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Calculation of self-consistent-field-$X\alpha$ wave functions. Core-exchange polarization calculation for free atoms

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Core-exchange polarization (CEP) effects in free atoms have been calculated for 15 different atomic configurations of Li, Be, B, C, N, O, F, Na, Cl, K, Rb, and Cs using the self-consistent-field-$X\alpha$ wave functions. Comparison with other results from the unrestricted Hartree-Fock (UHF) calculations and with experiments revealed that the $X\alpha$ approximation does not reproduce well the CEP effects for each s orbital, but it presents rather a good value for the total CEP effect.

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The recently developed self-consistent-field-$X\alpha$ (SCF-$X\alpha$) method[1,2] has been successfully applied to calculate such properties as electron densities, dipole[3–5] and quadrupole[5] moments, orbital energies and ionization potentials of heavy metal complexes[6–8] and many atom clusters,[9] total energy curves giving binding energies, equilibrium separations, and vibration frequencies of diatomic molecules including first-row atoms[10,11] or transition metal elements.[12] This method, however, raises the following point: Since in this method the approximate exchange potential including a single parameter α, is obtained from a free-electron gas model taking no account of spin polarization, there may be difficulties in the adequacy of the single α value to describe the charge density and spin polarization simultaneously. Thus it is recommended that the SCF-$X\alpha$ method be tested on the calculations of the properties concerning the spin densities rather than energies in order to determine the reliability of this method. In a previous paper[13] we showed that the (linear combination of atomic orbitals) LCAO-SCF-$X\alpha$ calculation of nuclear spin-spin coupling constants presented a good agreement with the *ab initio* LCAO-SCF-MO (molecular orbit) results. Herein we report our investigation on core-exchange polarization (CEP) effects[14] in free atoms, which has important contributions to atomic hyperfine structure, nuclear spin-spin coupling constant in molecules,[15] and the Knight shift in metals[16] *via* the Fermi contact term, and seems to be a desirable property to test exchange potential approximation in the SCF-$X\alpha$ method.

In atoms in which one or more electrons belonging to outer shells are unpaired with respect to their spin direction, core electrons with spins parallel to that of the unpaired electrons experience stronger total exchange forces than core electrons of opposite spin. This exchange polarization of the core electrons, that is, CEP results in nonzero values of the quantities,

$$\rho_{ns}^{s}(0)=|\psi_{ns}^{\uparrow}(0)|^2-|\psi_{ns}^{\downarrow}(0)|^2\,, \tag{1}$$

for each pair of s electrons in the atomic core and these contibute to the Fermi contact term.

Atomic orbitals $\psi_i^{\uparrow,\downarrow}$ of Eq. (1) are solutions to the following one-electron equation (in a.u.):

$$\left[-\frac{1}{2}\Delta-\frac{Z}{r}+\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' -3\alpha[(\tfrac{3}{4\pi})\rho^{\uparrow,\downarrow}(\vec{r})]^{1/3}\right]\psi^{\uparrow,\downarrow}=\epsilon^{\uparrow,\downarrow}\psi^{\uparrow,\downarrow}\,, \tag{2}$$

where $\rho=\rho^{\uparrow}+\rho^{\downarrow}$ and $\rho^{\uparrow,\downarrow}=\sum_i^{occ}|\psi_i^{\uparrow,\downarrow}|^2$. For the statistical exchange parameter α we used α_{vt} values by Schwarz.[17] Equation (2) was solved numerically with the spherically averaged potential.[18] Equation (2) has a pole at the nuclear position, so wave functions have to be extrapolated to get $\psi_{ns}^{\uparrow,\downarrow}(0)$. We used the Thomas-Fermi statistical model[19] to

TABLE I. Core-exchange polarization results (in a.u.) from SCF-$X\alpha$ and UHF[a] calculations.

		$\rho_{1s}^{s}(0)$		$\rho_{2s}^{s}(0)$		$\rho_{3s}^{s}(0)$		$\rho_{4s}^{s}(0)$		$\sum_n \rho_{ns}^{s}(0)$		$\sum_n \rho_{ns}^{s}(0)$
Atom	Term	SCF-$X\alpha$	UHF	SCF-$X\alpha$	UHF	SCF-$X\alpha$	UHF	SCF-$X\alpha$	UHF	SCF-$X\alpha$	UHF	Exp.
Li	^2S	−0.0107	0.0609	0.232	0.1638					0.221	0.2247	0.2313[b]
Li	^2P	−0.0464	−0.0184							−0.0464	−0.0184	
Be	^3P	−0.0916	0.0938	0.777	0.6299					0.685	0.7237	
B	^2P	−0.135	−0.0913	0.110	0.1085					−0.025	0.0172	
C	^3P	−0.394		0.353						−0.041		
N	^4S	−0.774	−0.7418	0.721	0.9301					−0.053	0.1883	
O	^3P	−0.668		0.633						−0.035		
F	^2P	−0.403	−0.5076	0.376	0.6411					−0.027	0.1335	
Na	^2S	0.023	0.0463	−0.047	0.0745	0.803	0.5261			0.779	0.6469	0.7492[b]
Na	^2P	−0.0054	−0.0098	−0.0106	0.0143					−0.0160	0.0045	−0.0008±0.0015[c]
Cl	^2P	−0.115	−0.211	−0.022	0.113	0.091	0.132			−0.046	0.034	
K	^2S	0.0159	0.0340	−0.0015	0.0409	−0.0532	0.0880	1.092	0.6913	1.053	0.8542	1.1067[b]
K	^2P	−0.0036		−0.0006		−0.0127				−0.0169		−0.0009±0.0044[c]
Rb	^2S									1.928		2.3446[b]
Cs	^2S									2.495[d]		3.9196[b]

[a] See Reference 14.

[b] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. 126, 1749 (1962).

[c] Cited in Reference 14.

[d] Calculated as $\alpha=0.7$.

get the initial charge density and potential for the self-consistent cycling. The SCF-$X\alpha$ calculations have been carried out for 15 different atomic configurations and the results are given in Table I with the UHF (unrestricted Hartree-Fock) results[14] and experimental values.

There are a number of interesting features about the results in Table I. Most obvious is the opposite signs of CEP between the SCF-$X\alpha$ results and the UHF ones. Namely, when the unpaired electrons are of s type, all $\rho^s_{ns}(0)$'s are positive in the exact UHF results, whereas in the SCF-$X\alpha$ results $\rho^s_{ns}(0)$'s are alternate in signs. This discrepancy is most striking in Li ($[^2S]$). We could not succeed in obtaining the positive CEP effect by neither changing Li's α value or using different α values for inner and outer shells.[20]

Another observation drawn from Table I is that the SCF-$X\alpha$ results of the total spin density at the nucleus, $\sum_n \rho^s_{ns}(0)$'s show closer agreement with experimental ones than do the exact UHF results. Therefore, we can suppose that the $X\alpha$ approximation is not a good approximation to the exchange potential for the individual orbital, but rather it presents a good approximation of the total exchange interaction effects. However, in Rb and Cs, the calculated total spin densities are too small. It seems because the relativistic effects are no longer negligible in Rb and Cs.

As a conclusion the SCF-$X\alpha$ method does not correctly describe the spin-density distribution. Recently Gunnarsson *et al.*[21–24] have proposed and extensively applied a modification of the SCF-$X\alpha$ method, the so-called local-spin-density (LSD) approximation, in which the exchange-correlation potential is given as the functional of the charge density and spin polarization. We feel that the LSD method should be tested to see whether or not it gives the accurate spin-density distributions.

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[1] J. C. Slater, Phys. Rev. 81, 385 (1951).
[2] J. C. Slater, *Advances in Quantum Chemistry,* edited by P. O. Löwdin (Academic, New York, 1972), Vol. 6, p. 1.
[3] E. J. Baerends, D. E. Ellis, and P. Ros, Chem. Phys. 2, 41 (1973).
[4] E. J. Baerends and P. Ros, Chem. Phys. 2, 52 (1973).
[5] S. B. Woodruff and M. Wolfsberg, J. Chem. Phys. 65, 3687 (1976).
[6] E. J. Baerends and P. Ros, Mol. Phys. 30, 1735 (1975).
[7] J. M. Dyke, N. K. Fayad, A. Morris, I. R. Trickle, and G. C. Allen, J. Chem. Phys. 72, 3822 (1980).
[8] J. F. Nixon, R. J. Suffolk, M. J. Taylor, J. G. Norman, Jr., D. E. Hoskins, and D. J. Gmur, Inorg. Chem. 19, 810 (1980).
[9] B. D. El-Issa and A. Hinchliffe, Mol. Phys. 39, 1463 (1980).
[10] J. W. Mintmire, Int. J. Quant. Chem. Symp. 13, 163 (1979).
[11] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. 71, 4993 (1979).
[12] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, Int. J. Quant. Chem. Symp. 11, 81 (1977).
[13] H. Fukui, J. Chem. Phys. 65, 844 (1976).
[14] D. A. Goodings, Phys. Rev. 123, 1706 (1961).
[15] C. J. Jameson and H. S. Gutowsky, J. Chem. Phys. 51, 2790 (1969).
[16] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. London Sec. A 73, 811 (1959).
[17] K. Schwarz, Phys. Rev. B 5, 2466 (1972).
[18] J. M. Blatt, J. Comput. Phys. 1, 382 (1967).
[19] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-relativistic Theory),* 3rd. ed. (Pergamon, Oxford, 1976), p. 259.
[20] I. Lindgren and K. Schwarz, Phys. Rev. A 5, 542 (1972).
[21] O. Gunnarsson, P. Johansson, S. Lundqvist, and B. I. Lundqviat, Int. J. Quant. Chem. Symp. 9, 83 (1975).
[22] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4272 (1976).
[23] O. Gunnarsson and P. Johansson, Int. J. Quant. Chem. 10, 307 (1976).
[24] O. Gunnarsson, J. Harris, and R. O. Jones, J. Chem. Phys. 67, 3970 (1977).