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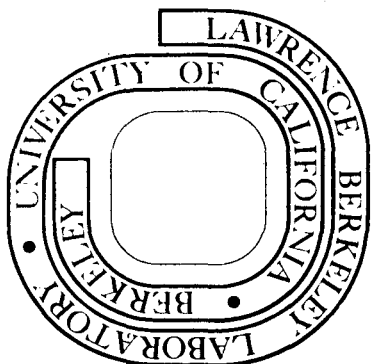
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A Theory of Self-Consistent Electron Pairs.

Computational Methods and Preliminary Applications

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Abstract

The recently developed theory of Self-Consistent Electron Pairs (SCEP) is an iterative variational method of obtaining correlated wavefunctions. The computational application of the theory has been fully implemented and tested for a variety of chemical systems. Some theoretical refinements which resulted from these tests are presented. The chemical systems selected for this first SCEP study of molecular electronic structure test most of the anticipated difficulties in using the theory and include H_2 , LiH , BeH^+ , BH , Be_2 , CH_2 , H_2O , H_2CO and $HCCH$. Some of the advantages of SCEP over conventional configuration interaction (CI) appear to be computational efficiency, variationally additive pair correlation energies and the capability to treat systems nearly as large as can be studied with one-configuration self-consistent field (SCF) theory. The method's efficiency results largely from the avoidance of any integrals transformation or construction and diagonalization of a large CI matrix. Because SCEP theory is formulated using Hartree-Fock-like operators, with the same dimensionality as the Fock operator, large basis sets are handled nearly as easily as with SCF calculations. The largest calculation reported here involved 42 contracted gaussian functions and accounts for $\sim 88\%$ of the valence shell correlation energy of singlet methylene. The equivalent CI wavefunction would include 2926 symmetry-adapted singlet configurations.

Introduction

As ab initio electronic structure calculations are used to study increasingly critical properties of a wide range of chemical systems (see, for example, reference 1), the need for easily obtaining correlated wavefunctions has intensified. A large number of different correlation energy methods have been developed over a long period of time, though the majority have appeared quite recently. Several review articles¹⁻³ have recently set forth the "state of the art" of electronic structure calculations, so only a brief, and certainly not inclusive, discussion of correlation methods is given here.

The most conceptually straightforward method is configuration interaction (CI) which, of course, is the diagonalization of the Hamiltonian matrix in the space of some selected set of configurations (linear combinations of Slater determinants). The matrix is typically quite large so that its construction and diagonalization are not trivial. Early ideas to get around the problems of CI were founded on perturbation theory.⁴⁻⁶ Notable among these was the Independent Electron Pair Approximation⁷ (IEPA) which gave independent pair contributions to the correlation energy. However, since the interaction between pairs was neglected, the resulting correlation energy was not variational and gave potentially disastrous results. A similar idea, but with a different formalism and using groups of electrons rather than just pairs, was McWeeny's theory of self-consistent group functions.⁸ The ideas which grew out of perturbation theory suggested a cluster development of the wavefunction as opposed to the individual configuration treatment of CI.

The recognized failure of IEPA left CI as the most reliable method, and substantial effort has been made at improving it. Bender, Davidson⁹ and Schaefer¹⁰ have done extensive work with the iterative natural orbital (INO) method. This method involves determining optimum orbital forms by diagonalizing the first-order density matrix between iterations and each step is a complete CI calculation. Another major development was the Pair Natural Orbital (PNO-CI) method of Meyer.¹¹ This method was highly successful in large scale calculations because it greatly reduced the number of configurations in the CI through the use of non-orthogonal orbitals, the PNO's. The method introduced by Roos¹² improves the computational efficiency of CI by determining expansion coefficients directly from two-electron integrals. The only weakness of this method is the rather complex logic required to do more than single and double excitations from closed shell singlet states.

Among the newest correlation energy methods is the treatment of two-electron systems by Driessler and Ahlrichs.¹³ They calculated the wavefunction iteratively using an operator formalism somewhat related to that of McWeeny's self-consistent groups. Beyond two-electron systems, their method is useful for selecting pair natural orbitals to do PNO-CI. The Vector Method (VM) of Bender¹⁴ represents another important development in CI techniques. VM uses the second quantized form of the Hamiltonian operator and solves for the wavefunction iteratively. In construction of matrix elements it has some similarity to Roos' method, but is totally general with respect to excitation level, types of states and selection of higher roots.

Other recent developments have occurred in the area of perturbation theory. Perhaps most important is the work of Pople's group³ on third-order

Møller-Plesset theory. As another example, Freeman and Karplus¹⁵ have recently used Goldstone diagrams in calculations on a few small molecular systems, providing an interesting comparison of variational and perturbation correlation energy approaches. The general trend among many of the newer methods¹²⁻¹⁴ has been to make use of perturbation theory to some extent. It is interesting to note, for example, that Bender's Vector Method had its historical development from nuclear shell models, which of course have utilized many-body perturbation theory. The distinction between many of the various correlation energy methods seems to be whether to use higher order perturbation theory or to use first- or second-order perturbation theory in an iterative manner to achieve a variational result. The variational methods are in the end equivalent to a CI calculation of some type.

Perhaps the most recent new method is the theory of Self-Consistent Electron Pairs (SCEP) due to Meyer.¹⁶ This method, which is the subject of the present paper, uses a highly efficient operator formalism to obtain necessary matrix elements. As such, it avoids an integrals transformation. It utilizes first-order perturbation theory in an iterative variational scheme. Currently, the method is limited to single and double excitations and closed shell reference states, but the theoretical formulation should not limit its extension. We also point out that the coupled electron pair approximation (CEPA) of Meyer¹⁷ is easily incorporated into SCEP, if desired, so that unlinked cluster effects may be approximately incorporated.

Theory

Though the theory of Self-Consistent Electron Pairs has been presented elsewhere,¹⁶ it is useful to briefly mention theoretical details which relate to work presented here. The SCEP wavefunction is given by

$$\psi = \psi_0 + \sum_P \psi_P \quad (1)$$

ψ_0 is a closed shell reference determinant and ψ_P is a doubly substituted pair function; $P = (ij,p)$ where i and j are internal orbitals (occupied in the reference determinant) and p is +1 or -1 for singlet or triplet spin coupled pairs, respectively. For the specific substitution of the internal pair P by an external pair, say (ab,p) , a coefficient matrix is defined using the orbital vectors $|a\rangle$

$$\tilde{C}_P^{ab} = (2 + 2\delta_{ab})^{-1/2} [|a\rangle\langle b| + p|b\rangle\langle a|] \quad (2)$$

A linear combination of all \tilde{C}_P^{ab} for a given P , multiplied by appropriate expansion coefficients is designated \underline{C}_P and is a representation of ψ_P .

(\underline{C}_P , boldface, is termed the external pair coefficient matrix for pair $P = (ij,p)$; C_P , however, is the internal pair coefficient for the pair $P = (ij,p)$ and is given by (2), if i and j are substituted for a and b .)

The expansion coefficients are not carried explicitly so that \underline{C}_P is directly in terms of basis functions rather than orbitals. The variational energy expression is

$$E = E_0 + \sum_P \epsilon_P \quad (3)$$

$$\epsilon_P = \langle \psi_0 + \psi | H - E_0 | \psi_P \rangle / \langle \psi | \psi \rangle \quad (4)$$

E_0 is the energy of the reference determinant and ϵ_p is the p^{th} pair contribution to the correlation energy.

Calculation of the wavefunction proceeds via matrix elements T_p^{ab} , which for the double excitation $ij \rightarrow ab$ is of the form

$$T_p^{ab} = \langle \psi_p^{ab} | H-E | \psi \rangle \quad (5)$$

The wave function is then improved according to first-order perturbation theory.

$$\psi^{(n+1)} = \psi^{(n)} - \sum_{P,cd} \psi_P^{ab} T_P^{ab} / E_P^{ab} \quad (6)$$

$$E_P^{ab} = \langle \psi_P^{ab} | H-E | \psi_P^{ab} \rangle \quad (7)$$

Iterating with (5) and (6) yields a self-consistent solution when each T_p^{ab} is zero. The calculation of the matrix elements in (5) and (6) requires primarily matrix addition and multiplication of easily constructed operators. Furthermore, all T_p^{ab} for a given pair P are obtained at the same time. Important in the iteration scheme is that different, non-orthogonal sets of external orbitals may be used for each internal pair. Clearly, these orbitals may be selected to optimize convergence.

Single excitations are treated apart from the double excitation iterations. Again, matrix elements are calculated from simple operators.

$$T_i^a = \langle \psi_i^a | H | \psi \rangle \quad (\text{excitation } |i\rangle \rightarrow |a\rangle) \quad (8)$$

$$E_i^a = \langle \psi_i^a | H-E | \psi_i^a \rangle \quad (9)$$

The wavefunction may then be improved by first order perturbation theory.

$$\psi' = \psi - \sum_{i,a} \psi_i^a T_i^a / E_i^a \quad (10)$$

In practice, it has been found that a more accurate treatment of the single excitations is achieved by iterating until the singles have zero Hamiltonian matrix elements with the total wavefunction. The original presentation of the theory did not include a discussion of this treatment, so an appendix has been included which gives explicit forms of the operators used in the singles iterations.

The singly-excited configurations are absorbed into ψ_0 by improving the internal orbitals using

$$|i'\rangle = |i\rangle - \frac{1}{\sqrt{2}} \sum_a |a\rangle T_i^a / E_i^a \quad (11)$$

The T_i^a are either the matrix elements of (8) or an iterative result (see the appendix). The orbitals are then symmetrically reorthogonalized. A projection operator is then used to insure orthogonality of the set of \tilde{C}_p 's with ψ_0 in the new internal orbital basis. This is the only orthogonality constraint in SCEP.

The general SCEP procedure, then, begins with a closed shell reference determinant and a set of internal and external (virtual) orbitals, presumably from an SCF calculation. Different sets of optimum external orbitals are found for each internal two-electron pair. Sets of doubles and singles iterations are performed until all single and double excitations have zero Hamiltonian matrix elements with the wavefunction. New sets of externals

and various operators are set up after each set of singles iterations because the orbitals have been changed.

Computational Aspects

The SCEP procedure begins with the construction of internal pair Coulomb and exchange operators from the two-electron integrals, $(\alpha\beta|\gamma\delta)$.

$$\begin{aligned}
 [J^{ij}]_{st} &= \sum_{\mu\nu} |i\rangle_{\mu} \langle j|_{\nu} (st|\mu\nu) \\
 [K^{ij}]_{st} &= \sum_{\mu\nu} |i\rangle_{\mu} \langle j|_{\nu} (s\mu|t\nu)
 \end{aligned}
 \tag{12}$$

If there are N occupied orbitals in the reference determinant, exclusive of those which are frozen to excitation, then there are only $N(N+1)/2$ J and K operators, since $J^{ij} = J^{ji}$ and $K^{ij} = (K^{ji})^{\dagger}$. The J and K operators can be formed in effectively one pass through the two-electron integral list and are then stored on disk. The closed-shell Fock operator in terms of these operators is given as

$$F_0 = H_0 + \sum_i (2J^{ii} - K^{ii})
 \tag{13}$$

with H_0 being the matrix of one-electron integrals over basis functions.

Pair Fock operators, designated F_{PP} and F_{PQ} (see ref. 16), are now set

up. F_{PQ} represents the interaction between the internal cores of two doubly substituted pairs. F_{PP} is used to find optimum external orbitals.

If there are M internal pairs, then there are $M(M+1)/2$ pair Fock operators,

because $F_{PQ} = F_{QP}^{\dagger}$. In the current program version, these operators are

constructed and then stored on disk. (They are, of course, unchanged throughout an entire set of doubles iterations.) However, the simple form of the operators suggests that it may be more efficient to obtain them directly from the J and K lists during each doubles iteration.

The only other use of two-electron integrals is in the construction of external exchange operators,

$$[K(\underline{C}_p)]_{st} = \sum_{\mu\nu} [C_p]_{\mu\nu} (s\mu|t\nu) \quad (14)$$

of which there are N^2 . This is done at each doubles iteration except the first, where $\underline{C}_p = 0$. Simple matrix manipulation of all the operators is used to construct a total pair operator, G_p , for each pair. G_p is used to calculate matrix elements according to

$$\begin{aligned} T_p^{ab} &= \langle \psi_p^{ab} | H-E | \psi \rangle = \text{Trace} \{ [p|a\rangle\langle b| + |b\rangle\langle a|] G_p \} \\ &= p \text{ Trace} \{ \underline{C}_p^{ab} G_p \} \end{aligned} \quad (15)$$

and

$$\langle \psi_p | H-E | \psi \rangle = p \text{ Trace} \{ \underline{C}_p G_p \} \quad (16)$$

The calculation is performed pair by pair and by using a "double transformation" of G_p ¹⁶ each \underline{C}_p can be improved directly without the intermediate step of (15). This has been found to be very efficient.

The form of the wavefunction here is a set of N^2 coefficient matrices, the \underline{C}_p 's. For convenience, the wavefunction is not explicitly renormalized at any point. Instead, one begins with $\langle \psi_0 | \psi_0 \rangle = 1$ and then $\langle \psi | \psi \rangle$ is calculated using

$$\langle \psi | \psi \rangle = \langle \psi_0 | \psi_0 \rangle + \sum_p p \text{ Trace} \{ \underline{C}_p S \underline{C}_p S \} \quad (17)$$

where S is the basis function overlap matrix.

Treatment of the single excitations follows convergence of the doubles. An operator is constructed immediately following the last doubles iteration

which gives matrix elements, T_i^a , of the singles with ψ . Then, $N(N+1)/2$ operators are constructed (see appendix) which are used to get matrix elements between the singly-excited configurations. The singles iterations are very fast since the two-electron integrals are not used and the number of matrix elements is small. Typically, the entire treatment of the singles, from constructing operators to improving the orbitals, requires less time than one doubles iteration. The symmetric reorthogonalization of orbitals after (11) is a three-step process. The internal orbitals are orthogonalized using Löwdin's procedure¹⁸ and a five-term series expansion is used to find $\Delta^{-1/2}$ where Δ is the overlap matrix of the improved orbitals. Schmidt orthogonalization is used to zero out the overlap of the externals with the internal orbitals. This is necessary because the optimum form of the internal orbitals is fixed after the first step. Finally, the Löwdin orthogonalization is applied to the externals alone.

Since the iterative SCEP method uses first-order perturbation theory to achieve self-consistency, it should be clear that the choice of energy denominators, E_p^{ab} and E_i^a , affects convergence but not the final result. Several of the systems studied were selected because of potentially small energy denominators. A very small energy denominator, say less than 0.1, may cause the first-order perturbation expression to greatly overshoot the correct result. Indeed, it was not difficult to find cases where this effect completely prevented convergence. To overcome this difficulty, two modifications have been tested for the energy denominators. The first is the addition of a small quantity to each E_p^{ab} or E_i^a , while the second is a multiplicative factor. The results of these tests, discussed below, showed

convergence was possible in all of the difficult cases. Clearly, some experience will be helpful in properly correcting energy denominators and some programmed criterion is anticipated.

A unique feature of SCEP is the ability to "restart" a calculation. Just as in conventional SCF methods, where an orbital vector or density matrix determined at one geometry provides a starting guess for a calculation at a new geometry, the SCEP list of C_p 's can be used as a guess in a calculation at a new geometry. To do this, the old set of C_p 's is orthogonalized with respect to the molecular orbitals at the new geometry using a projection operator (see ref. 16). This restart feature has been implemented in the program and tests show that it saves at least a few doubles iterations and as much as 1/3 of the total computation time.

SCEP is a particularly attractive method for use on mini-computers. This is because the maximum number of elements used in any array is the square of the number of basis functions; there are obviously no large CI matrices to deal with. Only a few such arrays are needed in core at one time. In the present version of the SCEP program we have selected a generous limit of six arrays. For the Harris Corporation Series 100 system (32K of 48-bit words), the program limit is 54 functions, compared to an SCF (POLYATOM) limit of 72 functions. We anticipate reducing the number of arrays in core to four which will increase the SCEP limit to 66 functions. (The program does take advantage of the total available memory in the construction of most of the operators, even when the number of functions is less than the limit.) Since there is no configuration list and no configuration limit, almost any problem which can be studied with SCF can be studied with SCEP.

Finally, it should be pointed out that the SCEP program is still in somewhat of a preliminary form. For example, all systems are treated assuming no symmetry. Meyer¹⁶ has shown there is definite advantage to including symmetry in the treatment, though the savings from symmetry will not be as great for SCEP as for CI. In the largest CH₂ calculation reported here (42 basis functions), the number of symmetry-adapted configurations required for a calculation equivalent to the SCEP result is 2926. Without symmetry, this number rises to 6669, a much more difficult problem for CI. SCEP is thus a very competitive method for systems without symmetry, and we plan to incorporate the advantages of symmetry, along with other improvements, in later versions of the program.

Results and Discussion

Pair Correlation Energies

An exciting result which is obtained from SCEP theory is the set of pair correlation energies which can be added to the reference one-configuration energy to give the total energy of the system. We expect that this will add a new level of understanding and interpretation to correlated wavefunctions. An example of pair correlation energies is given for methylene in Table I. The first two calculations were with the standard double-zeta basis set of Dunning¹⁹ contracted Gaussian functions. The third calculation used a much larger basis set of 32 contracted functions, the same as previously used by Bender, Schaefer and McLaughlin.²⁰ A comparison of the first two columns of pair correlation energies shows the effect of freezing the carbon 1s orbital. While excitations from the carbon 1s orbital can contribute more than 0.01 au to the total correlation energy, the contribution of pairs which do not include the 1s are nearly identical in both calculations. Since the SCEP method is strictly variational and explicitly accounts for inter-pair effects, this result demonstrates quantitatively the validity of freezing the carbon 1s orbital. That is, the carbon 1s orbital interacts little with other pairs, or more precisely, the ψ_p involving the $1a_1$ internal orbital are almost completely independent from the correlation corrections for the remaining electrons. The failure of IEPA indicates that this will not be true for all other orbitals. What SCEP has provided is a clear-cut quantitative argument for freezing orbitals with respect to excitation.

The capability to do large scale calculations with the SCEP method is shown by the results in the final column of Table I. This computation employed

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a basis set of 42 functions. Huzinaga's²¹ (10s 6p) carbon basis was contracted to (6s 4p) using Dunning's²² contraction scheme. For hydrogen the Huzinaga (5s) set was contracted to (3s) following Dunning. A set of p functions was added to hydrogen with exponent 1.0, and two sets of d functions with exponents 1.3088 and 0.38768 were added to carbon, as was done in the methylene calculation of Bender *et al.*²³ The geometry for all singlet methylene calculations was 1.11 Angstrom C-H bond length and an H-C-H angle of 102.4 degrees. To our knowledge, column D represents the largest methylene calculation performed to date, and the energy is lower than the previous best singlet methylene energy of Pakiari and Handy.²⁴

For comparison with the above ab initio results, we have attempted to predict the "experimental" correlation energy of singlet methylene. The lowest single configuration SCF energy obtained to date is that of Meadows and Schaefer,²⁵ $E_{\text{SCF}} = -38.8952$ hartrees, and we estimate the Hartree-Fock limit to be -38.8972 hartrees. Obtaining an estimate of the exact nonrelativistic energy is more difficult. We begin with Bunge's exact nonrelativistic energy²⁶ for the C atom -37.8436 ± 0.0015 hartrees, and add the energy (-1.0 hartree) of two H atoms, plus the dissociation energy for the process



The latter quantity is estimated to be 180.6 ± 1 kcal from the JANAF Thermochemical Tables,²⁷ and we have added an estimated 11.4 ± 2 kcal for the zero-point vibrational energy of CH_2 . Thus we arrive at -39.1496 ± 0.004 for the exact nonrelativistic energy of ground state (triplet) CH_2 . Adding to this the singlet-triplet separation²⁸ of 19.5 ± 0.7 kcal we finally

obtain -39.1185 ± 0.005 hartrees, corresponding to a correlation energy of 0.2213 hartrees. Our 42 basis function calculation yields a correlation energy of 0.1471 hartrees or 66.5% of the "experimental" result. However, we have made no attempt to account for the ψ_p involving the carbon 1s orbital. This part of the correlation energy due to the $1a_1$ orbital may be crudely estimated as -0.0549 hartrees, the analogous quantity from Bunge's study²⁶ of the C atom. Thus we may roughly estimate the valence shell correlation energy of CH_2 as -0.1665 hartrees. Our 42 basis function calculation accounts for 88.4% of this valence shell correlation energy.

Comparison of pair correlation energies for calculations with different basis sets shows some interesting features. Typically, one assumes a greater correlation energy contribution from a singlet coupled pair than from a triplet coupled pair.¹⁰ This is true in the double-zeta methylene calculations, but with larger basis sets, the $(1b_2, 3a_1)$ triplet coupled pair has a larger pair correlation energy than the $(1b_2, 3a_1)$ singlet coupled pair. Other pair energies, such as $(2a_1, 2a_1)$ and $(2a_1, 1b_2)$, show qualitative changes with different basis sets. These effects are probably due to the changes in the internal orbitals with different basis sets. However, the precise nature of the effects suggests additional study. It is clear at this point, though, that SCEP pair correlation energies will aid in understanding basis set effects on correlated wavefunctions.

Table II gives a summary of results of test calculations on a few small systems. The BeH^+ potential curve was studied at a variety of internuclear distances and the potential minimum was found to be at 2.557 bohrs. The

result of the water calculation, -76.13501 , compares well with the equivalent INO result of Schaefer and Bender,²⁹ -76.13497 hartrees.

Convergence

An example of the convergence of the SCEP method is shown in Table III for the 30 basis function LiH calculation. After the second iteration, changes in the wavefunction become rather small. The LiH calculation and most of the other calculations reported here seem to indicate that the singles treatment needs to be performed only two or three times. The exceptions to this are cases where singly-excited configurations would have a large matrix element, in the CI sense, with the reference determinant. This implies that the internal orbitals will change substantially after the singles iterations so that several sets of singles iterations are needed to achieve self-consistency. Examples are formaldehyde, where the reference determinant has been shown to have a large CI matrix element with the lowest A_1 singlet,³³ the dissociating BeH^+ , and Be_2 at large internuclear separations. While these calculations did require more singles iterations than LiH, the number of required sets was about four, with only a few doubles iterations required between sets.

Convergence is difficult for some systems. For basis sets larger than 28 functions with Be_2 , SCEP, in its undamped mode, does not converge at all. A general rule seems to be that with basis sets larger than double zeta, the energy denominators tend to be too small. In these cases, additive or multiplicative scaling factors were required. As mentioned earlier, these factors can be used to reduce the magnitude of the first-order perturbation correction to the wavefunction. As such, they can

greatly influence convergence, though not the final result. While water, with a double zeta basis, is not difficult to converge, it does show the effects of these scaling factors. The results of seven water calculations are given in Table IV. The fastest convergence was obtained with an additive factor of 0.09. The multiplicative scaling has the potential of overdamping as shown by the last column.

Overall, our results on the test cases discussed here seem to indicate that convergence of the doubles starting with $C_p = 0$ can be achieved in 9 or less iterations. Two to three sets of singles iterations are usually required with just a few doubles iterations between. Considerable savings can be accomplished by using a larger convergence limit for the first one or two sets of doubles iterations (see Table III) or by using the restart feature. Convergence of many systems is quite fast, but the important conclusion is that even for systems that converge with difficulty, one can still depend on convergence in 25 or less equivalent doubles iterations (this counts set up and singles iteration times to the extent to which they are equivalent to a doubles iteration).

Computation Time

Having considered some of the types of molecular systems which can be studied by SCEP and having demonstrated the convergence properties of the method, it remains to show computational efficiency to establish SCEP as a viable correlation method. The first and admittedly easy system to consider is H_2 . With a basis set of 22 gaussian functions,³⁴ SCEP required 3 minutes, 48 seconds on the Harris 100. The calculated energy was -1.171140 hartrees at 1.4 bohrs, in exact agreement with the CI calculation of

Bauschlicher et al.³¹ In comparison, the SCF calculation required 2 minutes 18 seconds. The SCEP calculation required 9 actual doubles iterations and the equivalent of 12 iterations when including the time for set-up, singles treatment and improvement of the orbitals. Each doubles iteration required about 19 seconds and each SCF iteration required about 18 seconds. This similarity is not surprising because the SCEP method is structured around Hartree-Fock like operators, which for a two-electron system are no more complex than the Fock operator. Driessler and Ahlrichs found similar efficiency in their PNO-CI method for two-electron systems.¹³

The results of a calculation on LiH have already been presented. The time for the SCEP calculation was about 40 minutes (on the Harris 100), while the SCF calculation required 9 minutes. The time for an SCF iteration was about 39 seconds while the time for one SCEP doubles iteration was 141 seconds. The ratio is nearly equal to the number of electron pairs, four. An additional calculation done on LiH used 21 basis functions. The run time for this calculation was about 970 seconds compared to 2526 seconds with 30 basis functions and identical numbers of iterations. Solving $(30/21)^R = 2526/970$ gives $R = 2.7$. That is, empirically, the process goes as less than N^3 for N basis functions. Calculations on Be_2 with 22, 28, 36, 40 and 44 basis functions and the methylene calculations gave about the same value of R .

Overall, it appears that SCEP may be a highly efficient method for many chemical problems. It is clear that in many cases the computation time is of the order of magnitude of SCF calculations, as originally suggested by Meyer, but the difference increases sharply with the number of electron pairs. This is, of course, due to the explicit inclusion of inter-pair

effects. The less than N^3 dependence of computation time with basis set size makes the method quite attractive for extended basis set calculations. As a final demonstration of the potential applications of the SCEP method, we report in Table V pair energies for formaldehyde. The calculations were done with a Dunning-contracted double zeta basis set¹⁹ for all atoms. Carbon and oxygen 1s orbitals were frozen to excitation, and the geometry was the experimental structure given by Herzberg.³⁵

Summary and Outlook

The increasing value of theoretical electronic structure calculations to fundamental physical chemistry research has made the search for efficient, accurate theoretical methods of major importance. As a result, a wide variety of variational and perturbation methods have been proposed. Nonetheless, the standard configuration interaction approach is the most persistently used and serves as a basis of comparison for new methods. CI calculations, however, even including the promising new formulations by Roos¹² or Bender,¹⁴ are still difficult and require extensive numerical effort. Essentially all CI methods, for instance, rely on an integrals transformation³⁶ and any improvement in orbitals requires another transformation.

Perturbation techniques show some promise for being computationally more efficient than CI, but may be more difficult to apply reliably, as evidenced by the few systems which have been studied with these methods. In addition, the energy values are, of course, not variational which may limit the use of such results where small energy differences are important. These methods, generally, also require an integrals transformation and calculation of many matrix elements.

An overview of the many correlation energy methods seems to point to a "convergence" in methods. The idea of pair contributions to the total energy has been an interesting concept for a long period of time; the direct determination of the wavefunction without construction of a Hamiltonian matrix is clearly an efficient scheme; and perturbation theory may be an ideal way to improve a wavefunction. All of these are a part of the SCEP method. SCEP uses first-order perturbation theory, but does so iteratively to achieve a self-consistent variational result. It never constructs a

complete Hamiltonian matrix and avoids the manipulation of individual matrix elements. As such, it determines the wavefunction in a most direct fashion and since it requires no configuration list, there is in principle no limit to the dimensionality of the configuration Hilbert space. SCEP includes pair-pair interaction explicitly and thus, gives truly variationally additive pair correlation energies.

In conventional CI or in any perturbation scheme, it is difficult to establish a clear-cut optimum set of molecular orbitals. Iterative natural orbital methods (INO) have been perhaps the most successful, but often require several or even many expensive CI calculations. The SCEP formalism yields the optimum set of orbitals within the space of single and double excitations. Finally, SCEP does not require any explicit integrals transformation. This accounts for its less than N^3 computation time dependence (when the number of electrons is fixed), while an integrals transformation is at best N^5 .

The advantages of SCEP and its formal structure suggest that it could possibly be the "converged result" of the many correlation energy methods. Supporting this assertion, however, will require substantial effort. First, the method must be extended to higher order excitations to be competitive with both CI and perturbation methods. The treatment of higher order excitations may be much more complex than singles and doubles, but should present no limitation to the method. Extension of SCEP to open shell systems is a more immediate, but fortunately, straightforward problem. Reservations about applying SCEP to open shells are primarily due to possible convergence difficulties. However, we have experimented with the method enough to believe any convergence difficulties can be overcome. In the BeH^+ calculations, the method was tested on a dissociating (to $\text{Be}^+ + \text{H}$) system and proved successful. In a CI

treatment, the dominant configuration at the dissociation limit may be expressed as a singly-excited configuration from the SCF closed shell state. Thus we have, in effect, treated an open shell state with this method, though not in an optimum fashion.

If SCEP is successfully extended, we believe it will be a most powerful method and possibly the most efficient approach to the correlation energy problem. In the meantime, it will serve as an excellent closed shell method, capable of treating large systems and equivalent to CI techniques including several thousand configurations, for instance. Our tests already show the capability for such large scale calculations and show computational efficiency competitive with existing variational methods. Theory and program developments, such as taking molecular symmetry into account, should increase the advantages of the SCEP method.

Acknowledgments

The computational development of the SCEP method began in September, 1975 at the University of California, Berkeley and the first version of the SCEP program was completed and tested at Der Johannes Gutenberg Universität during a visit by one of us (C.E.D.). Travel expenses were paid from the Alfred P. Sloan Fellowship of H.F.S. We thank Das Rechenzentrum in Mainz for computer time on the Telefunken TR 440 computer and Professor Martin Maier, Dr. P. Rosmus and Peter Botschwina for assistance in using this computer system. We also thank the Darmstadt Technische Hochschule for test runs made on their IBM 360 system. We are grateful to IBM of Germany for support for C.E.D. during the stay in Mainz.

The second SCEP program version, which was used for the calculations reported here, was developed on the Berkeley Electronic Structure Group's Harris 100 minicomputer supported by NSF Grants GP-39317 and GP-41509X. In addition to the above mentioned computer systems, the program has also been adapted for use with the Lawrence Berkeley Laboratory CDC 7600.

AppendixTreatment of Single Excitations

The wavefunction, including single excitation configurations, is

$$\psi_S = \psi + \sum_{i,a} c_i^a \psi_i^a \quad (\text{A1})$$

Notice that unlike the treatment of the doubles, explicit expansion coefficients are being used. The optimal coefficients are those for which the single excitation configurations have a zero Hamiltonian matrix element with ψ_S . The following matrix elements are calculated.

$$R_i^a = \langle \psi_i^a | H - E | \psi_S \rangle \quad (\text{A2})$$

$$E_i^a = \langle \psi_i^a | H - E | \psi_i^a \rangle \quad (\text{A3})$$

The iterative solution is given by an expression analogous to equation (6) for double excitations.

$$\psi_S^{(n+1)} = \psi_S^{(n)} - \sum_{i,a} \psi_i^a R_i^a / E_i^a \quad (\text{A4})$$

For the first iteration, for which $\psi_S = \psi$, $R_i^a = T_i^a$ as in (8).

Expressions for T_i^a have been given by Meyer.¹⁶

To find the matrix elements of (A2) and (A3) a set of operators F^{ij}

$$F^{ij} = \delta_{ij} F_0 + 2K^{ij} - J^{ij} - S \langle i | F_0 | j \rangle \quad (A5)$$

are constructed. Slater-Condon formulae³⁷ then give the following result

$$\langle \psi_i^a | H-E | \psi_j^b \rangle = \langle a | F^{ij} | b \rangle - (E-E_0) \delta_{ij} \delta_{ab} \quad (A6)$$

To perform the iteration of (A4) the following expression is used to determine the expansion coefficients of (A1).

$$C_i^{a(n+1)} = C_i^{a(n)} - \frac{1}{E_i^a} \left\{ T_i^a - (E-E_0) C_i^{a(n)} + \sum_{jb} \langle a | F^{ij} | b \rangle C_j^{b(n)} \right\} \quad (A7)$$

From (A6) and (A7) it is clear that the values $\langle a | F^{ij} | b \rangle$ need to be calculated only once. Convergence is achieved when the change in C_i^a 's is within some specified limit.

After the converged set of C_i^a 's is determined, the total variational energy is calculated starting with the expectation value expression

$$E = \langle \psi_S | H | \psi_S \rangle / \langle \psi_S | \psi_S \rangle \quad (A8)$$

Rearranging using (A1) gives

$$E \left\{ \langle \psi | \psi \rangle + \sum_{ia} C_i^a{}^2 \right\} = \langle \psi | H | \psi_S \rangle + \sum_{ia} C_i^a \langle \psi_i^a | H | \psi_S \rangle \quad (A9)$$

$$E \langle \psi | \psi \rangle = \langle \psi | H | \psi_S \rangle + \sum_{ia} C_i^a \langle \psi_i^a | H-E | \psi_S \rangle \quad (A10)$$

The last term in (A10) is just R_i^a , which is zero after the singly excited configurations have converged. Therefore, separating the first term in

(A10) gives

$$E\langle\psi|\psi\rangle = \langle\psi|H|\psi\rangle + \sum_{ia} C_i^a \langle\psi|H|\psi_i^a\rangle \quad (\text{A11})$$

Using (8), this leaves

$$E = \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle + \left\{ \sum_{ia} C_i^a T_i^a \right\} \sqrt{\langle\psi|\psi\rangle} \quad (\text{A12})$$

The first term is just the energy from the last doubles iteration and the second term is the energy improvement from the singly excited configurations.

The final step is absorbing the single excitation configurations into the closed shell reference determinant.

$$|i'\rangle = |i\rangle + \frac{1}{\sqrt{2}} \sum_a C_i^a |a\rangle \quad (\text{A13})$$

The wavefunction then has the form given in (1). However, because the orbitals have changed, double excitations will no longer have zero matrix elements with ψ and thus, another set of doubles iterations may be performed.

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Table I. Methylene electron pair correlation energies in hartrees. The sum of the pair energies and E_{ref} (the one-configuration energy in the final orbital basis) is the molecular energy, E_{total} . E_{corr} is the difference between the total energy and the SCF energy and is, therefore, the correlation energy. The pairs are ordered by orbital energy, and p indicates singlet ($p=1$) or triplet ($p=-1$) coupling. Sets A and B are double-zeta calculations and the remaining basis sets are discussed in the text. In all calculations except A, the lowest occupied orbital ($1a_1$, essentially the carbon $1s$ orbital) was frozen with respect to both single and double excitations.

Pair = (i	j	p)	A (14 fcns.)	B (14 fcns.)	C (32 fcns.)	D (42 fcns.)
$1a_1$	$1a_1$	1	-0.011 107			
$1a_1$	$2a_1$	1	-0.001 071			
$1a_1$	$2a_1$	-1	-0.000 038			
$1a_1$	$1b_2$	1	-0.000 011			
$1a_1$	$1b_2$	-1	-0.000 102			
$1a_1$	$3a_1$	1	-0.000 323			
$1a_1$	$3a_1$	-1	-0.000 106			
$2a_1$	$2a_1$	1	-0.012 120	-0.012 104	-0.016 662	-0.017 347
$2a_1$	$1b_2$	1	-0.011 385	-0.011 369	-0.022 224	-0.023 344
$2a_1$	$1b_2$	-1	-0.002 473	-0.002 462	-0.005 327	-0.005 858
$2a_1$	$3a_1$	1	-0.008 768	-0.008 758	-0.014 802	-0.016 293
$2a_1$	$3a_1$	-1	-0.002 923	-0.002 910	-0.006 052	-0.006 868
$1b_2$	$1b_2$	1	-0.014 355	-0.014 338	-0.020 471	-0.021 024
$1b_2$	$3a_1$	1	-0.008 701	-0.008 704	-0.012 657	-0.013 391
$1b_2$	$3a_1$	-1	-0.004 789	-0.004 784	-0.012 714	-0.014 740
$3a_1$	$3a_1$	1	-0.017 048	-0.017 245	-0.026 626	-0.029 274
E_{ref}			-38.861 274	-38.861 268	-38.888 751	-38.891 361
E_{total}			-38.956 595	-38.943 942	-39.026 286	-39.039 501
E_{SCF}			-38.861 533	-38.861 533	-38.889 788	-38.892 387
E_{corr}			-0.095 062	-0.082 409	-0.136 498	-0.147 114

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Table II. Correlation energies of LiH, BeH⁺, BH, H₂O, and HCCH

	Basis Functions	Number of Pairs	E _{ref}	E _{corr}	E _{SCF}	E _{total}
LiH	30 ^a	4	- 7.983 152	-0.055 692	- 7.983 771	- 8.039 463
BeH ⁺	13 ^b	4	-14.845 489	-0.038 586	-14.846 249	-14.884 835
BH	19 ^c	9	-25.106 831	-0.094 796	-25.107 545	-25.202 341
H ₂ O	14 ^d	16	-76.008 483	-0.125 711	-76.009 294	-76.135 005
HCCH	24 ^e	25	-76.796 256	-0.176 620	-76.797 686	-76.974 306

^a R = 3.015 bohrs. Huzinaga's Li 10s and H 5s sets were used (ref. 21). The Li 4p set of Williams (ref. 30) was added along with a set of H p functions with exponent of 1.0. None of the functions were contracted.

^b The Be-H distance was 2.557 bohrs, which was determined to be the potential minimum. The basis set was a double-zeta set using Dunning's contractions (ref. 19) with an additional s function released (see ref. 31).

^c R = 2.33 bohrs. Gaussian lobe function basis set, 13 functions for B and 6 for H (ref. 32).

^d Dunning contracted (9s 5p/4s 2p) oxygen basis and (4s/2s) hydrogen basis (ref. 19). Geometry was that used by Schaefer and Bender (ref. 29). The lowest orbital was frozen with respect to excitation, giving 16 instead of 25 pairs.

^e Same type of basis as in d above; experimental geometry is from reference 35.

Table III. Convergence of the LiH Calculation. In this calculation, the sets of doubles iterations have each been carried to the same convergence limit to show the nature of the iterative technique. However, the same final result is obtained by using a larger convergence limit for all but the last set(s) of doubles iterations. Thus, with a limit of 10^{-3} au for the first set, and 10^{-5} au for the second set, iterations 4, 5, 9 are not carried out resulting in a savings of about 20% of the total computation time.

Doubles Iteration	Energy	Energy Change	$\langle \psi \psi \rangle$	Variance ^a
1 ^b	-7.983 770 8		1.0	0.022 614 4
2	-8.038 043 5	-0.054 272 7	1.022 614	0.000 411 7
3	-8.038 885 5	-0.000 842 0	1.022 778	0.000 013 4
4	-8.038 901 9	-0.000 016 4	1.023 332	0.000 000 9
5	-8.038 902 8	-0.000 000 9	1.023 335	0.000 000 1
Singles Iterations ^c	-8.039 400 0	-0.000 497 2		
6	-8.039 404 8	-0.000 004 8	1.023 378	0.000 036 9
7	-8.039 440 6	-0.000 035 8	1.024 421	0.000 001 9
8	-8.039 442 7	-0.000 002 1	1.024 596	0.000 000 2
9	-8.039 442 9	-0.000 000 2	1.024 668	0.0
Singles Iterations	-8.039 459 3	-0.000 016 4		
10	-8.039 457 7	+0.000 001 6	1.024 685	0.000 003 8
11	-8.039 461 1	-0.000 003 4	1.024 917	0.000 000 2
12	-8.039 461 3	-0.000 000 2	1.024 971	0.0
Singles Iterations	-8.039 463 0	-0.000 001 7		
13	-8.039 463 0	0.0	1.025 058	0.0

Table III continued.

- ^a The variance is the sum of the square of the T_p^{ab} matrix elements divided by the square of E_p^{ab} . It represents the sum of the squares of the changes in expansion coefficients.
- ^b The first iteration requires substantially less computational effort than following iterations since $C_p = 0$ and matrix elements are being calculated only with ψ_0 . As such, this iteration amounts to a starting guess for the C_p 's and the energy is the SCF energy.
- ^c The energy expression for the wavefunction including singly excited configurations is given in the appendix. The values in the table are obtained after several singles iterations, when convergence is achieved.

Table IV. Convergence tests on H₂O. Convergence of the iterative perturbation improvement in the wavefunction was tested by either multiplying Hamiltonian matrix elements, T_P^{ab} , by some factor less than 1.0 or by adding a small constant to the energy denominator, E_P^{ab} . The singles elements, T_i^a and E_i^a , were adjusted in the same way.

	<u>Normal</u>	<u>$E_P^{ab} + 0.03$</u>	<u>$E_P^{ab} + 0.06$</u>	<u>$E_P^{ab} + 0.09$</u>	<u>$T_P^{ab} \times 0.9$</u>	<u>$T_P^{ab} \times 0.8$</u>	<u>$T_P^{ab} \times 0.7$</u>
Doubles Iterations	8	8	7	7	7	8	9
Singles Iterations	13	12	10	10	13	13	13
Doubles Iterations	3	3	3	3	3	3	3
Singles Iterations	12	10	9	8	11	12	10
Doubles Iterations	2	2	2	2	2	2	2

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Table V. Variational pair correlation energies ϵ_p (see equation (4) of text) of formaldehyde. The reference or SCF configuration is $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^2 1b_1^2 2b_2^2$.

Pair = (i	j	p)	
3a ₁	3a ₁	1	-0.006 001
3a ₁	4a ₁	1	-0.001 736
3a ₁	4a ₁	-1	-0.000 718
3a ₁	1b ₂	1	-0.002 863
3a ₁	1b ₂	-1	-0.001 302
3a ₁	5a ₁	1	-0.005 590
3a ₁	5a ₁	-1	-0.002 100
3a ₁	1b ₁	1	-0.009 839
3a ₁	1b ₁	-1	-0.004 522
3a ₁	2b ₂	1	-0.004 002
3a ₁	2b ₂	-1	-0.002 303
4a ₁	4a ₁	1	-0.008 182
4a ₁	1b ₂	1	-0.007 118
4a ₁	1b ₂	-1	-0.002 058
4a ₁	5a ₁	1	-0.005 851
4a ₁	5a ₁	-1	-0.001 474
4a ₁	1b ₁	1	-0.005 379
4a ₁	1b ₁	-1	-0.003 588
4a ₁	2b ₂	1	-0.005 452
4a ₁	2b ₂	-1	-0.001 293
1b ₂	1b ₂	1	-0.006 419
1b ₂	5a ₁	1	-0.003 759
1b ₂	5a ₁	-1	-0.003 289
1b ₂	1b ₁	1	-0.004 212
1b ₂	1b ₁	-1	-0.004 218
1b ₂	2b ₂	1	-0.008 457
1b ₂	2b ₂	-1	-0.000 588

Table V continued

Pair = (i j p)			
5a ₁	5a ₁	1	-0.008 816
5a ₁	1b ₁	1	-0.008 502
5a ₁	1b ₁	-1	-0.013 350
5a ₁	2b ₂	1	-0.005 162
5a ₁	2b ₂	-1	-0.005 183
1b ₁	1b ₁	1	-0.031 206
1b ₁	2b ₂	1	-0.005 316
1b ₁	2b ₂	-1	-0.008 453
2b ₂	2b ₂	1	-0.008 717
E _{ref}			-113.826 318
E tot			-114.033 335
<hr/>			
E _{SCF}			-113.829 539
E _{corr}			-0.203 796

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