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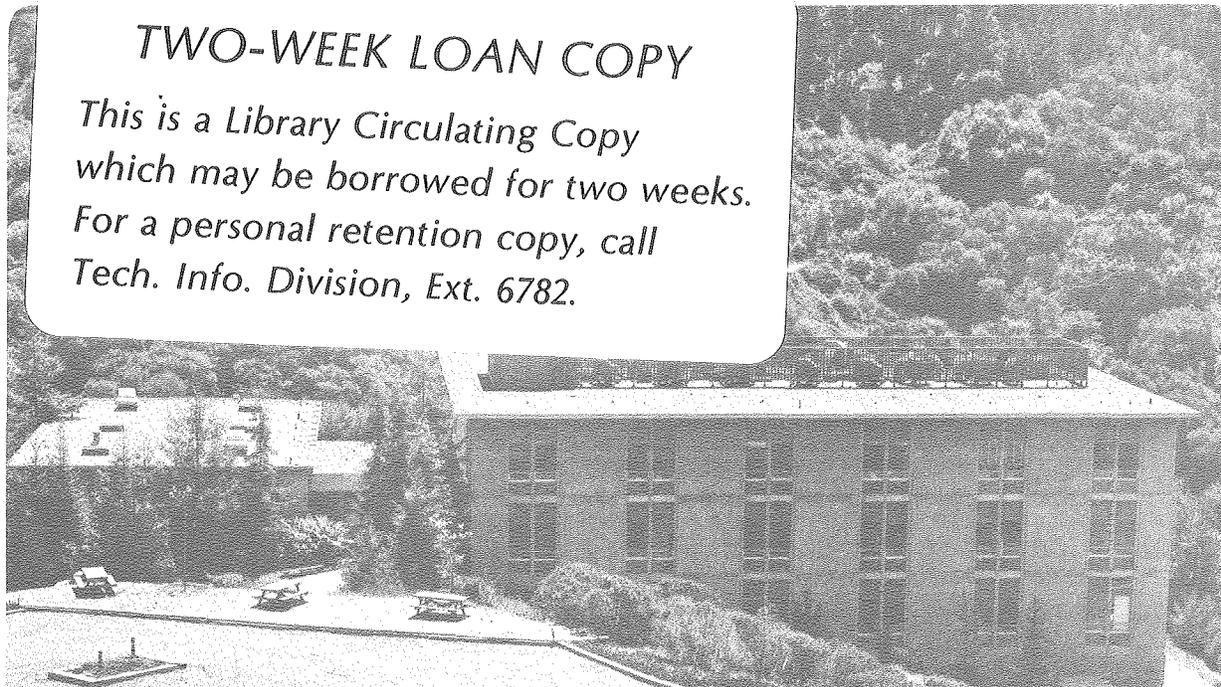
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WAVEFUNCTIONS

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Ab Initio Effective Core Potentials Including Relativistic Effects.

VI. A Procedure for the Inclusion of Spin-Orbit Coupling in Molecular
Wavefunctions

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Abstract

An 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.

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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 EP's which are derived from atomic Dirac-Fock wavefunctions [2] 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 Schroedinger 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 [4-9, 14, 16-18] have opted to eliminate altogether the spin-orbit terms from the effective potential. This is done either by deriving the EP's using atomic states from which the spin-orbit splitting has been averaged out [16,18] or averaging the

fully relativistic EP's themselves [7-9] to obtain a spin averaged relativistic effective potential (AREP). With AREP's 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 semiempirically 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 semiempirically 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 a spin-orbit operator for such applications.

In the following section we propose an 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.

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,

$$U^{\text{REP}} = U_{\text{LJ}}^{\text{REP}}(r) + \sum_{\ell=0}^L \sum_{j=|\ell-\frac{1}{2}|}^{\ell+\frac{1}{2}} [U_{\ell j}^{\text{REP}}(r) - U_{\text{LJ}}^{\text{REP}}(r)] \sum_{m=-j}^j |\ell j m\rangle \langle \ell j m|, \quad (1)$$

where the $U_{\ell j}^{\text{REP}}(r)$ are the EP's derived from individual pseudospinors with angular quantum numbers ℓ and j . For the "residual" potential, $U_{\text{LJ}}^{\text{REP}}(r)$, 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 insure that the $U_{\ell j}^{\text{REP}}$ operate only on spinors of the proper angular symmetry. Previous work has shown that, when the $U_{\ell j}$ 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 equation (1) have been limited to single configuration SCF [11] or relatively simple MCSCF [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,

$$U^{\text{AREP}} = U_{\text{L}}^{\text{AREP}}(r) + \sum_{\ell=0}^L \sum_{m=-\ell}^{\ell} [U_{\ell}^{\text{AREP}}(r) - U_{\text{L}}^{\text{AREP}}(r)] |\ell m\rangle \langle \ell m| \quad (2)$$

where the U_{ℓ}^{AREP} are defined as

$$U_{\ell}^{\text{AREP}}(r) = \frac{1}{2\ell+1} [\ell U_{\ell, \ell-\frac{1}{2}}^{\text{REP}}(r) + (\ell+1) U_{\ell, \ell+\frac{1}{2}}^{\text{REP}}(r)], \quad (3)$$

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" EP's of references [16] and [18] where the spin-orbit effects were averaged out prior to determining the EP's.

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

$$H^{\text{SO}} = U^{\text{REP}} - U^{\text{AREP}} = U_{\text{LJ}}^{\text{REP}}(r) - U_{\text{L}}^{\text{AREP}}(r) + \sum_{\ell=0}^{\text{L}} \sum_{j=|\ell-\frac{1}{2}|}^{\ell+\frac{1}{2}} \sum_{m=-j}^j [U_{\ell j}^{\text{REP}}(r) - U_{\ell}^{\text{AREP}}(r) - U_{\text{LJ}}^{\text{REP}}(r) + U_{\text{L}}^{\text{AREP}}(r)] |\ell j m\rangle \langle \ell j m|. \quad (5)$$

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

$$H^{\text{SO}} = \sum_{\ell=1}^{\text{L}-1} \Delta U^{\text{REP}}(r) \left\{ \frac{\ell}{2\ell+1} \sum_{m=-\ell-\frac{1}{2}}^{\ell+\frac{1}{2}} |\ell, \ell+\frac{1}{2}, m\rangle \langle \ell, \ell+\frac{1}{2}, m| - \frac{\ell+1}{2\ell+1} \sum_{m=-\ell+\frac{1}{2}}^{\ell-\frac{1}{2}} |\ell, \ell-\frac{1}{2}, m\rangle \langle \ell, \ell-\frac{1}{2}, m| \right\} \quad (6)$$

with

$$\Delta U_{\ell}^{\text{REP}}(r) = U_{\ell, \ell+\frac{1}{2}}^{\text{REP}}(r) - U_{\ell, \ell-\frac{1}{2}}^{\text{REP}}(r). \quad (7)$$

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

$$H_{pq}^{SO}(\rho_r \rho_s) = \langle \chi_{p\rho_r} | H^{SO} | \chi_{q\rho_s} \rangle, \quad (8)$$

where the χ 's are spatial basis functions and the Pauli spinors ρ define the α and β spins of the electron such that $\rho_i = \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ or $\rho_i = \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. 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, $m=1,2,\dots,M$ is defined by

$$H_{nm}^{SO} = \langle \Psi_n | H^{SO} | \Psi_m \rangle, \quad (9)$$

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.

$$H_{nm}^{SO} = \sum_I \sum_J C_I^n C_J^m \sum_i \sum_j a_i^I a_j^J \langle D_i | H^{SO} | D_j \rangle. \quad (10)$$

The Slater determinants can be written as

$$D_i = A \prod_{k=1}^{n_e} \phi_k^{\rho_k} \quad (11)$$

where A is the antisymmetrization operator, n_e the number of electrons, the ϕ_k 's are molecular orbitals (MO), and ρ_k is either α or β depending

on the electron configuration of D_i . The MO's are defined in terms of linear combinations of primitive basis functions as

$$\phi_k = \sum_{p=1}^{n_p} c_{pk} \chi_p \quad (12)$$

where n_p is the number of (spatial) primitive basis functions in the basis set.

Substitution for the Slater determinants with these expressions and use of the fact that H^{SO} is a one-electron operator together with the properties of the antisymmetrizer gives

$$H_{nm}^{SO} = \sum_I \sum_J C_I^n C_J^m \sum_i \sum_j a_i^I a_j^J \sum_k^{2n} \sum_\ell^{2n} f_k^i f_\ell^j \langle \phi_{k\rho_k} | H^{SO} | \phi_{\ell\rho_\ell} \rangle \quad (13)$$

In Equ. (13) $\phi_{k\rho_k}$ is a one-electron spinorbital, f_k^i the occupation number of $\phi_{k\rho_k}$ in determinant D_i , and the sums on the one-electron spinorbitals go to $2n_p$ to include both α and β spins. If the sum on the ρ 's is explicitly written out and the substitution made in terms of the spatial basis functions one obtains

$$H_{nm}^{SO} = \sum_I \sum_J C_I^n C_J^m \sum_i \sum_j a_i^I a_j^J \sum_k^{n_p} \sum_\ell^{n_p} f_k^i f_\ell^j \sum_p^{n_p} \sum_q^{n_p} c_{pk} c_{q\ell} \langle \chi_{p\rho_k} | \hat{H}^{SO} | \chi_{q\rho_\ell} \rangle. \quad (14)$$

The integrals in this equation, which are of the desired form defined by Eq. (8), can be obtained by a straightforward modification of the existing REP integral program [11].

The Hamiltonian matrix constructed from the above elements is of the same form as that given by Cohen, Wadt, and Hay [4]. Diagonalization of \hat{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 MCSCF or SCF wavefunctions. Thus correlation and spin-orbit phenomena can be considered separately or simultaneously at varied levels of approximation.

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 spin-orbit operator proposed for application is a significantly better approximation than the effective charge operator while 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 rare 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.

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