AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVISTIC EFFECTS. A PROCEDURE FOR THE INCLUSION OF SPIN–ORBIT COUPLING IN MOLECULAR WAVEFUNCTIONS

Walter C. ERMLER
Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030, USA

Yoon S. LEE
James Franck Institute, Department of Chemistry, University of Chicago, Chicago, Illinois 60637, USA

and

Phillip A. CHRISTIANSEN and Kenneth S. PITZER
Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

Received 23 January 1981; in final form 20 March 1981

The first ab initio procedure for the treatment of spin–orbit coupling in molecules based on the use of relativistic effective potentials derived from Dirac–Fock atomic wavefunctions is presented. A rigorous definition for the spin–orbit operator is given and its use in molecular calculations discussed.

1. Introduction

The inclusion of relativistic effects in electronic structure calculations for molecules containing heavy elements has recently received a great deal of attention [1–18]. Inasmuch as relativistic corrections are predominantly core effects, the effective potential (EP) scheme [19] offers a particularly simple approach to the inclusion of relativistic effects with (at least in principle) remarkably little loss in accuracy [20]. Pitzer and co-workers [7–13] have developed EPs which are derived from atomic Dirac–Fock wavefunctions [21] and include explicitly the relativistic corrections as given by the Dirac formalism [22]. This EP procedure greatly reduces the difficulties associated with the large number of core electrons and at the same time eliminates the need to treat explicitly (at least in molecular calculations) the small components of the Dirac wavefunction. The relativistic and core effects (including the non-negligible two-electron contributions) appear in the form of a one-electron operator which is added to the Schrödinger equation for the valence electrons.

Although these methods have been successfully employed in the study of very heavy molecular systems, the explicit inclusion of the spin–orbit effects makes such calculations difficult. Furthermore, for the somewhat lighter elements such as Xe, Kr, etc., the spin–orbit term is probably small enough that it can be adequately treated as a perturbation following an initial SCF or CI calculation.

For the above reasons most workers [5–9, 14, 16–18] have opted to eliminate together the spin–orbit terms from the effective potential. This is done either by deriving the EPs using atomic states from which the spin–orbit splitting has been averaged out [16,18] or averaging the fully relativistic EPs themselves [7–9] to obtain a spin averaged relativistic effective potential (AREP). With AREPs molecular calculations can be carried out using

standard non-relativistic formalisms. The spin–orbit correction is then added as a perturbation. In practice this has been done either by semi-empirically estimating the spin–orbit matrix elements which couple the various L–S type molecular states [7–9] or else the matrix elements are evaluated using some convenient spin–orbit operator [4] such as Z^{eff}/r^3 where the adjustable parameter Z^{eff} is chosen to reproduce the atomic splittings.

The above procedures, though possibly inadequate for the heaviest elements [13], provide a particularly convenient technique for treating molecules containing somewhat lighter atoms. Unfortunately, selecting matrix elements semi-empirically becomes difficult if not impossible if very many states are involved. Furthermore, the form of the operator, Z^{eff}/r^3, though justifiable in terms of atomic all-electron calculations, may be seriously inappropriate for calculations involving pseudo-orbitals whose behavior in the heavily weighted core region differs dramatically from that of the original atomic orbitals or spinors from which they were derived [19,20]. In fact, at first inspection it is not obvious how one would go about defining, ab initio, a spin–orbit operator for such applications. Thus, until now there has been no alternative to the semi-empirical procedures discussed above.

In section 2 we propose the first ab initio procedure by which a spin–orbit operator appropriate for use in molecular effective potential calculations may be rigorously determined and we discuss its use in molecular calculations.

2. Formal procedure

The effective potentials of Pitzer and co-workers [7–13] (and also of Hafner and Schwarz [15]) may be written in the general form

$$U^{\mathrm{REP}} = U_{LJ}^{\mathrm{REP}}(r) + \sum_{l=0}^{L} \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} [U_{lj}^{\mathrm{REP}}(r) - U_{LJ}^{\mathrm{REP}}(r)] \sum_{m=-j}^{j} |ljm\rangle\langle ljm|, \tag{1}$$

where the $U_{lj}^{\mathrm{REP}}(r)$ are the EPs derived from individual pseudospinors with angular quantum numbers l and j. For the "residual" potential, $U_{LJ}^{\mathrm{REP}}(r)$, L is ideally chosen to be at least one greater than the highest angular quantum number for the core electrons. The projection operators on the right ensure that the U_{lj}^{REP} operate only on spinors of the proper angular symmetry. Previous work has shown that, when the U_{lj} are properly defined in terms of all-electron atomic wavefunctions, the effective potential formalism is capable of reproducing molecular all-electron calculations to a high degree of reliability. Unfortunately, to date, calculations using the full potential of eq. (1) have been limited to single-configuration SCF [11] or relatively simple MC SCF [12,13] calculations. Whenever large-scale configuration interaction has been included, the spin–orbit effects implicit in U^{REP} were first averaged out resulting in an averaged relativistic effective potential, U^{AREP}, of the form

$$U^{\mathrm{AREP}} = U_L^{\mathrm{AREP}}(r) + \sum_{l=0}^{L} \sum_{m=-l}^{l} [U_l^{\mathrm{AREP}}(r) - U_L^{\mathrm{AREP}}(r)] |lm\rangle\langle lm|, \tag{2}$$

where the U_l^{AREP} are defined as

$$U_l^{\mathrm{AREP}}(r) = (2l+1)^{-1} [l U_{l,l-1/2}^{\mathrm{REP}}(r) + (l+1) U_{l,l+1/2}^{\mathrm{REP}}(r)], \tag{3}$$

and the projector on the right is now defined in terms of orbitals with the usual angular quantum numbers, l and m. The effective potential operator, U^{AREP}, therefore includes all relativistic effects except for spin–orbit. This potential can therefore be added to the usual non-relativistic hamiltonian and molecular calculations, including configuration interaction, carried out in the non-relativistic formalism. The U^{AREP} of Pitzer and co-workers [7–9] (or of Hafner and Schwarz [15]) is then roughly equivalent to the "relativistic" EPs of refs. [16,18] where the spin–orbit effects were averaged out prior to determining the EPs.

From the above discussion it is clear that the spin–orbit operator appropriate for use with molecular pseudo-orbitals can be defined simply as the difference of the U^{REP} and U^{AREP},

$$H^{\mathrm{so}} = U^{\mathrm{REP}} - U^{\mathrm{AREP}} = U_{LJ}^{\mathrm{REP}}(r) - U_{L}^{\mathrm{AREP}}(r) + \sum_{l=0}^{L} \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} \sum_{m=-j}^{j} [U_{lj}^{\mathrm{REP}}(r) - U_{l}^{\mathrm{AREP}}(r) - U_{LJ}^{\mathrm{REP}}(r) + U_{L}^{\mathrm{AREP}}(r)] \, |ljm\rangle\langle ljm| . \tag{4}$$

Note that the projection operators of eq. (2) have been expanded in terms of the corresponding operators for two-component spinors in order to combine terms with eq. (1). With increase in l the difference between the effective potentials for $j = l + \frac{1}{2}$ from that for $j = l - \frac{1}{2}$ decreases rapidly. Thus the difference $U_{LJ}^{\mathrm{REP}}(r) - U_{L}^{\mathrm{AREP}}(r)$ in most cases will be very small and can be neglected. If we also introduce the relationship of eq. (3), we obtain as an excellent approximation

$$H^{\mathrm{so}} = \sum_{l=1}^{L-1} \Delta U^{\mathrm{REP}}(r) \left[\frac{l}{2l+1} \sum_{-l-\frac{1}{2}}^{l+\frac{1}{2}} |l, l+\tfrac{1}{2}, m\rangle\langle l, l+\tfrac{1}{2}, m| - \frac{l+1}{2l+1} \sum_{-l+\frac{1}{2}}^{l-\frac{1}{2}} |l, l-\tfrac{1}{2}, m\rangle\langle l, l-\tfrac{1}{2}, m| \right], \tag{5}$$

with

$$\Delta U_{l}^{\mathrm{REP}}(r) = U_{l,l+1/2}^{\mathrm{REP}}(r) - U_{l,l-1/2}^{\mathrm{REP}}(r). \tag{6}$$

The matrix elements of H^{so} with respect to the atomic orbital basis set will have the form,

$$H_{pq}^{\mathrm{so}}(\rho_r \rho_s) = \langle \chi_p \rho_r | H^{\mathrm{so}} | \chi_q \rho_s \rangle, \tag{7}$$

where the χ are spatial basis functions and the Pauli spinors ρ define the α and β spins of the electron such that $\rho_i = \alpha = \binom{1}{0}$ or $\rho_i = \beta = \binom{0}{1}$. The matrix elements of H^{so} between the various L–S type states for a given molecule can then be obtained as an expansion over one-electron integrals employing the various CI, MO, and spin symmetry coefficients. An outline of this procedure follows.

The hamiltonian matrix element corresponding to the L–S states that correlate to the same M atomic asymptotes $n, m = 1, 2, \ldots M$ is defined by

$$H_{nm}^{\mathrm{so}} = \langle \Psi_n | H^{\mathrm{so}} | \Psi_m \rangle, \tag{8}$$

where Ψ_i is the CI wavefunction in L–S coupling. This is then expressed in terms of the sum of Slater determinants, D_i, with the appropriate CI coefficients C_I^n and individual Slater determinant coefficients a_i^I that define the spin eigenfunctions in L–S coupling,

$$H_{nm}^{\mathrm{so}} = \sum_I \sum_J C_I^n C_J^m \sum_i \sum_j a_i^I a_j^J \langle D_i | H^{\mathrm{so}} | D_j \rangle. \tag{9}$$

Substitution for the Slater determinants using the fact that H^{so} is a one-electron operator together with the properties of the antisymmetrizer gives

$$H_{nm}^{\mathrm{so}} = \sum_I \sum_J C_I^n C_J^m \sum_i \sum_j a_i^I a_j^J \sum_k^{2n_{\mathrm{p}}} \sum_l^{2n_{\mathrm{p}}} f_k^i f_l^i \langle \phi_k \rho_k | H^{\mathrm{so}} | \phi_l \rho_l \rangle, \tag{10}$$

where $\phi_k \rho_k$ is a one-electron molecular spin orbital (ρ_k is either α or β depending on the electron configuration), f_k^i is the occupation number of $\phi_k \rho_k$ in determinant D_i, and the sums on the one-electron spin orbitals go to $2n_{\mathrm{p}}$ to include both α and β spins. n_{p} is the number of spatial orbitals. The integrals in eq. (10) can be obtained by a straightforward transformation of the integrals from eq. (7) using the molecular orbital expansion coefficients.

Although (10) is formally identical to standard configuration-interaction property expansions, the limits for the k and l summations are now $2n_{\mathrm{p}}$ rather than n_{p} as is typical in CI programs. Furthermore, the integrals on the

right may be complex. Except for the now rigorous definition of the spin–orbit operator and our inclusion of two-center integrals, the matrix constructed from the above elements is of a form similar to that used by Hay et al. [6]. Diagonalization of $\mathbf{H}^{SO}$ will yield the appropriate energies and coupling vectors for the desired manifold of spin–orbit states in the ω–ω coupling framework. It is also noted that this general development in terms of CI wavefunctions can be used to treat the special cases of MC SCF or SCF wavefunctions. Thus correlation and spin–orbit phenomena can be considered separately or simultaneously at varied levels of approximation.

3. Concluding remarks

Understanding the chemistry of molecules comprised of heavy atoms is inexorably bound to the proper inclusion of spin–orbit and other relativistic effects in the molecular wavefunctions. The operator proposed above is to our knowledge the only ab initio spin–orbit operator rigorously applicable to effective potential calculations. At the same time, being in the form of a one-electron operator, it circumvents the necessity for the costly large-scale calculations required when the full microscopic spin–orbit hamiltonian is retained. The present ab initio approach thus emerges as a promising alternative to the existing procedures.

Applications to the homonuclear inert-gas excimer systems are among the initial objectives owing to the widespread interest in our earlier, limited accuracy SCF calculations on the Xe_2^* states [7] in which one of the empirical approaches for the inclusion of spin–orbit coupling was employed. Calculations on molecules where the bonding interactions are significantly stronger are also planned to investigate the dependence of molecular spin–orbit coupling as a function of internuclear distance.

Acknowledgement

This research was partially supported by the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy through Contract W-7405-ENG-48. In addition, one of us (WCE) acknowledges the Research Corporation and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

References

[1] K.S. Pitzer, Accounts Chem. Res. 12 (1979) 271.
[2] P. Pyykkö, Advan. Quantum Chem. 11 (1978) 353.
[3] G. Malli and J. Oreg, J. Chem. Phys. 63 (1975) 1032;
O. Matsuoka, N. Suzuki, T. Aoyama and G. Malli, J. Chem. Phys. 73 (1980) 1320;
T. Aoyama, H. Yamakawa and O. Matsuoka, J. Chem. Phys. 73 (1980) 1329.
[4] J.S. Cohen, W.R. Wadt and P.J. Hay, J. Chem. Phys. 71 (1979) 2955.
[5] W.R. Wadt and P.J. Hay, J. Am. Chem. Soc. 101 (1979) 5198.
[6] P.J. Hay, W.R. Wadt, L.R. Kahn, R.C. Raffenetti and D.H. Phillips, J. Chem. Phys. 71 (1979) 1767.
[7] W.C. Ermler, Y.S. Lee, K.S. Pitzer and N.W. Winter, J. Chem. Phys. 69 (1978) 976.
[8] Y.S. Lee, W.C. Ermler, K.S. Pitzer and A.D. McLean, J. Chem. Phys. 70 (1979) 288.
[9] W.C. Ermler, Y.S. Lee and K.S. Pitzer, J. Chem. Phys. 70 (1979) 293.
[10] Y.S. Lee, W.C. Ermler and K.S. Pitzer, J. Chem. Phys. 67 (1977) 5861.
[11] Y.S. Lee, W.C. Ermler and K.S. Pitzer, J. Chem. Phys. 73 (1980) 360.
[12] P.A. Christiansen and K.S. Pitzer, J. Chem. Phys. 73 (1980) 5160.
[13] P.A. Christiansen and K.S. Pitzer, J. Chem. Phys., to be published.
[14] G. Das and A.C. Wahl, J. Chem. Phys. 64 (1976) 4672; 69 (1978) 53.
[15] P. Hafner and W.H.E. Schwartz, J. Phys. B11 (1978) 217, 2975; Chem. Phys. Letters 65 (1979) 537.
[16] L.R. Kahn, P.J. Hay and R.D. Cowan, J. Chem. Phys. 68 (1978) 2386.

[17] S.N. Dutta, C.S. Ewig and J.R. van Wazer, Chem. Phys. Letters 57 (1978) 83.
[18] H. Basch and S. Topiol, J. Chem. Phys. 71 (1979) 802.
[19] L.R. Kahn, P. Baybutt and D.G. Truhlar, J. Chem. Phys. 65 (1976) 3826;
R.N. Dixon and I.L. Robertson, in: Theoretical chemistry, eds. R.N. D ixon and C. Thomson (Chem. Soc., London, 1978).
[20] P.A. Christiansen, Y.S. Lee and K.S. Pitzer, J. Chem. Phys. 71 (1979) 4445.
[21] J.P. Desclaux, Computer Phys. Commun. 9 (1975) 31.
[22] H.A. Bethe and E.E. Salpeter, Quantum mechanics of one- and two-electron atoms (Springer, Berlin, 1957).