. Mavroyannis and M. J. Stephen, Mol. Phys. 5, 629 (1962).

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

5. A. R. Edmonds, "Angular Momentum in Quantum Mechanics" (John Wiley and Sons, Inc., New York, 1957).

6. M. Blume and R. E. Watson, Proc. Roy. Soc. A270, 127 (1962).

7. R. M. Pitzer, C. W. Kern and W. N. Lipscomb, J. Chem. Phys. 37, 267 (1962); M. Geller and R. W. Griffith, J. Chem. Phys. 40, 2309 (1964); D. M. Schrader, J. Chem. Phys. 41, 3266 (1964).

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

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

10. This Hamiltonian has recently been derived using quantum electrodynamics by T. Itoh, Rev. Mod. Phys. 37, 159 (1965).

11. 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.

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

13. The phase convention we use for the $Y_\ell^m(\theta,\varphi)$ is the same as that used, for example in E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra" (Cambridge University Press, London, 1935) and in refs. 4 and 5.

14. See for example ref. 4, p. 61.

15. Closed form expressions for these coefficients are available (see refs. 4 and 5), and they are tabulated in E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra" (Cambridge University Press, London, 1935). The 3-j symbols, which are closely related to the Clebsch -Gordan coefficients hav 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).

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

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

18. R. A. Sack, J. Math. Phys. 5, 245 (1964); 5, 252 (1964).

19. P. R. Fontana, J. Math. Phys. 2, 825 (1961); Y. N. Chiu, J. Math. Phys. 5, 283 (1964).

20. The transformed Hamiltonian has the following form

$$H_{LL} = -\tfrac{1}{2}\sum_{k>j}\frac{1}{r_{jk}^3}\Big[2r_{jk}^2(\underline{p}_j\cdot\underline{p}_k) - (\underline{r}_j\times\underline{p}_k)(\underline{p}_j\times\underline{p}_k) - (\underline{r}_{jk}\times\underline{p}_k)\cdot\underline{\ell}_j - (\underline{r}_{kj}\times\underline{p}_j)\cdot\underline{\ell}_k\Big]$$

The terms of the form $(\underline{r}_{jk}\times\underline{p}_k)\cdot\underline{\ell}_j$ represent the coupling of the angular momentum of electron k relative to electron j with the angular momentum of electron j.

21. M. E. Rose, "Multipole Fields" (John Wiley and Sons, Inc., New York, 1955), p. 28.

22. R. J. Beuhler and J. O. Hirschfelder, Phys. Rev. 83, 628 (1951); 85, 149 (1952).

23. P. R. Fontana, Phys. Rev. 123, 1865 (1961).

24. R. A. Sack, J. Math. Phys. 5, 260 (1964).

25. The result for n = 1 agrees with the previous work of R. C. Carlson and L. S. Rushbrooke, Proc. Cambridge Phil. Soc. 46, 626 (1950) and refs. 17 and 22.

26. See appendices 1.A - 1.C of W. J. Meath, The University of Wisconsin Theoretical Chemistry Institute Technical Report WIS-TCI-75, April, 1965. For explicit expressions through $(1/R^3)$ see W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. (to be published).

27. See for example ref. 4, p. 62.

28. See for example ref. 4, p. 89.