NOTIZEN

A New Method for the Calculation of Correlated Pair Functions

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A method for the calculation of correlated pair functions was first developed by FOCK, WESSELOW, and PETRASHEN [1, 2]; more recently several other methods had been developed [3]. All these methods have in common the feature that the correlated pair function is the solution of an equation of the form $H_{12}\,\Phi = E\,\Phi$ where H_{12} is a two-electron HAMILTONIAN and Φ must be strongly orthogonal [2] to the one-electron spin orbitals. The orthogonality requirement is the source of extreme mathematical difficulties. If Φ_0 is a function not orthogonal to the one-electron orbitals, it is orthogonalized [2] with the operator $(1-\Omega_{12})$ which is a two-electron, integral, projection operator. Consequently if Φ_0 contains r_{12}, the interelectronic distance, the application of H_{12} and $(1-\Omega_{12})$ to Φ_0 will result in integrals containing the combinations [4] $(r_{12}\,r_{23})$, $(r_{12}\,r_{13}\,r_{14})$, $(r_{12}\,r_{23}\,r_{34})$, and $(r_{12}\,r_{23}\,r_{13})$. The calculation of such integrals is extremely time consuming for atoms [5] and quite impossible for molecules.

We report that we developed a method in which this difficulty is avoided. Consider an atom with N electrons in closed shells plus two valence electrons. The total wave function is [1, 2] $\psi = (N+2)^{-1/2}\,\tilde{A}\{\varphi_1\,\varphi_2 \dots \varphi_N\,\Phi\}$ where $\tilde{A}$ is an antisymmetrizer, $\varphi_1 \dots \varphi_N$ are the core functions, and Φ is the correlated two-electron function for the valence electrons. Φ is strongly orthogonal to the φ_i's. The energy expression has the form [1, 2]

$$E_{\mathrm{T}} = \langle \Phi \,|\, H_{\mathrm{F}}(1) + H_{\mathrm{F}}(2) + r_{12}^{-1} \,|\, \Phi \rangle + E_{\mathrm{c}}\,,$$

where H_{F} is the HARTREE–FOCK (H–F) HAMILTONIAN of the core and E_{c} is the (H–F) energy of the core. We put [6]

$$\Phi = \varphi_{\mathrm{A}}(1)\,\varphi_{\mathrm{B}}(2)\,.$$

(In order to make the result simple we do not antisymmetrize Φ. This deficiency can be corrected later.) Application of the energy minimum principle leads to the equations

$$(H_{\mathrm{F}} + V_{\mathrm{B}})\,\varphi_{\mathrm{A}} = E_{\mathrm{A}}\,\varphi_{\mathrm{A}}\,,$$

and

$$(H_{\mathrm{F}} + V_{\mathrm{A}})\,\varphi_{\mathrm{B}} = E_{\mathrm{B}}\,\varphi_{\mathrm{B}}\,,$$

where V_{A} and V_{B} are the potentials resulting from φ_{A} and φ_{B}. Putting φ_{A} and φ_{B} in the SCHMIDT-orthogonalized form we get

$$\{H_{\mathrm{F}} + V_{\mathrm{B}} + \sum_i C_i^{\mathrm{A}}\,[E_{\mathrm{A}} - E_i - V_{\mathrm{B}}]\,\varphi_i/\varphi_{\mathrm{A}}^0\}\,\varphi_{\mathrm{A}}^0 = E_{\mathrm{A}}\,\varphi_{\mathrm{A}}^0 \tag{1}$$

and a similar equation for φ_{B}^0. In (1) φ_{A}^0 is the pseudowave function defined by

$$\varphi_{\mathrm{A}} = N_{\mathrm{A}}\,(\varphi_{\mathrm{A}}^0 - \sum_i C_i^{\mathrm{A}}\,\varphi_i)\,,$$

where

$$C_i^{\mathrm{A}} = \langle \varphi_i \,|\, \varphi_{\mathrm{A}}^0 \rangle\,;$$

E_i is the (H–F) core orbital parameter, and N_{A} is a normalization constant. There is a similar formula for φ_{B}^0.

We solve the equations for φ_{A}^0 and φ_{B}^0 and obtain E_{A} and E_{B}. Then using (1) and the equations defining φ_{A}^0 and φ_{B}^0 we eliminate φ_{A} and φ_{B} from the energy expression. By putting $\Phi_0 = \varphi_{\mathrm{A}}^0\,\varphi_{\mathrm{B}}^0$ and using the energy minimum principle we obtain the equation for Φ_0 in the form

$$H_{12}^{\mathrm{M}}\,\Phi_0 = E\,\Phi_0$$

where Φ_0 is *not orthogonal* to the core functions and H_{12}^{M} the *modified Hamiltonian* has the form:

$$\begin{aligned} H_{12}^{\mathrm{M}} = {} & H_{\mathrm{F}}(1) + H_{\mathrm{F}}(2) + (N_{\mathrm{A}}^2 + N_{\mathrm{B}}^2 - N_{\mathrm{A}}^2\,N_{\mathrm{B}}^2)/r_{12} + \sum_i C_i^{\mathrm{A}}\,[E_{\mathrm{A}} - E_i - (2\,N_{\mathrm{A}}^2 - 2\,N_{\mathrm{A}}^2\,N_{\mathrm{B}}^2 + N_{\mathrm{B}}^2)\,V_{\mathrm{BB}}(1)]\,\varphi_i(1)/\varphi_{\mathrm{A}}^0(1) \\ & + \sum_i C_i^{\mathrm{B}}[E_{\mathrm{B}} - E_i - (2\,N_{\mathrm{B}}^2 - 2\,N_{\mathrm{A}}^2\,N_{\mathrm{B}}^2 + N_{\mathrm{A}}^2)\,V_{\mathrm{AA}}(2)]\,\varphi_i(2)/\varphi_{\mathrm{B}}^0(2) \\ & + [N_{\mathrm{B}}^2 - N_{\mathrm{A}}^2\,N_{\mathrm{B}}^2] \sum_{ik} (C_i^{\mathrm{B}}\,C_k^{\mathrm{B}}\,V_{ik}(1) + 2\,C_i^{\mathrm{A}}\,C_k^{\mathrm{B}} V_{\mathrm{B}k}(1)\,\varphi_i(1)/\varphi_{\mathrm{A}}^0(1)) \\ & + [N_{\mathrm{A}}^2 - N_{\mathrm{A}}^2\,N_{\mathrm{B}}^2] \sum_{ik} (C_i^{\mathrm{A}}\,C_k^{\mathrm{A}} V_{ik}(2) + 2\,C_i^{\mathrm{A}}\,C_k^{\mathrm{B}} V_{\mathrm{A}i}(2)\,\varphi_k(2)/\varphi_{\mathrm{B}}^2(2)) \end{aligned} \tag{2}$$

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$$+ [2\,N_A^2 N_B^2 - N_B^2] \sum_{ikl} (C_i^A C_k^B C_l^B V_{kl}(1)\, \varphi_i(1)/\varphi_A^0(1)) + [2\,N_A^2 N_B^2 - N_A^2] \sum_{ikl} (C_i^B C_k^A C_l^A V_{kl}(2)\, \varphi_i(2)/\varphi_B^0(2))$$

$$- [N_A^2 N_B^2/2] \sum_{ijkl} C_i^A C_j^A C_k^B C_l^B V_{kl}(1)\, \varphi_i(1)\, \varphi_j^*(1)/|\varphi_A^0(1)|^2 +$$

$$- [N_A^2 N_B^2/2] \sum_{ijkl} C_i^A C_j^A C_k^B C_l^B V_{ij}(2)\, \varphi_k(2)\, \varphi_l^*(2)/|\varphi_B^0(2)|^2,$$

where

$$V_{\alpha\beta}(i) = \int (\varphi_\alpha^*(j)\, \varphi_\beta(j))\,(1/r_{ij})\, \mathrm{d}v_j\,.$$

This Hamiltonian is exact (apart from exchange terms which can be included later) if Φ_0 is the product of one-electron pseudo-wave functions. *We suggest that the equation $H_{12}^M \Phi_0 = E\,\Phi_0$ is a good approximation also if Φ_0 is a correlated pair function.* This assumption is strongly supported by the following argument. The operator H_{12}^M is derived in such a way that the orthogonality projection operator $(1-\Omega_{12})$ is transformed into pseudopotentials. But we orthogonalize correlated and uncorrelated two-electron functions with the same operator; i. e. $(1-\Omega_{12})$ is the same regardless whether it operates on a correlated or uncorrelated function [2].

By transforming $(1-\Omega_{12})$ we have eliminated the troublesome integrals from the calculations. By solving

$$H_{12}^M\, \Phi_0 = E\, \Phi_0$$

variationally we can put Φ_0 in a Hylleraas form and only two-electron integrals will occur since all terms in H_{12}^M have the character of potentials.

The method is developed here for the two valence electrons of an atom. Generalization for an arbitrary electron pair is straightforward. The wave function will be the same again with Φ representing any electron pair. The derivation of H_{12}^M will follow the same steps but the equations for φ_A^0 and φ_B^0 will be different and therefore also H_{12}^M will be slightly different.

As a first, demonstrative calculation we computed a correlated pair function for the (2s) shell of the Be atom. Since the pseudo-wave functions are not available for the Be (2s) electrons we used the pseudo-wave function for the (2s) electron of Be^+ ion [7]. It can be shown that the pseudopotentials are not sensitive to small changes in the pseudo-wave function [8]. Using a 6 term Hylleraas type function with a Slater function as the leading term we obtained a correlation energy of $E_c = -0.0302$ a. u. By carrying out the orthogonalization explicitly one obtains with the same ansatz $E_c = -0.0321$ a. u. [5]. The agreement is very good; the small difference is probably a result of using Be^+ pseudopotentials instead of the correct ones for Be.

The work is being continued and the results will be presented in forthcoming publications.

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Proton Spin Relaxation in Paramagnetic Ion Solutions: Deuterium Isotope Effect

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In aqueous paramagnetic ion solutions the observed rate of proton spin relaxation $(1/T_2)$ is controlled by the rate of relaxation in the primary hydration shell of the paramagnetic ion $(1/T_{2x})$, and by the rate of proton exchange between the hydration shell and the solvent. The relaxation rate is given by

$$1/T_2 = P\,(T_{2x} + \tau_{xw})^{-1}\,, \tag{1}$$

where P is the fraction of protons in hydration shells, and τ_{xw} is the mean lifetime of a proton in the hydration shell. The effects of isotopic substitution have been studied by measurement of deuteron spin relaxation in D_2O solutions [1, 2], and of proton and deuteron relaxation in solutions of mixed isotopic composition [3–6]. The present discussion will apply to cases like Cr^{3+} and VO^{2+}, where the dominant exchange mechanism is proton transfer across hydrogen bonds, rather than exchange of whole water molecules. We seek to account for changes in the T_2 of protons (and deuterons) with variation in the isotopic composition of the solution, as have been observed by Mazitov and Rivkind [5, 6].

If the solution contains a mixture of the isotopes H and D, the factor P in Eq. (1) is given by

$$P = (n\,x/w)\,(\beta_x/\beta_w)\,, \tag{2}$$

where n is the hydration number, x is the paramagnetic ion concentration, w is the concentration of water molecules, and β is the fractional concentration of protons – i. e., $\beta_x = H_x/(H_x + D_x)$, and $\beta_w = H_w/(H_w + D_w)$. Due to the difference in zero-point vibrational energy, the chemical rate constants for H and D exchange dif-

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