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Application of configuration interaction for the study of relativistic effects in atoms and molecules

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Abstract - The configuration interaction method has proven to be quite effective for the treatment of correlation effects in atoms and small molecules. The non-relativistic electrostatic Hamiltonian employed in such calculations is not adequate for the description of a number of key electronic structure effects, however, particularly when term splittings for states of high multiplicity are of interest or quite generally when heavy atoms are involved (from transition metals onward). The extension of CI techniques to the treatment of relativistic effects is not straightforward because of the spin-dependent nature of the interactions involved, but also because the operators most generally considered in this connection are not bounded from below and thus do not lend themselves to the use of standard variational methods. In this work two different approaches are surveyed which deal with these difficulties, the Breit-Pauli perturbative formalism and the use of projected Hamiltonians for which variational procedures are valid, and results for both types of calculations are discussed.

INTRODUCTION

Over the past two decades there has been much progress in developing computational methods which describe the electronic structure of atoms and molecules. These techniques generally employ basis set expansions and correspond to an approximate solution of the non-relativistic electronic Schrödinger equation at either the self-consistent field (SCF) or configuration interaction (CI) levels of treatment. The use of a purely electrostatic Hamiltonian has the drawback of being incapable of describing a number of relativistic effects, including various types of zero-field splittings which become increasingly important for systems whose constituent atoms come from the second and higher rows of the periodic table. The most successful approach to including such relativistic effects in the theoretical treatment involves the solution of the Dirac equation, but its use of four-component spinors instead of the two-component basis functions of the Schrödinger equation poses significant obstacles which preclude a straightforward extension of the above non-relativistic SCF and CI computational methods beyond the level of an electrostatic Hamiltonian. To preserve the two-component structure to a maximum extent in a relativistic treatment, various reductions of the Dirac equation have been proposed (1), which in effect provide a more comprehensive Hamiltonian operator containing the spin-orbit, spin-spin, orbit-orbit and other relativistic potential interactions as well as a correction to the kinetic energy. Because these terms vary as r^{-3} or p^4 it is not possible to treat them in a strictly variational manner (1), however, since such a procedure inevitably results in the generation of unphysical charge distributions and total energies lying well below their experimental counterparts. Essentially two approaches have been attempted to date to circumvent this difficulty and still retain as far as possible the two-component methodology of the SCF and CI computational techniques. The first of these, the Breit-Pauli method, simply treats the short-range operators to at most second-order in perturbation theory, based on non-relativistic zero-order solutions of the Schrödinger equation, while the second involves the use of a somewhat altered version of the Breit-Pauli Hamiltonian (2) which does afford itself to a variational treatment. Both of these approaches will be illustrated in the present contribution, with the emphasis on the manner in which the computational techniques of more conventional ab initio many-electron calculations need to be altered to obtain an optimal description of the desired relativistic effects of systems containing heavy atoms.

APPLICATION OF BREIT–PAULI FORMALISM EMPLOYING CI (CONFIGURATION INTERACTION) WAVEFUNCTIONS

From a computational point of view the first step in carrying out the Breit-Pauli treatment of relativistic phenomena is to obtain a zero-order set of solutions for the corresponding non-relativistic Schrödinger equation. The wavefunctions generated by conventional CI programs are clearly very well suited for this purpose. The next step involves the evaluation of matrix elements between pairs of such multi-determinantal

functions over the various Breit-Pauli operators H'. The spin-orbit interaction (term H_3 of Ref.1) is most commonly employed in such calculations because it leads to important multiplet splittings not accounted for in non-relativistic theory. The major technical difficulties which arise in such computations may be appreciated from the following considerations. The first-order correction to the energy of a given state vanishes for the type of real functions produced by CI programs, so it is necessary to go to second order in perturbation theory in general. An exception of sorts occurs for spatially degenerate states, in which case the main effect often comes from the matrix element between their different components. The simplest such class of systems are the $^2\Pi$ species, in which case the $<^2\Pi_x|H_{so}|^2\Pi_y>$ spin-orbit matrix element is required. As a result the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$ multiplets are separated in contrast to their degenerate status in non-relativistic theory. A whole series of such calculations are available in the literature (3-5) and the indication is that such a theoretical treatment results in a uniformly accurate prediction of the experimentally observed zero-field splittings, generally underestimating the measured results by from 5 to 10%.

To go further in this development, however, it is necessary to employ second-order perturbation theory, in which case interactions with the whole range of zeroeth-order solutions need to be considered in principle. At this point it is clear that the method can succeed only if the infinite series implied by second-order perturbation theory can be safely truncated. In order to test this possibility it is important to have a large series of zeroeth-order solutions available, but in processing the corresponding numerical data it is evident that the more weakly interacting exctied states can safely be employed at a lower level of approximation without adversely affecting the overall accuracy of the computations. For this purpose it is convenient to employ relatively small CI expansions (6) for the more weakly interacting states, for which purpose the use of configuration selection techniques (7) is particularly well suited. A configuration-driven CI algorithm such as the Table CI technique (8) allows for the evaluation of only those Hamiltonian matrix elements which are actually required when employing selected CI subspaces. A variation of the same technique has also been implemented for evaluation of the spin-orbit matrix elements between the zeroeth-order CI wavefunctions (9). The dependence of the magnitude of the spin-orbit matrix elements on the size of the CI wavefunctions employed is shown in Table 1 for the NBr molecule (10). Expecially when attention is centered on the ultimate goal of these computations, it is seen that considerable computation time can be saved by restricting the size of the CI expansions in this manner without any significant change in the final calculated results such as zero-field splittings or transition probabilities.

Table 1. Comparison of calculated spin-orbit matrix elements (cm^{-1}) obtained for two different configuration selection thresholds T (μhartree) for various pairs of zeroeth-order CI wavefunctions for the NBr molecule.

	$^1\Delta$,		$^1\Sigma^+$		$2^1\Delta$		$2^1\Sigma^+$	
	T=10	T=40	T=10	T=40	T=10	T=40	T=10	T=40
$3^1\Sigma^-$	-0.10234	0.05971	439.62592	445.24558	0.49771	-0.04359	416.09390	427.67499
$^3\Delta$	626.03914	625.39814	-0.15857	2.72708	-820.61001	-832.35531	1.12188	3.62547
$2^3\Sigma^-$	0.10227	2.62267	-610.51128	-666.80461	-1.01364	-3.51867	-862.84421	-866.31999
$3^3\Sigma^-$	-0.00336	-0.02198	-4.45584	-5.95292	0.00664	0.02002	-3.00013	-2.03021

In practice the most convenient way of proceeding is simply to form the spin-perturbed wavefunctions of the zeroeth-order CI wavefunctions with the help of the first order expression

$$c_{ik}^{(1)} = H'_{ik}/(E_k^o - E_i^o), \qquad (1)$$

where

$$\psi_k^{(1)} = \psi_k^{(o)} + \sum_i c_{ik}\psi_i^{(o)} \qquad (2)$$

Alternatively a small secular problem can be solved involving ψ_k^o and all perturbing species employing the combined Hamiltonian H^o+H_{so} which leads to quite similar results, but care must always be taken not to include excited species which possess very compact charge distributions and thus lead to the inevitable variational collapse expected for this operator. With the use of $\psi_k^{(1)}$ in eq.(2) it is then possible to evaluate its corresponding properties, including the energy.

Ancther possible simplification in this second-order procedure is to employ only the one-electron part of H_{so} in the matrix element computation. Again the advisability of this procedure must be judged on the basis of the importance of a given matrix

element in the overall computations. Sample data for the SeS molecule (11) are given in Table 2. In this case the approximation is generally not good enough for quantitative practice, but rather for more analytical purposes. The fact that the two-electron interaction is less important numerically than the nuclear term is a direct consequence of the short-range nature of the spin-orbit operator. The concept of shielding of the nucleus by the electrons so familiar to the quantum chemist is a consequence of Gauß's law and thus a specific characteristic of an r^{-1} potential. The relative diffuseness of the electron cloud greatly decreases the effect of the two-electron term relative to its one-electron counterpart, particularly as the charge of the nucleus increases. Since the other Breit-Pauli operators are also characterized by an r^{-3} dependence it can be assumed that a similar situation exists for them, at least for those species for which both one-electron and two-electron terms exist, and it will be seen that considerable advantage can be taken of this fact when the discussion turns to variational two-component treatments in the following section.

Table 2. Comparison of spin-orbit matrix elements (cm^{-1}) obtained with different levels of treatment (A: single configuration, one-electron operator only; B: CI wavefunction, one- and two-electron operator) for various pairs of states for the SeS molecule in its equilibrium geometry. Absolute values are given, but the phases agree in each case for the two treatments.

State 1	State 2	Treatment A	Treatment B	State 1	State 2	Treatment A	Treatment B
$^1\Delta$	$^3\Delta$	694.4	533.0	$^3\Sigma^y$	$^3\Pi$	605.0	542.2
$^3\Sigma^+$	$^3\Sigma^-$	484.5	498.5	$^3\Sigma^-$	$^1\Pi^x$	605.0	519.7
$^1\Sigma^+$	$^3\Sigma^-$	1267.0	1111.6	$^3\Pi$	$^1\Delta^x$	605.0	527.8
$^3\Pi$	$^3\Pi$	633.5	596.6	$^3\Pi^x$	$^3\Sigma^+$	229.8	190.7
$^1\Pi^x$	$^3\Pi^y$	633.5	604.9	$^1\Pi^x$	$^3\Sigma^+$	229.8	175.4
$^1\Pi^x$	$^3\Pi^y$	633.5	604.1	$^3\Pi^x$	$^1\Delta$	607.5	539.2
$^3\Pi^y$	$^3\Sigma^+$	232.9	191.5	$^3\Pi^x$	$^3\Sigma^-$	607.5	542.9
$^1\Pi^y$	$^3\Sigma^+$	232.9	199.2	$^1\Pi^y$	$^3\Sigma^-$	607.5	518.8
$^3\Pi^y$	$^1\Sigma^+$	605.0	492.8	$^3\Pi^y$	$^1\Delta$	607.5	528.6

Advantage of the dominance of the one-electron spin-orbit term can also be taken in another context, namely in determining the key phase relationships which exist between different degenerate components of the zeroeth-order basis. In the classic work of McWeeny describing the implementation of spin-orbit procedures (12), repeated use is made of the Wigner-Eckart theorem in conjunction with Wigner 3j coefficients, but in practice it must be recalled that the definition of the latter quantities is predicated upon the existence of certain phase relationships for the pertinent basis functions, in this case CI wavefunctions, employed in the treatment. For different M_s components of degenerate states it is straightforward to impose the necessary phase relationships since typically only the component with M_s=S is explicitly computed for the zero-order (spin-independent) Hamiltonian. For spatial degeneracies the situtation is far less clear, however, because species of more than one irreducible representation of the full point group are generally obtained together in conventional CI programs because of the convenience of working in effective Abelian group symmetries. As a result the phase relationship between such spatially degenerate components is left to chance and it is necessary to employ caution in the application of standard formulae for matrix elements involving such species. Perhaps the simplest means of determining the required phase relationships in this situation is to work out the corresponding one-electron matrix element for the leading terms in the respective CI wavefunctions. Because of the dominance of the nuclear contribution to such matrix elements the signs of these quantities are invariably determined by the one-electron portion of the operator. In practice then it is only necessary to know the absolute value of a given H_{so} matrix element obtained with the full two-electron operator and the corresponding multi-determinantal CI wavefunctions, while using the above results for the dominant terms with the one-electron portion to determine the phase needed for a particular application. At the very least this procedure allows one to confirm the computed results with very little additional effort and thus avoid the pitfalls of working with degenerate pairs with non-standard mutual phase relationships.

In order to check the convergence of the pertubative series it is well to calculate a large number of zeroeth-order CI wavefunctions. Typically for a linear molecule treated in C_{2v} symmetry four roots are obtained for each spin and spatial type ($^{3,1}A_1$, $^{3,1}A_2$ etc.), giving a total of 32 such functions if attention is restricted to singlet and triplet species only. These functions are then used as input to obtain all possible

non-zero matrix elements between them for both the perturbing Hamiltonian and various transition moment operators (usually electric dipole and quadrupole and magnetic dipole). The $C_{ik}^{(I)}$ quantities are then calculated by means of eq.(1) and the final spin-mixed wavefunctions of eq.(2) are formed accordingly. Since all the transition moment operators mentioned above are spin-independent, it is not necessary to employ other than the conventional CI property routines for this purpose, in which it is assumed that both participating wavefunctions possess the same values of the S, M_s quantum numbers. For most applications it appears that a set of zeroeth-order functions of the above dimensions is adequate for the purpose at hand, but obviously this is a point which requires careful attention in a given application. One possible concern is the fact that Rydberg states exist in large numbers in the neighborhood of a given perturbed state. Even if the corresponding spin-orbit matrix elements H'_{ik} are relatively small between such species, it is possible for the Rydberg states to have a non-negligible effect because their very diffuseness tends to increase the magnitude of their dipole and quadrupole matrix elements. Experience seems to indicate that such convergence problems are most likely less critical than those connected with the choice of AO basis for the overall treatment, as well as the more deeply founded theoretical deficiencies inherent to the method as a whole.

This situation is illustrated by Table 3 in which the computation of the transition probabilities for various mechanisms is shown for the $b\,^1\Sigma^+ - X\,^3\Sigma^-_o$ transition in the SeS molecule (11). The corresponding experimental lifetime data have recently been measured experimentally by Fink and coworkers (13) and they indicate that the computed electric dipole transition moment μ_o is 2.5 times smaller than that observed. The ratio of the electric and magnetic dipole moments ($^1\Sigma^+ - X\,^3\Sigma^-_1$) comes out much better in the calculations, with μ_o/M_1 being computed as 20.20 while the experimental value is 19.69. It should also be added that the experimental determination of the above ratio can be obtained to notably better accuracy than either μ_o or M_1 themselves, so there is some hope that the calculations are more accurate than might first have been thought. It also should be emphasized that the circumstances accompanying such experimental determinations are such that even order-of-magnitude accuracy can be of considerable benefit. The present results for SeS are comparable in accuracy to those obtained in an earlier theoretical study involving the isovalent species O_2, S_2 and SO (14), so it seems likely that such methods are capable of a quite consistent description of spin-orbit splitting and intensity data for systems including atoms at least as heavy as selenium. It also is well to point out that the Breit-Pauli approach has also been successfully applied to the calculation of non-radiative transition probabilities, notably in the case of the O_2^+ molecule (15), with the aid of the Fermi Golden rule and the spin-orbit perturbation.

Table 3. Computation of transition moments (atomic units) for various operators employing the Breit-Pauli approximation. Given are the electric dipole M_σ and quadrupole Q_σ matrix elements for pairs of zeroeth-order wavefunctions (multiplied by the appropriate spin functions) and their contributions ($\bar{M}_\sigma$ and $\bar{Q}_\sigma$) to the overall result of $-0.02236i(M_\sigma)$ and $-0.22902i(Q_\sigma)$ a.u. respectively for the corresponding spin-perturbed CI states ($b\,^1\Sigma^+ - X\,^3\Sigma^-_o$)

State 1	State 2	$C_1^* C_2/i$	M_σ	$\bar{M}_\sigma/i$	Q_σ	$\bar{Q}_\sigma/i$
$^3\Sigma^-$	$^3\Sigma^-$	-0.1516	0.2874	0.04357	-0.8736	0.132442
$^3\Sigma^-$	$2\,^3\Sigma^-$	-0.0131	1.3786	-0.01806	11.0720	-0.145043
$^1\Sigma^+$	$^1\Sigma^+$	0.1516	-0.2652	-0.04021	-0.9784	-0.148328
$^3\Pi$	$^3\Pi$	-0.00026	-0.2777	0.00007	6.6352	-0.001745
$^3\Pi^x$	$^3\Pi^x$	-0.00026	-0.2698	0.00007	6.7059	-0.001763
$^3\Pi^y$	$2\,^3\Pi^y$	0.00017	0.0107	0.000001	0.1122	0.000020
$^3\Pi^x$	$2\,^3\Pi^x$	0.00017	0.0107	0.000001	0.1052	0.000018
$2\,^3\Pi^y$	$^3\Pi^y$	-0.00015	0.0107	-0.000001	0.1122	-0.000017
$2\,^3\Pi^x$	$^3\Pi^x$	-0.00015	0.0107	-0.000001	0.1053	-0.000016
$2\,^3\Pi^y$	$2\,^3\Pi^y$	0.00010	-0.4003	-0.000041	-14.2306	-0.001452
$2\,^3\Pi^x$	$2\,^3\Pi^x$	0.00010	-0.3975	-0.000041	-14.2081	-0.001449
$2\,^1\Sigma^+$	$^1\Sigma^+$	0.00780	-1.0421	-0.008128	- 8.3212	-0.064906
$2\,^3\Sigma^-$	$^3\Sigma^-$	0.00030	1.3786	0.000413	11.0720	0.003322
$2\,^3\Sigma^-$	$2\,^3\Sigma^-$	0.00003	-0.3705	-0.000010	- 3.9772	-0.000103

VARIATIONAL TREATMENT OF RELATIVISTIC EFFECTS IN TWO-COMPONENT METHODS

The preceding section serves to illustrate both the advantages and disadvantages of the Breit-Pauli approach for the calculation of relativistic phenomena. On the one hand the nature of the effects for a large range of applications is perfectly consistent with such a low-order perturbation theory approach, while on the other, it is clear from a technical standpoint that the approximations being made are not always justified. Especially when the agreement with experimental data is not satisfactory, one is faced with the realization that traditional means of improving the calculations in non-relativistic treatments may not be employed in the context of the Breit-Pauli approximation because of the short-range nature of the quantum mechanical operators involved. With this observation one may justifiably ask whether another set of operators might not exist which does not suffer from the unboundedness property which prevents the use of variational techniques in the Breit-Pauli approximation. Especially since the Dirac equation involves only bounded operators, it would seem that a suitable reduction to a two-component theory could be found which does not involve the use of unbounded species. The affirmative answer to this question was provided by Foldy and Wouthuysen in the early 1950's (16). To appreciate this development it is helpful to recall that the Dirac equation may be looked upon as a four-dimensional matrix equation. The Dirac Hamiltonian H_D is a non-diagonal matrix of quantum-mechanical operators, whose off-diagonal elements are responsible for the coupling between electron and positron components of the overall wavefunction. Whenever one sees a matrix equation of the form

$$\mathbf{A}\,\psi = \mathbf{E}\,\psi \tag{3}$$

there is always the possibility of applying a similarity transformation U to it so as to obtain a diagonal form and thus uncouple the associated differential equation into its individual parts. In the present case this would simply be a series of four Schrödinger-type equations; each of the diagonal elements of the resulting operator matrix $\mathbf{U}^{\dagger}\mathbf{A}\mathbf{U}$ would serve as the Hamiltonian for these Schrödinger equations. The only difficulty with this line of approach is to find the matrix **U** which accomplishes the desired diagonalization, but Foldy and Wouthuysen were also able to provide answers on this point. To begin with they were able to diagonalize the free-particle Dirac equation exactly with the help of the matrix of operators defined as:

$$\mathbf{U} = (\beta\alpha\cdot\mathbf{p} + \mathbf{E}_p + \mathbf{m})\ (2\mathbf{E}_p\ (\mathbf{E}_p + \mathbf{m}))^{-1/2} \tag{4}$$

where α and β are the familiar matrices in Dirac theory, **m** and $\mathbf{E}_p$ are diagonal matrices whose elements are respectively the particle masses and the free-particle kinetic energies

$$E_p = (p^2 + m^2)^{1/2} \tag{5}$$

introduced by Einstein in 1905. The result of the diagonalization of the free-particle Dirac matrix of operators H_D^{FP} is

$$\mathbf{U}^{\dagger}\,\mathbf{H}_D^{FP}\,\mathbf{U} = \beta\,\mathbf{E}_p \tag{6}$$

whereby it can also be shown that

$$\mathbf{U}^{\dagger}\,\mathbf{U} = \mathbf{1} \tag{7}$$

i.e. **U** is a unitary matrix.

When the Coulomb potential is introduced into the Dirac equation, it is necessary to look for another unitary operator to accomplish the analogous uncoupling of the differential equations. For this purpose Foldy and Wouthuysen were only able to offer a formal solution (17), but recently Sucher and coworkers have suggested other closely related approaches to this problem. In the first variant of this type it was suggested to simply employ the free-particle transformation **U** of eq.(4) to the Dirac equation for a system of particles in a central field. As noted above the resultant four-dimensional Dirac matrix is not diagonal but it was proposed in effect to proceed as if it were; this step is accomplished formally by adding a projection operator to U which eliminates all but the positive-energy components in the Dirac spinor. More importantly these authors were able to prove that the remaining Hamiltonian-like operators on the diagonal of the transformed matrix are bounded from below, in contrast to these employed in the Breit-Pauli approach. For example the one-electron spin-orbit operator appears in this approach with an additional factor $(E_p(E_p+m))^{-1}$, which is easily seen to vary as p^{-2} in the limit of high velocities. The presence of this factor has the effect of transforming the r^{-3} dependence of the spin-orbit interaction to a more long-range r^{-1} behavior whenever relativistic speeds are approached, thereby

avoiding the unboundedness property associated with the corresponding Breit-Pauli version of this interaction. Similar damping factors are obtained in this way for each of the potential terms in the Breit-Pauli formulation, including the quantity $((E_p+m)/2E_p)$ for the Coulomb operator itself, which varies from unity to a value of one-half in the limit of large momenta. It also leads to a one-electron term $-p_1(Z/r_1)p_1$ damped with same $(E_p(E_p+m))^{-1}$ factor as for the spin-orbit term, which can be shown to contain the Darwin interaction, another key element in the Breit-Pauli Hamiltonian.

From a practical standpoint the main difficulty in employing the resulting operators is to evaluate matrix elements for them in some appropriate functional basis. Although many of the one-electron integrals required can be evaluated in closed form in momentum space (18), another approach has been studied which simply makes use of a matrix representation of the corresponding operators (19). For the free-particle kinetic energy of eq.(5), which replaces the unbounded p^4 mass-velocity correction of the Breit-Pauli Hamiltonian in the transformed Dirac equation, for example, the required matrix can be constructed by first diagonalizing the non-relativistic kinetic energy operator, replacing the resultant diagonal elements with the corresponding E_p quantities represented as functions of these eigenvalues, and then performing the reverse transformation to the original AO basis. This technique leads to the same integral values in the limit of a complete AO basis as are obtained by direct integration, but for normal basis sets the results are different. Explicit checks in which the E_p integrals over gaussian orbitals were compared when obtained with both methods (19,20) indicate that the matrix representation of such complex operators performs quite reliably. For moderately large basis sets there is still the slight disadvantage that the variation principle is not strictly obeyed when this technique is employed to form the Hamiltonian matrix representation, but in practice this difficulty is far outweighed by the flexebility it affords in the use of relatively complicated operators in quantum mechanical calculations including various types of relativistic corrections. In particular it allows existing non-relativistic SCF and CI computer codes to be easily modified for the purpose of carrying out the desired calculations. All that is required is an additional transformation step similar to that employed to obtain the required integrals in an orthonormal basis in non-relativistic computations; the procedure is also applicable to two-electron operators (20).

Basis set calculations with the free-particle projected Hamiltonian were first reported by Almlöf, Faegri and Grelland (21) and by Heß of the laboratory (20,22) for the hydrogenic ion series. The first and most important result of these calculations is that they demonstrate that relativistic corrections can be treated with variational methods when certain classes of Hamiltonian operators are employed. The agreement between ionization energies computed with this method and those predicted by the Dirac equation is by no means perfect, but even for Z=82 (lead) the free-particle projector result for the 1s ground state of 0.5812 hartree/Z^2 is in better concordance with the Dirac value of 0.5552 hartree than is the non-relativistic result (0.5000 hartree). At still larger Z values the free-particle projector results tend toward even larger overestimations of the one-electron binding energy, but it must also be recalled that in the type of ab initio computations of greatest interest the degree of ionization, even when shielding effects are taken into account, is well below that of the type of heavy atom ion for which the computed results begin to deviate strongly from those of the Dirac four-component relativistic treatment. Moreover, by employing a different unitary transformation which takes account of external field effects, much better agreement is possible between the results of the two- and four-component treatments for one-electron atoms (23).

In the present context the key question is how to carry these encouraging results for the relativistic treatment of hydrogenic ions over to more complicated many-electron atoms and molecules. The first level of approximation which can be employed is to retain only the one-electron spin-independent operators which occur in the two-component relativistic Hamiltonian operators described above. In particular the damped Coulomb and $p_1 r_1^{-1} p_1$ terms can be added to the free-particle kinetic energy E_p of eq.(5) to replace the conventional Coulomb plus $p^2/2m$ one-electron operator of standard non-relativistic calculations. In this approach the key zero-field splittings most often sought in the Breit-Pauli formalism discussed in the first part of this paper are still not accounted for, but a number of key relativistic effects which are important for the accurate representation of the charge distributions in heavy atoms and molecules can be handled effectively in this manner. The first such application of this type has been reported recently by Heß and Chandra (24) of this laboratory for the silver hydride molecule, and this work was able to show that the required contraction in the equilibrium internuclear distance arising from the influence of relativistic corrections does occur when such a one-electron Hamiltonian is employed. This finding naturally raises the question as to the desirability of going to the next highest level of approximation, namely to also include two-electron versions of the relativistically corrected potential terms. To date there has been no thorough study of this question as to the relative merits of these two levels of approximation.

The other direction which can be taken in this connection is to also include the spin-dependent operators in the variational treatment, beginning perhaps with only the one-electron spin-orbit operator. This development is much more ambitious from a technical point of view because it requires a thorough reorganization of conventional SCF and CI computer codes, since these are heavily dependent on the use of a spin-independent Hamiltonian. The situation is somewhat simpler for atomic systems because then a complex (j-j coupled) basis can be employed which leads to a set of exclusively real one-and two-electron integrals, but for molecules the difficulties are notably greater. It is probably safe to say that for the next few years at least that a compromise procedure for including spin-dependent effects will be favored, namely to employ relativistically optimized charge distributions, based on the use of a modified spin-independent Hamiltonian, to treat the spin-orbit and spin-spin interactions via perturbation theory. In any event it seems fair to say that the advent of projected relativistic two-component methods will have a decisive impact on the field of heavy atom and molecule electronic calculations in the immediate future.

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