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THE THEORY AND APPLICATIONS OF THE METHOD
OF SELF-CONSISTENT ELECTRON PAIRS

C.E. Dykstra
(Ph.D. Thesis)

September 1976

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The Theory and Applications of the Method of Self-Consistent Electron Pairs

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Ph.D. Thesis

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Abstract

The recently introduced theory of self-consistent electron pairs is shown to be a viable computational method for the determination of *ab initio* correlated molecular wavefunctions. Features of this method over conventional approaches are presented including the convenient calculation of variationally additive pair correlation energies, the representation of the wavefunction directly in terms of basis functions, and computational efficiency for many types of studies of molecular systems.

The self-consistent electron pairs method is an iterative scheme which, in its variational form, is equivalent to a configuration interaction treatment including all single and double substitutions from a closed shell reference determinant. The computational efficiency of the method results from the use of simple operators. These operators are defined in terms of pair coefficient matrices which serve as a compact representation of the total wavefunction. With this formulation of the method, explicit use and manipulation of a configuration list is completely avoided. Furthermore, since at any point in the calculation of a wavefunction only a few simple operators or other matrices are needed at the same time, the size limitations on computation approach those of one-configuration self-consistent field theory. This amounts to increasing the capability to study chemical systems with the inclusion of correlation

effects, especially with small-scale computing facilities.

The computational application of the theory has been fully implemented and tested for a variety of chemical systems. The operations and manipulations required for the determination of a wavefunction are considered in detail and it is demonstrated that the efficiency of this method over conventional techniques increases with increasing basis function set size. A number of reductions of the general formulas used to express the theory of self-consistent electron pairs are derived and further enhance the computational efficiency of the method. Finally, the results of some representative studies of chemical systems are presented. These include calculations performed for comparison with configuration interaction results and more extensive studies on a small beryllium metal cluster and planar and non-planar forms of allene. The interpretive value of pair correlation energies is indicated in the latter two studies.

Henry F. Schaefer III

Chairman, Committee in Charge

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He allowed immense freedom in study, complemented by exceptional scientific opportunity, and added insight and exposure to working independently in the field.

Finally, I thank Mrs. Carol Hacker for a lot of things, including typing this thesis, all done efficiently and without any mistake ever!

Overview

The development of science, according to T. S. Kuhn,[1] is guided by a set of paradigms. These paradigms are abstractly defined to include traditions and examples of scientific practice, theory, applications, and the models of scientific research. Now and then, contradictions or other difficulties arise within the paradigm of some field. Attempts are made to save the existing paradigm by classifying exceptions to it. Finally, however, the paradigm is replaced by a new and more useful one, which typically shows some similarity to ideas in force before the fall of the old paradigm. A scientific revolution is marked by the general acceptance of the new paradigm throughout the field.

Theoretical molecular electronic structure is a field whose paradigm is closely linked with a technological advance, the development of large-scale high-speed computers. Uprooted by this development was the notion that precise descriptions of molecular electronic structure were impossible. And thus a revolution in the development of modern physical chemistry occurred and its impact was the creation of a whole new field where chemistry is studied with computer programs completely dissected from laboratory experience. This new field, however, has been marked by segmentation and, one may argue, proliferation of different paradigms corresponding to different approaches used to approximate an exact answer. Part of the cause of this trend is that computational demands for studying real chemical systems are surpassing advancements in computer technology. Therefore, there has been a breakdown in the acceptance of traditional methods and a concomitant search for new

methods and new concepts. Even the technology which supports the field is being questioned as calculations are increasingly being performed on small rather than large-scale computers.

Using Kuhn's analysis, we could identify these trends as signposts of an impending revolution. This revolution will manifest itself by the general acceptance of some new powerful way of answering questions raised by today's theoretical chemists. The self-consistent electron pairs method provides a clearly useful restructuring of the problem of electron correlation in molecules. As such, it might well be anticipated that this new method will play a participating role in some future change in the paradigm which underlies electronic structure research.

Introduction

Increasingly over the past few years, electronic structure theory has become valuable in diverse areas of chemical research (see, for example, ref. 2). This has been made possible by the development of new computational methods which make real chemical problems tractable theoretical problems. Restricting the discussion to non-empirical or *ab initio* theoretical approaches, the standard division of methods is between one-configuration self-consistent field theory and methods which include correlation effects. The last division can be further broken down into variational and non-variational methods. Non-variational methods, while not as widely employed as variational techniques, have been used effectively in important calculations[3-4] and show a lot of potential for future use; however, no discussion of these methods will be given since the self-consistent electron pairs method is most closely related to variational approaches.

Before discussing ways of treating the electron correlation problem, it is, of course, necessary to identify the electron correlation problem and this requires a brief discussion of self-consistent field theory or SCF. The important concepts of SCF can be shown by considering only closed shell states, but SCF is certainly not limited to such types of systems. A closed shell SCF wavefunction is a product of spin-orbitals with an appropriate antisymmetrizer and normalization factor. (Ref. 5 gives a careful discussion and unambiguous description of electronic structure terminology.) Each spin-orbital is a product of a spatial orbital, ϕ_i, and a spin function to indicate the relative spin projection,

i.e., + ½ or - ½ . Letting ψ_0 be the wavefunction, $\hat{A}$ be an antisymmetrizing operator,[5-6] N be a normalization factor chosen so that $\langle\psi_0|\psi_0\rangle = 1$, then with N electrons, the wavefunction is

$$\psi_0 = N\,\hat{A}\,\phi_1(1)\,\alpha(1)\,\phi_1(2)\,\beta(2)\,\phi_2(3)\,\alpha(3)\,\phi_2(4)\,\beta(4) \cdots \phi_{N/2}(N-1)\,\alpha(N-1)\,\phi_{N/2}(N)\,\beta(N) \qquad (1)$$

A wavefunction where no orbitals are only partially occupied, such as (1), is termed a closed shell and can be written more compactly by deleting the identification of electrons as 1, 2, ..., N and realizing that there are the same number of α and β electrons in each spatial orbital. Furthermore, since the antisymmetrizer means forming the Slater determinant from the product in (1), we have

$$\psi_0 = N \det |\phi_1^2\ \phi_2^2 \cdots \phi_{N/2}^2| \qquad (2)$$

The rationalization for accepting this type of wavefunction is that for the most part electrons tend to move in the average field of the remaining particles.[7] Thus, their motion is instantaneously independent of one another and the total wavefunction can be written as a product of wavefunctions of individual particles.

After applying the Born-Oppenheimer approximation[8] to our molecular system the Hamiltonian operator corresponding to the energy due to the electrons (in atomic units[5]) is

$$\hat{H} = \sum_i^N \left(-\frac{\nabla_i^2}{2} - \sum_\alpha^L \frac{Z_\alpha}{r_{i\alpha}} \right) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} \qquad (3)$$

where there are L nuclei. The Hamiltonian can be rewritten as a sum of individual particle operators in the following way.

$$\hat{F}_i = -\frac{\nabla_i^2}{2} - \sum_{\alpha}^{L} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{j\neq i} \frac{1}{r_{ij}} \tag{4}$$

$$\hat{H} = \sum_{i}^{N} (\hat{F}_i - \frac{1}{2} \sum_{j\neq i} \frac{1}{r_{ij}}) \tag{5}$$

The second term in (5) means that the problem is not strictly separable and thus, (2) must be regarded as an approximation to the true wavefunction. If we are satisfied with this approximation and restrict the wavefunction to the one configuration, we can write an operator, $\hat{F}_i$, for each electron which assumes that the orbitals for the other electrons are fixed, and form an average field for the ith electron to move in.

$$\hat{F}_i^{\phi} = -\frac{\nabla_i^2}{2} - \sum_{\alpha}^{L} \frac{Z_\alpha}{r_{i\alpha}} + \hat{g}_i^{\phi} \tag{6}$$

The superscript, ϕ, on $\hat{F}$ and $\hat{g}$ is used to indicate that the form of this operator depends on the choice of the wavefunctions for the individual electrons and as such, it does not correspond to the exact operator in (4).

To understand the nature of $\hat{g}_i^{\phi}$, let us first define a two-electron integral over orbitals.

$$(ij|k\ell) = \langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_k\phi_\ell\rangle$$

$$= \int d\tau_1\ \phi_i^*(1)\ [\int d\tau_2\ \phi_k^*(2)\ \frac{1}{r_{12}}\ \phi_\ell(2)]\phi_j(1) \tag{7}$$

Using the two-electron integrals we can define Coulomb, J, and exchange operators, K, that satisfy the following.[6,9]

$$<\phi_k|J^{ii}|\phi_\ell> = (ii|k\ell) \tag{8}$$

$$<\phi_k|K^{ii}|\phi_\ell> = (ik|i\ell) \tag{9}$$

Clearly, J^{ii} and K^{ii} depend on the choice of orbitals, ϕ. Furthermore, the expressions for these operators are somewhat involved integral formulas requiring the use of permutation operators. However, since only matrix elements like those in (8) and (9) will be needed, the integration can be performed completely apart from the determination of the wavefunction. With our definition of $\hat{g}_i^\phi$, the value $<\phi_i|\hat{g}_i^\phi|\phi_i>$ should be the interaction of one electron in the ith orbital with all remaining electrons. Using (7), performing all spin integrations, and collecting terms yielding

$$<\phi_i|\hat{g}_i^\phi|\phi_i> = \sum_j^N <\phi_i|2J^{jj} - K^{jj}|\phi_i> \tag{10}$$

This gives

$$\hat{g}_i^\phi = \sum_j^N (2J^{jj} - K^{jj}) \tag{11}$$

It should be clear from this construction that $\hat{g}_i^\phi$ will equal $\sum_j \frac{1}{r_{ij}}$ exactly only when the electrons are completely separated as in, say, two hydrogen atoms at infinite internuclear distance. Otherwise, $\hat{g}_i^\phi$ and $\hat{F}_i^\phi$ are approximations to the true operator derived from the Hamiltonian and the approximation making $\hat{F}$ dependent on the choice of orbitals is a

consequence of restricting the wavefunction to have the form given by (2).

The goal of an SCF calculation is to determine the lowest energy forms of the occupied molecular orbitals using a finite expansion of the orbitals in terms of basis functions, χ.

$$\phi_i = \sum_r W_{ri}\chi_r \tag{12}$$

We will assume that the functions, χ, are orthonormal but as shown below this is not a requirement. From (11), it can be seen that the subscript in (6) is superfluous and we can operate with $\hat{F}$ on any given orbital. $\hat{F}$ can be given as a numeric matrix operator provided that integral values (13) - (14) over the basis functions are available.

$$I_{\alpha\beta} = \int d\tau\ \chi_\alpha^* \left[-\frac{\nabla^2}{2} - \sum_S^L \frac{Z_S}{r_S}\right]\chi_\beta \tag{13}$$

$$(\alpha\beta|\mu\nu) = \langle\chi_\alpha\chi_\beta|\frac{1}{r_{12}}|\chi_\mu\chi_\nu\rangle \tag{14}$$

The Coulomb and exchange operators can now be explicitly defined[6,10] using the orbital vector coefficients of (12).

$$[J^{ii}]_{st} = \sum_{\mu\nu} W_{\mu i}\ W_{\nu i}\ (st|\mu\nu) \tag{15}$$

$$[K^{ii}]_{st} = \sum_{\mu\nu} W_{\mu i}\ W_{\nu i}\ (s\mu|t\nu) \tag{16}$$

Therefore, the matrix operator, F^ϕ, called the Fock operator is

$$F^\phi = I + \sum_i^N (2J^{ii} - K^{ii}) \tag{17}$$

The eigenvalue problem is to vary the elements of W to obtain minimum values for $<\phi_i|\hat{F}^{\phi}|\phi_i>$. This means that the operator, F^{ϕ}, should be transformed to the orbital basis (i.e., from the proper matrix elements) and diagonalize the result.

$$<\phi_i|\hat{F}^{\phi}|\phi_i> = \sum_s \sum_t W_{si} W_{ti} F^{\phi}_{st} = F^{\phi\phi}_{ii} \tag{18}$$

$$F^{\phi\phi} = W^{\dagger} F^{\phi} W \tag{19}$$

The unitary transformation obtained from diagonalizing $F^{\phi\phi}$ is applied to the orbital vectors. However, this is not the final solution since the Fock operator is dependent, through the J and K operators, on the orbital basis. Thus, transforming the orbitals changes the Fock operator. SCF, then, is not a one step diagonalization, which is possible only when the operator is not basis dependent, but is iterative. The procedure can be listed as four simple steps as has been done by Flygare:[8]

1. Choose a guess set of orbitals, W^0.
2. Determine $F^{\phi\phi}$.
3. Diagonalize $F^{\phi\phi}$ with U, a unitary matrix, and form

$$W^{(n+1)} = W^{(n)} U \tag{20}$$

4. If U is not equal to the identity matrix, return to 2. When U is the identity matrix, the process has achieved self-consistency.

Defining the first order density matrix, largely for convenience,

$$[D_0]_{st} = 2 \sum_i^N W_{si} W_{ti} \tag{21}$$

and using (5), but replacing $\sum_j \frac{1}{r_{ij}}$ with $\hat{g}$ gives the total electronic energy.

$$E_{el} = \frac{1}{2} \sum_{ij} [D_0]_{ij} (I_{ji} + F^{\phi}_{ji}) \tag{22}$$

Adding the nuclear repulsion energy, R, gives the total SCF energy, E_0.

$$E_0 = E_{el} + R \tag{23}$$

The final point to be made concerning an SCF calculation is the use of non-orthogonal basis functions. One can rewrite all of the above expressions in a form that resembles a simultaneous diagonalization of the overlap matrix and the Fock operator.[5,6,9] However, the transformation of orbitals between iterations is unitary and thus, if linear combinations of basis functions which are orthonormal are used in the first iteration, the orbitals in all following iterations will necessarily be orthonormal. Thus, a non-orthogonal basis can be used with all of the above expressions if the overlap matrix of trial functions is diagonalized and the resulting vectors normed to unity before iterating. The usefulness of closed shell SCF theory can be seen in the thousands of studies which have been done with it, an example of which is ref. 11.

One purpose for discussing SCF is to make clear the approximation for the r_{ij}^{-1} part of the Hamiltonian operator. This approximation is what may be termed the electron correlation problem. Conceptually, the one-configuration form of the SCF wavefunction suggests independent electrons moving in average fields of the other electrons. But the instantaneous interaction of two electrons is ignored. Including this interaction, and thus, solving

the Schrödinger equation with an exact Hamiltonian causes the motions of the electrons to be correlated with respect to each other. The approximation in the Hamiltonian in SCF was shown to be a direct consequence of restricting the wavefunction to a one-configuration form. Thus, to account for electron correlation we must include more configurations in the wavefunction.

A configuration is a linear combination of Slater determinants which transform according to some spin and spatial symmetry representations.[12] The Slater determinants are constructed by putting electrons into available spin-orbitals limited only by the dimensionality of the basis function set. A wavefunction can consist of some linear combination of configurations with expansion coefficients chosen to minimize the total energy. The procedure for calculating such a wavefunction involves constructing matrix elements of the true Hamiltonian operator between configurations. The eigenvector corresponding to the lowest root found from diagonalizing this matrix contains the optimum expansion coefficients of the configuration in the wavefunction. This method is called configuration interaction[5,6,8] or CI. If all possible configurations are included, termed a full-CI calculation, then the only approximation in finding an eigenstate of (3) is that imposed by using a finite basis set expansion.

Including all configurations can become an immense problem for many chemical systems. Thus, one attempts to reduce the computational effort while still minimizing the approximation of r_{ij}^{-1} by removing configurations which are the least important in the expansion of the wavefunction. The most obvious cut off point, and probably the most often used in CI calculations, is excluding configurations that have more than two-electrons in orbitals differing from some reference configurations. Slater-Condon[13] formulae show that the Hamiltonian matrix element between the reference

configuration and the excluded configurations will be identically zero. If the reference configuration dominates the wavefunction, the effect of the excluded higher-order substituted configurations will be small. All that is needed is a reference configuration and the discussion of SCF theory makes the SCF wavefunction a likely choice.

CI is certainly a straightforward method for obtaining correlated wavefunctions, but it should be realized that typically the CI matrix is quite large, so that its construction and diagonalization are not trivial tasks. An early idea to reduce the effort involved in a CI calculation was the Independent Electron Pair Approximation[14] (IEPA). This approach neglected the interaction between substituted configurations from different pairs of orbitals occupied in the reference configuration. This gave independent pair contributions to the correlation energy, but they were not variational and the results were potentially disastrous.[15]

The effectiveness of conventional CI in studying chemical problems is shown by the many efforts made to extend or otherwise improve the method. Bender, Davidson and Schaefer[5,16] have performed numerous calculations with the iterative natural orbital method where the form of the orbitals is improved by diagonalizing the first order reduced density matrix. Each iteration, of course, is a complete CI calculation. A major accomplishment was the pseudo natural orbital (PNO-CI) method of Meyer.[17] PNO-CI takes advantage of the use of sets of non-orthogonal orbitals and in so doing can greatly reduce the number of configurations which need to be included in the wavefunction. Because of this, the method is quite useful in large-scale calculations.

The direct CI method introduced by Roos[18] makes use of an iterative scheme to achieve substantial computational efficiency. In this method,

configuration expansion coefficients are calculated directly while processing the two-electron integrals list. The new vector method of Bender[19] has some similarity as an iterative scheme to Roos' method. It uses a second quantized form of the Hamiltonian operator and has the same generality in usage as conventional CI. One other recent development has been the treatment of two-electron systems using a simple operator formalism by Ahlrichs and Driessler.[20]

The newest correlation energy method is the theory of self-consistent electron pairs (SCEP) due to Meyer,[21] and is the subject of this writing. SCEP makes use of an efficient operator formalism and determines the wavefunction iteratively. A report[22] on the computational implementation of the method has been presented along with several sample calculations. Given here is a detailed account of the operations and manipulations involved in SCEP and the simplifications which can be made in the general theoretical formulas when actually calculating a wavefunction. The computational development and testing of SCEP has occurred over a period of nearly one year. During this time, the efficiency of the computer program has been improved by several orders of magnitude and the time dependence of the method on basis set size, number of electrons, etc., has been carefully analyzed. This is essential for critically evaluating the method and for applying SCEP theory in the best manner.

The SCEP method is currently limited to closed shell reference configurations and in its variational form, is equivalent to a CI expansion including singly and doubly substituted configurations from the reference determinant. Extension of the method is certainly anticipated, but with the effort made in developing the closed shell form, it may be of interest to provide some perspective on the types of <u>ab initio</u> studies

undertaken in current research. Figure 1 represents one impression of the kinds of calculations performed ranging up to nearly exact results in one corner. With increasing accuracy, though, increasing effort is required. The range of applicability of SCEP is shown by a dotted line. As discussed later, the method becomes more attractive for extended basis sets and current experience indicates it may not be competitive with conventional CI for small basis sets. Figure 2 attempts to display a comparison of how much interesting chemistry involves primarily closed shell systems while in fairness showing that the effort required to study closed shells is substantially less than other types of states. The conclusion to be drawn from these representations is that SCEP, even in its current limited form, can be applied to a lot of chemical problems and is a method which can be used for achieving relatively quite accurate results.

Figure 1.

The approach to an exact solution of the Schrödinger equation within the Born-Oppenheimer approximation depends on the inclusion of correlation effects and the adequacy of the basis function set. On one axis are given arbitrary and qualitative cut-offs such as calculations involving a minimum basis set, double zeta (DZ) set, and extended basis sets, e.g., double zeta plus polarization functions (DZ + P). The vertical axis ranges from one-configuration through a full-CI expansion. The estimated range of practicable application of SCEP is given by the dotted line. The three blocks represent divisions into which a lot of calculations fall. As shown, calculations become more difficult and extensive when approaching the upper right corner, representing the greatest accuracy.

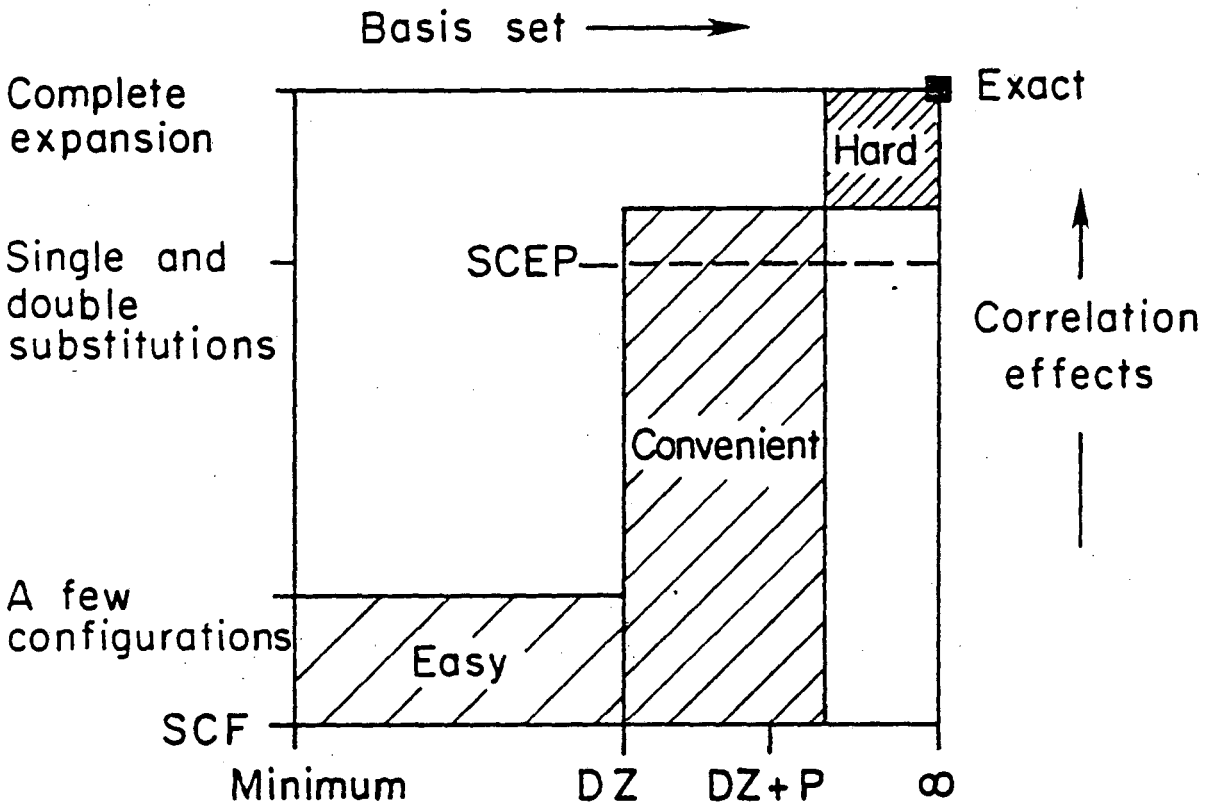
Basis set
Complete expansion
Single and double substitutions
A few configurations
SCF
Exact
Hard
SCEP
Convenient
Easy
Correlation effects
Minimum
DZ
DZ+P
∞

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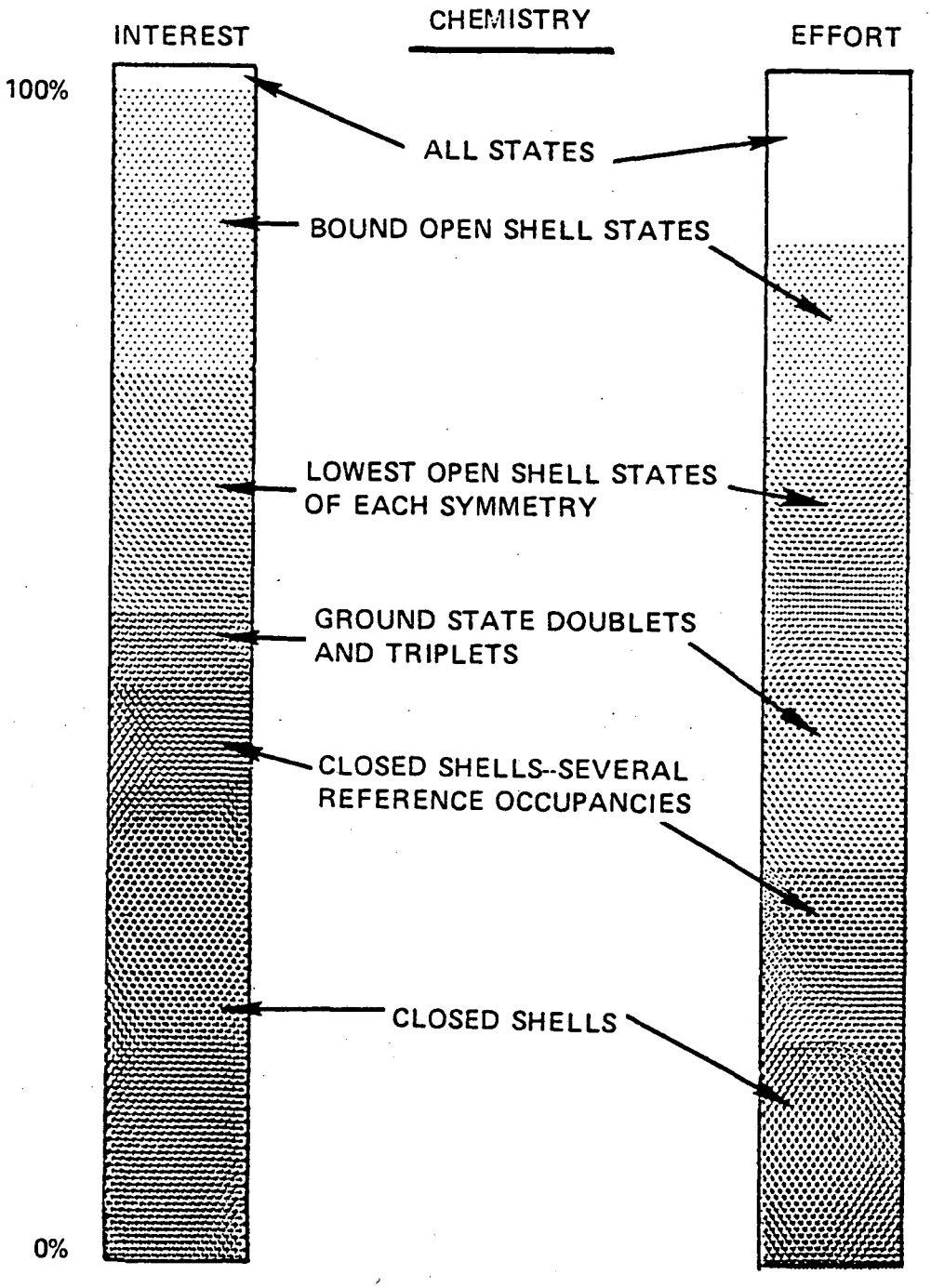
Figure 2.

Some arbitrary divisions among types of studies of electronic states in chemical systems is given. On the left is an estimate, if possible, of how much of today's interesting chemistry may fall into each division. An even more difficult estimate, considering the many different theoretical approaches, is the amount of effort required to study various states in an equivalent way and this is shown on the right.


CHEMISTRY
INTEREST
EFFORT
100%
0%
ALL STATES
BOUND OPEN SHELL STATES
LOWEST OPEN SHELL STATES
OF EACH SYMMETRY
GROUND STATE DOUBLETS
AND TRIPLETS
CLOSED SHELLS--SEVERAL
REFERENCE OCCUPANCIES
CLOSED SHELLS

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Self-Consistent Electron Pair Theory

To demonstrate the computational efficiency of SCEP, it is necessary to discuss its simple operator formalism and pair coefficient matrix structure of the wavefunction. With the earlier discussion of SCF and CI, it is easiest to lead into this by using an explicit configuration representation of the wavefunction as in CI. So, let us consider a wavefunction confined to the Hilbert space which includes a closed shell reference determinant, ψ_0, and all doubly substituted configurations which can be constructed from ψ_0 within a given finite set of basis functions. The wavefunction, ψ, will then have the form

$$\psi = \psi_0 + \sum_{i,j} \sum_{a,b} \sum_{p} C_{ij,ab,p}\, \psi_{ij,ab,p} \tag{24}$$

where $\psi_{ij,ab,p}$ is a linear combination of Slater determinants formed by replacing orbitals $|i\rangle$ and $|j\rangle$ in ψ_0 with $|a\rangle$ and $|b\rangle$ virtual orbitals. $|i\rangle$ and $|j\rangle$ will be referred to as internal orbitals and the virtuals will also be called external orbitals. The linear combination of determinants, or a configuration, is formed to transform as the closed shell reference configuration with respect to space and spin symmetry. Since a closed shell is totally symmetric in spatial symmetry and is a singlet spin state, $|i\rangle$ and $|j\rangle$ must be coupled as $|a\rangle$ and $|b\rangle$. For $i \neq j$ and $a \neq b$, $p = 1$ will imply a singlet coupling of $|i\rangle$ and $|j\rangle$ while $p = -1$ will imply triplet coupling. Now, defining the index $P \equiv (ij,p)$ as corresponding to an internal pair, and defining ψ_P as a doubly substituted function,

$$\psi_P = \sum_{ab} C_{ij,ab,p}\, \psi_{ij,ab,p} \tag{25}$$

the wavefunction can be rewritten as,

$$\psi = \psi_0 + \sum_p \psi_p \tag{26}$$

The usefulness of (26) is seen by looking at elements of the Hamiltonian matrix between configurations. The configuration $\psi_{ij,ab,p}$ with p = 1 is a sum of four Slater determinants.

$$\begin{aligned}\psi_{ij,ab,p} = \frac{1}{2} \{&\det |\Phi\ i\alpha\ j\beta\ a\alpha\ b\beta| \\ &+ \det |\Phi\ j\alpha\ i\beta\ a\alpha\ b\beta| \\ &+ \det |\Phi\ i\alpha\ j\beta\ b\alpha\ a\beta| \\ &+ \det |\Phi\ j\alpha\ i\beta\ b\alpha\ a\beta|\}\end{aligned} \tag{27}$$

where Φ is the set of doubly occupied orbitals and α and β indicate spin. Slater-Condon formulae[6,13] can be used to evaluate the Hamiltonian matrix element between this configuration and the reference configuration.

$$\langle\psi_{ij,ab,p}|H|\psi_0\rangle = \frac{1}{2} \{(ja|ib) + (ia|jb) + (jb|ia) + (ib|ja)\} \tag{28}$$

where the two-electron integrals are those defined by (7). This result can be generalized for any configuration, e.g., i = j, or a = b, or p = -1.

$$\begin{aligned}\langle\psi_{ij,ab,p}|H|\psi_0\rangle = &\frac{1}{2} [(1 + \delta_{ab})(1 + \delta_{ij})]^{-1/2} \sqrt{2-p} \\ &\{(ja|ib) + p(ia|jb) + p(jb|ia) + (ib|ja)\}\end{aligned} \tag{29}$$

The relationship between a two-electron integral over orbitals (7) and a two-electron integral over basis functions (14) is, of course just a simple transformation.

$$(ij|k\ell) = \sum_{\alpha\beta} \sum_{\mu\nu} |j\rangle_\alpha \langle\ell|_\beta \, |i\rangle_\mu \langle k|_\nu \, (\mu\alpha|\nu\beta) \tag{30}$$

Substituting (30) into (29) and rearranging gives

$$\langle\psi_{ij,ab,p}|H|\psi_0\rangle = \frac{1}{2} [(1 + \delta_{ab})(1 + \delta_{ij})]^{-1/2} \sqrt{2-p}$$

$$\sum_{\alpha\beta} \sum_{\mu\nu} (\mu\alpha|\nu\beta) \, [|i\rangle\langle j| + p|j\rangle\langle i|]_{\mu\nu} \, [p|a\rangle\langle b| + |b\rangle\langle a|]_{\alpha\beta} \tag{31}$$

With $|i\rangle_r = W_{ri}$ as in (12), then the vector cross product $|i\rangle\langle j|$ yields a square matrix

$$[|i\rangle\langle j|]_{\alpha\beta} = |i\rangle_\alpha \langle j|_\beta \tag{32}$$

This is similar to the expression for the SCF density matrix, D_0, given by (21) and indeed, one can write

$$D_0 = 2\sum_{k}^{N} |k\rangle\langle k| \tag{33}$$

Expression (31) looks somewhat like a matrix multiplication operation and so, it is convenient to break it into matrices. First, we generalize (16) and write an expression for a generalized exchange operator, K^{ij}. Though it's not yet needed, the expression for a generalized Coulomb operator is similar.

$$[K^{ij}]_{st} = \sum_{\mu\nu} |i\rangle_\mu \langle j|_\nu \, (s\mu|t\nu) \tag{34}$$

$$[J^{ij}]_{st} = \sum_{\mu\nu} |i\rangle_\mu \langle j|_\nu \, (st|\mu\nu) \tag{35}$$

The other matrix will be $\underline{C}_p^{ab}$, an external pair coefficient matrix for the specific ab substitution.

$$\underline{C}_p^{ab} = (2 + 2\delta_{ab})^{-1/2} \, [|a\rangle \langle b| + p|b\rangle \langle a|] \tag{36}$$

Expression (31) can now be rewritten as

$$\langle\psi_{ij,ab,p}|H|\psi_o\rangle = p\sqrt{2-p}\,(2 + 2\delta_{ij})^{-1/2}\, \mathrm{Tr}[\underline{C}_p^{ab}\,(K^{ij} + pK^{ji})] \tag{37}$$

The relationship between K^{ij} and K^{ji} is trivial.

$$[K^{ji}]_{st} = \sum_{\mu\nu} |j\rangle_\mu \langle i|_\nu \, (s\mu|t\nu)$$

$$= \sum_{\mu\nu} |i\rangle_\nu \langle j|_\mu \, (s\mu|t\nu) \qquad \text{since } \{\phi_i\} \text{ are real}$$

$$= \sum_{\nu\mu} |i\rangle_\nu \langle j|_\mu \, (t\nu|s\mu) \qquad \text{since } (\alpha\beta|\gamma\delta) = (\gamma\delta|\alpha\beta)$$

$$= [K^{ij}]_{ts}$$

That is,

$$K^{ij} = K^{ji\,\dagger} \tag{38}$$

$$J^{ij} = J^{ji} \tag{39}$$

where the relation for the Coulomb operators can be proved in a similar way.

Since (34) and (35) define operators in terms of vector cross products or matrices we can write generally,

$$[K(R)]_{st} = \sum_{\mu\nu} R_{\mu\nu} (s\mu|t\nu) \tag{40}$$

$$[J(R)]_{st} = \sum_{\mu\nu} R_{\mu\nu} (st|\mu\nu) \tag{41}$$

where R is some matrix. If we now define the internal pair coefficient matrix, C_p, analogous to (36)

$$C_p = (2 + 2\delta_{ij})^{-1/2} [|i\rangle\langle j| + p|j\rangle\langle i|] \tag{42}$$

then we can futher reduce (37) using (40) and (34) to show (43).

$$K(C_p) = (2 + 2\delta_{ij})^{-1/2} (K^{ij} + pK^{ji}) \tag{43}$$

$$J(C_p) = (2 + 2\delta_{ij})^{-1/2} (J^{ij} + pJ^{ji}) \tag{44}$$

This leaves

$$\langle\psi_{ij,ab,p}|H|\psi_o\rangle = p\sqrt{2-p}\ \mathrm{Tr}(\underline{C}_p^{ab}\ K(C_p)) \tag{45}$$

From (42) and (36) it can be seen that a coefficient matrix is symmetric if p = 1 and antisymmetric if p = -1. Thus, the transpose of a coefficient matrix for triplet coupled electrons is just the negative of the coefficient matrix. For convenience in writing expressions, we notice that the transpose of any coefficient matrix is, then, p times the matrix. Following Meyer[21] in using brackets, < >, to indicate the trace of a matrix or possibly matrix expression, gives

$$\langle\psi_{ij,ab,p}|H|\psi_o\rangle = \sqrt{2-p}\ \langle\underline{C}_p^{ab\dagger}\ K(C_p)\rangle \tag{46}$$

From (46) and the steps leading up to it, it can be seen that the only thing that depends on the external orbitals of the doubly substituted configuration is $\underline{C}_p^{ab}$. Thus, the Hamiltonian matrix element for another substitution from the internal pair is easily found by replacing $\underline{C}_p^{ab}$ with the appropriate external pair coefficient matrix for another specific substitution, e.g.

$$<\psi_{ij,cd,p}|H|\psi_o> = \sqrt{2-p}\ <\underline{C}_p^{cd\,\dagger}\ K(C_p)> \tag{47}$$

At this point, it should be clear that the reason for using an operator formalism in SCEP is the convenience in obtaining a whole set of matrix elements. If there are N occupied orbitals, then there are $M = N^2$ internal pairs. In the type of matrix elements considered so far all we need are a few generalized exchange operators, specifically $N(N + 1)/2$ by using (43), and then from matrix operations alone and no additional manipulation of the two-electron integrals, we obtain all Hamiltonian matrix elements between the reference determinants and the set of doubly substituted configurations. If there are K basis functions, then there are $\frac{1}{2}\, N(K - N)\ (1 + N(K - N))$ such Hamiltonian matrix elements.

Representation of the Wavefunction

Consideration of the Hamiltonian matrix elements between substituted configurations leads to the construction of another type of generalized exchange operator and an expression analogous to (47). This in turn suggests a representation for the total wavefunction. Let us first look at the matrix element between two doubly substituted configurations where the substitutions are from the same internal pair, the configurations have no external orbitals in common, and the remaining internal electrons are singlet coupled. Each configuration will have the form of (27) and applying the Slater-Condon rules once again to the sum of determinants and collecting the unique two-electron integrals gives

$$\langle\psi_{ij,cd,p}|H|\psi_{ij,ab,p}\rangle = [(1 + \delta_{cd})(1 + \delta_{ab})]^{-1/2}\{(ad|bc)+(ac|bd)\} \quad (48)$$

As was done for matrix elements with the reference determinant, we can generalize this result for triplet coupling, substitute in the expansion for the two-electron integrals in (30) and are left with

$$\langle\psi_{ij,cd,p}|H|\psi_{ij,ab,p}\rangle = [(1 + \delta_{cd})(1 + \delta_{ab})]^{-1/2} \sum_{\alpha\beta} \sum_{\mu\nu} (\mu\alpha|\nu\beta) \quad (49)$$

$$[|d\rangle\langle c| + p|c\rangle\langle d|]_{\mu\nu}\ [|a\rangle\langle b| + p|b\rangle\langle a|]_{\alpha\beta}$$

This result can be written in operator form in two ways:

$$\langle\psi_{ij,cd,p}|H|\psi_{ij,ab,p}\rangle = \langle\underline{C}_p^{cd\dagger}\ K(\underline{C}_p^{ab})\rangle \quad (50)$$

$$= \langle\underline{C}_p^{ab\dagger}\ K(\underline{C}_p^{cd})\rangle \quad (51)$$

It may seem at this point that SCEP is merely an operator scheme for constructing the Hamiltonian CI matrix. If this were true, there would be little advantage to SCEP, since the effort required to obtain all the matrix elements considered so far from the generalized Coulomb and exchange operators is about equal to the effort to transform the two-electron integrals from basis functions to the orbital basis as in (30). What SCEP does to reduce the effort to obtain the wavefunction is use an iterative scheme where, in effect, only matrix elements between configurations and the total wavefunction (from the last iteration) are needed. If there are J configurations, there are J(J + 1)/2 unique CI matrix elements to be constructed. SCEP will need only J elements per iteration and while these elements will typically be more complex than the CI elements, which are between individual configurations rather than with the total wavefunction, their construction will be facilitated by reductions made possible by the operator formalism.

If ψ is a solution to $H|\psi\rangle = E|\psi\rangle$ then we may write

$$\langle\psi_i|H-E|\psi\rangle = 0 \tag{52}$$

where ψ_i is some vector in the Hilbert space in which ψ is defined, for example, one configuration in a CI wavefunction. Let us assume we have a trial wavefunction, ψ', and wish to test it with (52) to see if it is the desired solution. In SCEP, the form of the wavefunction is that given by (26), so we can test each configuration or each ψ'_P.

$$\langle\psi'_P|H-E|\psi\rangle = \langle\psi'_P|H-E|\psi_0\rangle + \langle\psi'_P|H-E|\sum_Q \psi_Q\rangle \tag{53}$$

The first term on the right of (53) is particularly easy to calculate. Using (46) and (25) produces

$$<\psi_p'|H-E|\psi_o> = \sqrt{2-p} \sum_{a\geq o} c_{ij,ab,p}' <\underline{C}_p^{ab\dagger} K(C_p)> \tag{54}$$

At this point, we define the external pair coefficient matrices, $\underline{C}_p$,

$$\underline{C}_p = \sum_{a\geq b} c_{ij,ab,p} \underline{C}_p^{ab} \tag{55}$$

so that (54) becomes

$$<\psi_p'|H-E|\psi_o> = \sqrt{2-p} \quad <\underline{C}_p'^{\dagger} K(C_p)> \tag{56}$$

These external pair coefficient matrices can be shown to be a representation of the wavefunction. That is, given the set of internal orbitals which represent ψ_o, the set of $\underline{C}_p$'s provides all information about the wavefunction as do the set of orbitals and expansion coefficients of the CI wavefunction of (24).

Before showing how the external pair coefficient matrices can be used to obtain the desired wavefunction it is useful to establish more clearly the relationship between a CI representation and an SCEP representation. Expression (55) somewhat assumes that we will use a CI wavefunction to construct each $\underline{C}_p$. In fact, (55) is never performed explicitly and, as will be shown, the pair coefficient matrices are obtained quite directly. The question which arises, then, is can we relate some given $\underline{C}_p$ to CI expansion coefficients. Beginning with (55) the following operations may be performed.

$$\underline{C}_p = \sum_{a \geq b} c_{ij,ab,p} \, [|a\rangle \langle b| + p|b\rangle \langle a|] \, (2 + 2\delta_{ab})^{-1/2}$$

$$\underline{C}_p S \underline{C}_p^{rs} = \sum_{a \geq b} c_{ij,ab,p} \, [|a\rangle \langle b| + p|b\rangle \langle a|] \, S[|r\rangle \langle s| + p|s\rangle \langle r|]$$

$$(2 + 2\delta_{ab})^{-1/2} \, (2 + 2\delta_{rs})^{-1/2}$$

$$= \sum_{a \geq b} c_{ij,ab,p} \, [|a\rangle \langle s|\delta_{br} + p|a\rangle \langle r|\delta_{bs} + p|b\rangle \langle s|\delta_{ar} + p^2|b\rangle \langle r|\delta_{as}]$$

$$(2 + 2\delta_{ab})^{-1/2} \, (2 + 2\delta_{rs})^{-1/2}$$

The overlap matrix, S, is used since the orbitals are defined in terms of non-orthogonal basis functions. To obtain the CI expansion coefficient for the rs doubly substituted configuration, we multiply by the overlap matrix again and take the trace.

$$\langle \underline{C}_p S \underline{C}_p^{rs} S \rangle = \sum_{a \geq b} c_{ij,ab,p} \, (\delta_{as}\delta_{br} + p\delta_{ar}\delta_{bs} + \delta p_{bs}\delta_{ar} + \delta_{br}\delta_{as})$$

$$(2 + 2\delta_{ab})^{-1/2} \, (2 + 2\delta_{rs})^{-1/2}$$

$$= p \, c_{ij,rs,p} \tag{57}$$

From this result, we can write

$$\langle \psi_p | \psi_p^{ab} \rangle = \langle \underline{C}_p^{\dagger} \, S \, \underline{C}_p^{ab} \, S \rangle \tag{58}$$

which highlights the representation of components of the wavefunction by coefficient matrices.

By using (40), external pair coefficient generalized exchange operators, $K(\underline{C}_p)$, can be defined. Then the value $\langle \underline{C}_p^{ab\dagger} \, K(\underline{C}_p) \rangle$ will

be the sum of Hamiltonian matrix elements between the ab configuration and all configurations differing by two external orbitals, e.g., the cd configuration with $a \neq c$, $b \neq c$, and $b \neq d$, multiplied by the expansion coefficient of the cd configuration plus part of the Hamiltonian matrix elements for configurations differing by less than two external orbitals. Furthermore, analogous to (56), the value $\langle \underline{C}_p^\dagger K(\underline{C}_p) \rangle$ is part of the value $\langle \psi_p | H-E | \psi_p \rangle$ which is used in (53).

Pair Fock Operators

The iterative improvement in the wavefunction performed in an SCEP calculation is by first order perturbation theory. Let us assume that we have some arbitrary wavefunction which does not satisfy (52): that is $\langle\psi_i|H-E|\psi\rangle \neq 0$. We can make a first order improvement in the wavefunction by adding ψ_i times some factor to the wavefunction. The condition for choosing the factor is that the new wavefunction satisfy (52):

$$\langle\psi_i|H-E|(\psi + \alpha_i\psi_i)\rangle = 0 \tag{59}$$

Defining two matrix elements determines α_i.

$$T_i = \langle\psi_i|H-E|\psi\rangle \tag{60}$$

$$E_i = \langle\psi_i|H-E|\psi_i\rangle \tag{61}$$

$$\alpha_i = -{}^{T_i}/_{E_i} \tag{62}$$

If ψ has only two components, say ψ_0 and ψ_i, then this improvement gives the desired wavefunction. However, if there are more than two components, the correction for each ith component is made independent of all other components. Thus, it will be necessary to iterate until no further improvement in the wavefunction is possible which occurs when $T_i = 0$ for all i. The iterative result is a self-consistent result since the matrix elements T_i depend on the improvement in the wavefunction made with elements T_j. That is, the T matrix elements are changed when the

wavefunction is improved by (62) in much the same way as the Fock operator in SCF is changed when the orbitals are changed after diagonalizing the Fock matrix.

In SCEP similar matrix elements are defined:

$$T_p^{ab} = \langle\psi_p^{ab}|H-E|\psi\rangle \tag{63}$$

$$E_p^{ab} = \langle\psi_p^{ab}|H-E|\psi_p^{ab}\rangle \tag{64}$$

In practice, an exact value for E_p^{ab} is not necessary since this energy denominator will affect convergence, but not the final result which depends only on T_p^{ab}. With (63) and (64), the first order improvement in the wavefunction is

$$\psi_p^{(n+1)} = \psi_p^{(n)} - \sum_{a\geq b} \psi_p^{ab} \quad T_p^{ab}/E_p^{ab} \tag{65}$$

Remembering the definition of the external pair coefficient matrices we improve the representation of the wavefunction in a similar way.

$$\underline{C}_p^{(n+1)} = \underline{C}_p^{(n)} - \sum_{a\geq b} \underline{C}_p^{ab} \quad T_p^{ab}/E_p^{ab} \tag{66}$$

What is needed at this point is the means for calculating the set of matrix elements, T_p^{ab}. It is clear from the earlier discussion that we can obtain part of T_p^{ab} using $\underline{C}_p^{ab}$ and various operators. In fact, it is possible to define a total operator, G_p, such that

$$T_p^{ab} = \langle\psi_p^{ab}|H-E|\psi\rangle = \langle\underline{C}_p^{ab^\dagger} \; G_p\rangle \tag{67}$$

The operator G_P corresponds to $(H-E)|\psi>$ but can be constructed only so that it is appropriate for the one pair, P. Hence, G_P, G_Q, G_R ... must all be constructed to get the complete set of T matrix elements needed to perform (66) for all $\underline{C}_P$. The definition of G_P, showing why it is specific to one pair, is

$$G_P = \sqrt{2-p}\, K(C_P) + \{K(\underline{C}_P) + 2F_{PP}\underline{C}_P S - (E-E_o)S\underline{C}_P S\} \tag{68}$$

$$+ 2 \sum_{Q\neq P} F_{PQ}\, \underline{C}_Q S$$

where F_{PP} and F_{PQ} are pair Fock operators. The first term in (68) corresponds to $H|\psi_o>$ which is seen by comparing with (47) or (56). The second term corresponds to $(H-E)|\psi_P>$ while the last term is $H|\sum_{Q\neq P}\psi_Q>$.

The manipulations involving the pair Fock operators are about the most extensive of any in SCEP. Rather than deriving the expression for the F_{PQ}'s as has been done by Meyer,[21] we will instead use the expression to show how these operators give the desired matrix elements in some representative cases. First,

$$F_{QP} = \delta_{QP}F_o + K(D_{QP})\sqrt{(2-p)(2-q)}\,/2 \tag{69}$$

$$- \delta_{qp}\, \{J(D_{QP}) + S[<F_o D_{QP}> - <C_Q^{\dagger}\, K(C_P)>]/2\}$$

where

$$D_{QP} \equiv 2\, C_Q S C_P^{\dagger} \tag{70}$$

If Q = (kl,q) and P = (ij,p), then D_{QP} becomes

$$D_{QP} = [(1+\delta_{ij})(1+\delta_{kl})]^{-\frac{1}{2}} [|k><l|+q|l><k|]S[p|i><j|+|j><i|]$$

$$= [(1+\delta_{ij})(1+\delta_{kl})]^{-\frac{1}{2}} (|k><j|p\delta_{li}+|k><i|\delta_{lj}+|l><j|pq\delta_{ki}$$

$$+|l><i|q\delta_{kj}) \qquad (71)$$

As will be shown in Section III, (71) will always reduce to two or fewer terms. $K(D_{QP})$ and $J(D_{QP})$ can then be constructed from one or two K^{ij} and J^{ij} operators. It can easily be shown that $F_{PQ} = F_{QP}^{\dagger}$ and therefore, for M internal pairs, at most $M(M + 1)/2$ pair Fock operators are required. One thing to be noticed about the F_{QP} operators is that they only involve <u>internal</u> pair operators and internal pair coefficient matrices. Thus, these operators will not change between iterations. In CI terms, the F_{QP} operators will give all matrix element information which involves two-electron integrals over the orbitals where none of the four orbital indices of the integral correspond to external orbitals. The $K(\underline{C}_P)$ operator in G_P (68) is used where two-electron integrals over externals are needed. In this manner, all information about the wavefunction which is not changed from one iteration to the next is completely separated from that which has to be updated.

The first specific example of using F_{QP} operators is to calculate the matrix element $E^{ab} = <\psi_P^{ab}| H |\psi_P^{ab}>$ which is needed to obtain a value of T_P^{ab}. For illustration, we will use P = (ii,1) and a = b. With I as the one-electron operator matrix, the energy of the reference configuration is

$$E_0 = \sum_{k}^{\text{occupied}} <k| 2I + \sum_{l}^{\text{occupied}} (2J^{ll} - K^{ll})|k> \qquad (72)$$

ψ_P^{aa} is also a closed shell so the energy of this configuration is like

(72).

$$E^{aa} = \sum_{k\neq i} < k|2I + 2J^{aa} - K^{aa} + \sum_{l\neq i}(2J^{ll} - K^{ll})|k >$$

$$+ < a|2I + 2J^{aa} - K^{aa} + \sum_{l\neq i}(2J^{ll} - K^{ll})|a > \qquad (73)$$

Orbital energies for the ith and a^{th} orbitals are

$$\varepsilon_i = < i|\ I\ |i > + < i| \sum_{l}^{occupied} (2J^{ll}-K^{ll})|i > \qquad (74)$$

$$\varepsilon_a = < a|\ I\ |a > + < a| \sum_{l}^{occupied} (2J^{ll}-K^{ll})|a > \qquad (75)$$

Then, $E^{aa} - E_o$ can be rewritten as

$$E^{aa} - E_o = 2\varepsilon_a - 2\varepsilon_i + < i|K^{ii}|i > + < a|K^{aa}|a >$$

$$+ 2 < a|K^{ii} - 2J^{ii}|a > \qquad (76)$$

For the specific case being considered, the required pair Fock matrix is F_{pp} which, after using (71), is

$$F_{pp} = F_o + K^{ii} - 2J^{ii} - S < i|F_o|i > + \tfrac{1}{2}S < i|K^{ii}|i > \qquad (77)$$

Using (67) and (68) and taking $\underline{C}_p = \underline{C}_p^{aa}$ we form the matrix element for the aa double substitution in an attempt to determine E^{aa} in terms of F_{pp}:

$$< \underline{C}_p^{aa\dagger}|2F_{pp}|\underline{C}_p^{aa}S > = 2 < a|F_o|a > + 2 < a|K^{ii}-2J^{ii}|a >$$

$$-2 < i|F_o|i > + < i|K^{ii}|i > \qquad (78)$$

Realizing that $\varepsilon_a = < a|F_o|a >$ and comparing (78) with (76) indicates

$$E^{aa} - E_0 = \langle \underline{C}_P^{aa\dagger} | 2F_{PP} | \underline{C}_P^{aa} S \rangle + \langle a | K^{aa} | a \rangle \tag{79}$$

This result can be rewritten as

$$\langle \psi_P^{aa} | H - E_0 | \psi_P^{aa} \rangle = \langle 2\underline{C}_P^{aa\dagger} F_{PP} \underline{C}_P^{aa} S \rangle + \langle \underline{C}_P^{aa\dagger} K(\underline{C}_P^{aa}) \rangle \tag{80}$$

Another case to consider is the matrix element between two doubly substituted configurations from the same internal pair where the two configurations have no external orbitals in common. The pair Fock operator will be that of (77) and for convenience we will use the configurations ψ_P^{aa} and ψ_P^{bb}. As discussed earlier, the Hamiltonian matrix element between these two configurations is, according to (50)

$$\langle \psi_P^{bb} | H | \psi_P^{aa} \rangle = \langle \underline{C}_P^{bb\dagger} K(\underline{C}_P^{aa}) \rangle \tag{81}$$

Since this term will be included in the $K(\underline{C}_P)$ operator in G_P, we must expect $\langle \underline{C}_P^{bb\dagger} 2F_{PP} \underline{C}_P^{aa} S \rangle$ to give a zero contribution. Writing this out explicitly,

$$\langle \underline{C}_P^{bb\dagger} 2F_{PP} \underline{C}_P^{aa} S \rangle = 2 \langle b | S | a \rangle \langle a | F_0 + K^{ii} - 2J^{ii} - S \langle i | F_0 | i \rangle + \tfrac{1}{2} S \langle i | K^{ii} | i \rangle | b \rangle \tag{82}$$

Since $\langle b | S | a \rangle = 0$ by orthogonality of the orbitals, the term does indeed become zero.

A different type of case than the first two is the matrix element between double substitutions from different internal pairs. Reductions of (69) for all possible internal pair groupings are considered in Section III and given in detail in the Supplementary Tables, so for this example a fairly trivial case is selected for illustration: P = (ii,1) and Q = (jj,1). Since no internal orbitals are in common,

$D_{QP} = 0$ as can be seen by (71). Thus, the pair Fock operator consists of only one term:

$$F_{QP} = \tfrac{1}{2}S < j|K^{ii}|j > \tag{83}$$

The Hamiltonian matrix element of interest is

$$< \psi_P^{aa}|\ H\ |\psi_Q^{aa} > = (ij|ij) \tag{84}$$

$$= < j|K^{ii}|j > \tag{85}$$

Now this can be easily related to the pair Fock operator.

$$< \psi_P^{aa}|\ H\ |\psi_Q^{aa} > = < \underline{C}_P^{aa\dagger} 2F_{QP} \underline{C}_Q^{aa} S > \tag{86}$$

If the external orbitals for the two double substitutions were not the same, then the two configurations would differ by more than two orbitals and Slater-Condon rules would give a zero Hamiltonian matrix element. This, of course, is accounted for with the overlap matrix elements as in (82). However, since the overlap matrix is part of the operator, we could use a linear combination of the orbitals a, b, c, ..., for the internal pair P to form the external orbitals a', b', c', ..., for the internal pair Q. All the above expressions would remain valid because if c' has a non-zero overlap with a, it would have a Hamiltonian matrix element proportional to $< c'|S|a >$. This, in fact, is quite important for it means that different sets of external orbitals can be used with the different internal pairs and that orthogonality between the sets of externals is not required. The sets of externals, as shown below, can then be chosen to improve the convergence behavior of the iterative scheme.

The discussion of the relation between Hamiltonian matrix elements and pair Fock operators for the three cases mentioned above neither proves nor derives the expression for the F_{QP} operators. However, it is intended that these examples establish that: 1) CI type matrix elements between individual configurations can be determined from SCEP type operators, 2) the representation of the wavefunction can be collected into pair coefficient matrices, $\underline{C}_p$, and that operators can be defined in terms of the $\underline{C}_p$ which will give Hamiltonian matrix elements with the <u>total</u> wavefunction, 3) overall pair operators, G_p in (68), can be written generally enough to give all $< \psi_p^{ab} | H - E | \psi >$ for all double substitutions from P, and 4) different non-orthogonal sets of external orbitals can be used with different internal pairs in defining the $\underline{C}_p$'s and the specific substitutions.

Selection of External Orbitals

Optimal convergence conditions of the first order perturbation iteration scheme used in SCEP is achieved when the configurations are least interacting. Indeed, in the limit of completely noninteracting configurations, which of course cannot really be achieved, one iteration would be sufficient. An approach which has been used in SCEP calculations to date to reduce the interaction between configurations is to select special sets of external orbitals for each internal pair. These externals are selected to minimize, on the average, matrix elements of the type $\langle\psi_P^{ab}|H|\psi_P^{cd}\rangle$ where no more than one external in the two configurations is in common. As considered above, the pair Fock operator will give the necessary matrix elements which we seek to minimize. Part of these elements are the following:

$$\langle\psi_P^{ab}|H|\psi_P^{cd}\rangle = \langle\underline{C}_P^{ab^\dagger}\ K(\underline{C}_P^{cd})\rangle \qquad a \neq c,\ b \neq c,\ b \neq d \tag{87}$$

$$\langle\underline{C}_P^{ab^\dagger}\ K(\underline{C}_P^{ad})\rangle = [(2 + 2\delta_{ab})(2 + 2\delta_{ad})]^{-1/2}\{2\langle b|K^{ad}|a\rangle + 2\langle d|J^{aa}|b\rangle\} \tag{88}$$

where $\langle d|J^{aa}|b\rangle = \langle b|K^{da}|a\rangle$

Two approximations are made. First, the exchange operator contributions will generally be smaller than the Coulomb operator matrix elements. Thus, the exchange operators are neglected. The Coulomb operator in (88) would require an integrals pass and the number of such operators would be potentially large since the operators are over external rather than internal orbitals. Fortunately, approximations can be made at this

stage since the choice of externals does not affect the final result and will hopefully only improve convergence. The chosen approximation is, with P = (ij,p)

$$J^{aa} \approx \frac{1}{2}(J^{ii} + J^{jj}) \tag{89}$$

As Meyer has explained,[21] this is a reasonable approximation when assuming that the more important external orbitals, as far as minimizing the interaction of the configurations is concerned, are located in the space of the i and j internal orbitals. This approximation is particularly convenient since the same substitution of operators is made for all externals. Thus, adding $\frac{1}{2}(J^{ii} + J^{jj})$ to F_{pp} gives an operator which will give the matrix elements which we seek to minimize. We then transform this operator to the orbital basis with the matrix of orbital vectors, W,

$$V = W^{\dagger}\{F_{pp} + \frac{1}{2}(J^{ii} + J^{jj})\}W \tag{90}$$

The transformation which diagonalizes V yields the desired set of orbitals. However, we have assumed throughout that the same set of internal orbitals are used to define each internal pair and that any set of externals are orthogonal to the internals. Thus, in transforming W we cannot allow the internals to mix with the externals. This, of course, is easily accomplished by zeroing out elements of V between internals and externals.

The eigenvalues of V serve as good approximations for the energy denominators of (64).

$$E_p^{ab} = V'_{aa} + V'_{bb} - (E-E_o) \tag{91}$$

Inclusion of Singly Substituted Configurations

In the previous section, only double substitutions from the reference determinant have been considered. Operators were developed which give the necessary matrix elements to find an iterative self-consistent solution of the wavefunction. The final result is the lowest energy expansion of the wavefunction in the space of the reference determinant plus double substitutions. Single substitutions, however, are likely to be important. If the reference determinant is constructed from SCF orbitals, then the single substitutions will have zero Hamiltonian matrix elements with the reference determinant (see appendix) but will still have an interaction with the doubly substituted configurations. The approach which will be used to include singly substituted configurations into the wavefunction will be to hold $\psi = \psi_0 + \sum_p \psi_p$ fixed and iteratively diagonalize a Hamiltonian CI matrix whose rows and columns are labeled by ψ and the singly substituted configurations, ψ_i^a.

The wavefunction including the singles is designated

$$\psi_s = \psi + \sum_{i,a} c_i^a \psi_i^a \tag{92}$$

The iterative diagonalization follows the first-order perturbation improvement used with the doubles.[22] Matrix elements are found

$$R_i^a = \langle\psi_i^a|H-E|\psi_s\rangle \tag{93}$$

$$E_i^a = \langle\psi_i^a|H-E|\psi_i^a\rangle \tag{94}$$

and the wavefunction is improved according to

$$\psi_s^{(n+1)} = \psi_s^{(n)} - \sum_{i,a} \psi_i^a \, R_i^a / E_i^a \tag{95}$$

To find E_i^a and R_i^a, matrix elements of the general form $\langle\psi_i^a|H-E|\psi_j^b\rangle$ are required. For R_i^a, matrix elements of the singles with ψ are also needed. Construction of these matrix elements, designated T_i^a, is fairly involved but only requires operators which are all known after the last doubles iteration. The expression for T_a^i as given by Meyer[21] is

$$T_i^a = \langle\psi_i^a|H|\psi\rangle \tag{96}$$

$$= \sqrt{2}\,\langle a|F_o - \sum_p S\underline{C_p}K(C_p^\dagger)\sqrt{2-p}\;|i\rangle$$

$$+ \sum_{P=(ik,p)} \sqrt{2-p}\sqrt{(2+2\delta_{ik})}\,\langle a|S\underline{C_p}F_o - K(\underline{C_p})|k\rangle$$

By defining a simple set of singles Fock operators, F^{ij},

$$F^{ij} = \delta_{ij}F_o + 2K^{ij} - J^{ij} - S\langle i|F_o|j\rangle \tag{97}$$

and once again applying Slater-Condon rules gives

$$\langle\psi_i^a|H-E|\psi_j^b\rangle = \langle a|F^{ij}|b\rangle - (E-E_o)\delta_{ij}\,\delta_{ab} \tag{98}$$

On the first iteration $R_i^{a(1)} = T_i^a$. After collecting all terms, R_i^a on later iterations is

$$R_i^{a(n)} = T_i^a - (E-E_o)\,C_i^{a(n-1)} + \sum_{j,b} \langle a|F^{ij}|b\rangle\, C_j^{b(n-1)} \tag{99}$$

Thus, the iterative improvement in the singles expansion coefficients indicated by (95) is

$$C_i^{a(n+1)} = C_i^{a(n)} - \frac{1}{E_i^a} R_i^{a(n+1)} \tag{100}$$

Since ψ was held fixed when the singles were included, the effect of the singles on the doubly substituted configurations has been neglected; that is, the doubles were not relaxed to account for the effect of the singles. This effect is quite small and as discussed in Section IV will usually be negligible compared to the total correlation energy. However, it is worth noting this restriction, because in a conventional CI calculation the doubles are naturally fully relaxed with respect to all other configurations. Thus, the energy of a singles and doubles CI treatment will not be identical to the SCEP energy.

Pair Correlation Energies

Given the wavefunction of (26), the energy is obtained from the simple variational energy expression:

$$E = \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle \tag{101}$$

$$= E_o + \langle\psi|H-E_o|\psi\rangle/\langle\psi|\psi\rangle$$

$$= E_o + \{\langle\psi_o|H-E_o|\sum_P \psi_P\rangle + \langle\sum_P \psi_P|H-E_o|\psi\rangle\}/\langle\psi|\psi\rangle$$

$$= E_o + \sum_P \langle\psi_P|H-E_o|\psi_o + \psi\rangle/\langle\psi|\psi\rangle \tag{102}$$

We now define pair correlation energies, ε_P, as

$$\varepsilon_P = \langle\psi_P|H-E_o|\psi_o + \psi\rangle/\langle\psi|\psi\rangle \tag{103}$$

Then with (102) these are seen to be variationally additive:

$$E = E_o + \sum_P \varepsilon_P \tag{104}$$

The pair correlation energies in (103) are easily calculated with the external pair coefficient matrices and the operators used to improve the wavefunction. $\langle\psi|\psi\rangle$ is given by

$$\langle\psi|\psi\rangle = 1.0 + \sum_P \langle\underline{C}_P^{\dagger}\, S\, \underline{C}_P\, S\rangle \tag{105}$$

Calculating the total energy of the wavefunction including single configurations as given by (92)

$$E = \langle\psi_s|H|\psi_s\rangle / \langle\psi_s|\psi_s\rangle$$

$$= \{\langle\psi|H|\psi_s\rangle + \sum_{i,a} C_i^a \langle\psi_i^a|H|\psi_s\rangle\} / \{\langle\psi|\psi\rangle + \sum_{ia} C_i^{a^2}\} \tag{106}$$

$$E\langle\psi|\psi\rangle = \langle\psi|H|\psi_s\rangle + \sum_{ia} R_i^{a(\infty)} \tag{107}$$

At convergence, R_i^a is of course zero. Thus,

$$E\langle\psi|\psi\rangle = \langle\psi|H|\psi\rangle + \sum_{i,a} C_i^a \langle\psi|H|\psi_i^a\rangle \tag{108}$$

$$E = E_o + \sum_p \varepsilon_p + \sum_{ia} C_i^a T_i^a / \langle\psi|\psi\rangle \tag{109}$$

Pair correlation energies are somewhat useful quantitites since they give the correlation contribution of each individual pair of electrons. Such a detailed breakdown of correlation effects is likely to be as useful as an interpretative aid in understanding electronic structure as orbital energies are in SCF. The pair correlation energies obtained in SCEP are not unique to this method. From the discussions above concerning the relationship between CI configurations and the ψ_p functions, it should be obvious that one can collect up energy contributions using (103) and (25) and obtain the ε_p. The distinction between SCEP and CI is that SCEP gives pair correlation energies directly from its operator structure and, in fact, this is the only way the total energy is found. In addition, the pair correlation energies defined by (103) are unambiguous: they are always additive with the reference configuration energy to give the total energy. To maintain this unambiguity, CI calculated ε_p must follow (103) even though other redistributions of the contributions to the total energy are possible.

Improvement of the Orbitals

The method as described so far amounts to finding the best wavefunction in the space of a reference determinant and all double substitutions and then including singly substituted configurations. We term a calculation which follows the method through this point a "fixed-ψ_0" calculation, since no attempt has been made to find a better set of internal orbitals. However, since the representation of the wavefunction is directly in terms of basis functions, one would hope that not much additional effort would be required to determine the wavefunction after making some small improvement in the internal orbitals. In fact, the set of $\underline{C}_p$'s can be rotated to any new orbital basis and another set of iterations performed using the rotated $\underline{C}_p$'s as the starting point.

To improve the internal orbitals the singly substituted configurations are approximately absorbed into the reference configuration. After several such cycles, the orbitals would have the form where singly substituted configurations would have identically zero expansion coefficients in the wavefunction and the orbitals are termed Brueckner orbitals.[23-26] Some additional discussion is given in the appendix. Several schemes are possible for making an approximate absorption of the singles and the one which has been used exclusively to date is

$$|i'\rangle = |i\rangle + \frac{1}{\sqrt{2}} \sum_{a}^{\bar{}} C_i^a \quad |a\rangle \tag{110}$$

where $|i'\rangle$ are the new set of orbitals. Following (110), the new orbitals are symmetrically reorthogonalized in a three step procedure:

Löwdin's orthogonalization[27] method is applied to the internal orbitals, Schmidt orthogonalization is used to zero out the overlap of the externals with the internals, and finally the Löwdin procedure is applied to the externals.

Defining a rotation operator, R, as

$$R = \sum_t |t'\rangle \langle t|S \tag{111}$$

gives the $\underline{C}_p$ in the $|t'\rangle$ basis:

$$\underline{C}_p' = R\, \underline{C}_p\, R^{+} \tag{112}$$

Since the $\underline{C}_p$ are linear combinations of $\underline{C}_p^{ab}$ we can see how this rotation operator works by looking at one specific doubly substituted pair coefficient matrix.

$$\underline{C}_p^{ab'} = \{\sum_t |t'\rangle \langle t|S\} \, (2 + 2\delta_{ab})^{-1/2} \, [|a\rangle \langle b| + p|b\rangle \langle a|] \, \{\sum_r S|r\rangle \langle r'|\} \tag{113}$$

$$= (2 + 2\delta_{ab})^{-1/2} \sum_{t,r} |t'\rangle \{\langle t|S|a\rangle \langle b|S|r\rangle + p\langle t|S|b\rangle \langle a|S|r\rangle\} \langle r'| \tag{114}$$

$$= (2 + 2\delta_{ab})^{-1/2} \sum_{t,r} |t'\rangle \langle r'| \, (\delta_{ta}\delta_{br} + p\delta_{tb}\delta_{ar}) \tag{115}$$

$$= (2 + 2\delta_{ab})^{-1/2} \, [|a'\rangle \langle b'| + p|b'\rangle \langle a'|] \tag{116}$$

In (116) the pair coefficient matrix is formed from the new set of orbitals so that all orthogonality conditions used in SCEP are maintained. Looking at (113) to (116), one may realize that R can be used to rotate

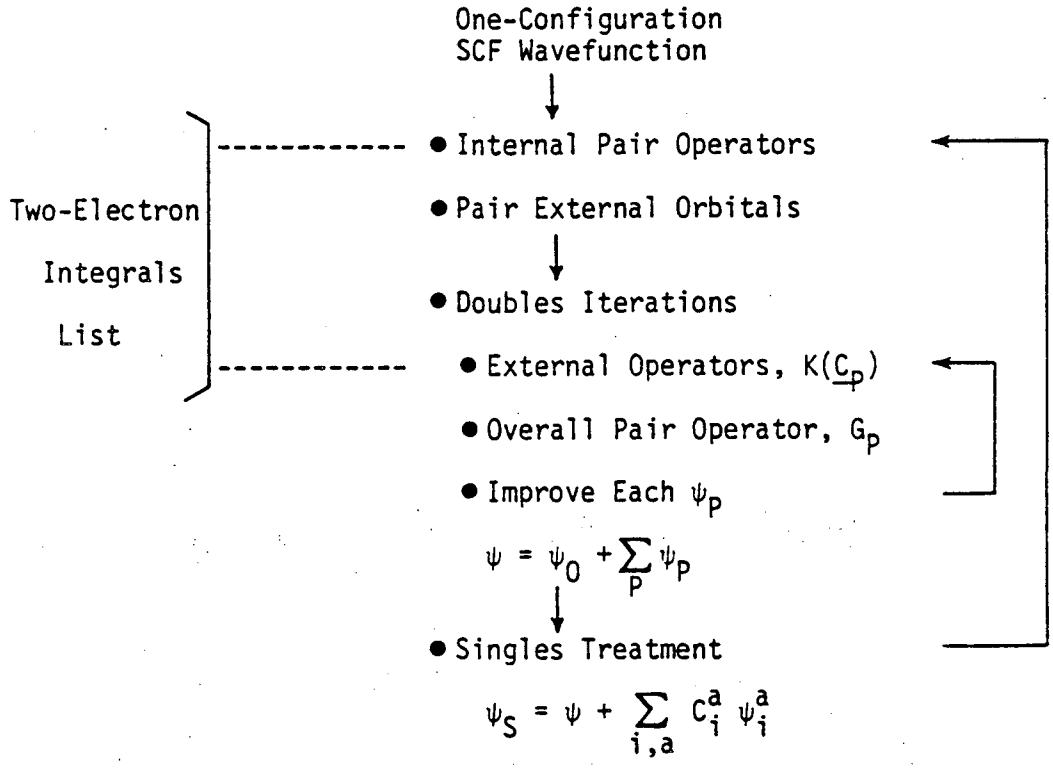
the $\underline{C}_p$'s determined at one molecular geometry to the orbital basis at another geometry so long as S is taken as the overlap matrix at the initial geometry.

The overall SCEP method, then, begins with a closed-shell reference determinant and a set of internal or occupied orbitals and external or virtual orbitals, presumably from an SCF calculation. Two sets of internal operators, J^{ij} and K^{ij}, are constructed for all internal pairs using the two-electron integrals list. With these operators, pair Fock operators, F_{PQ}, are defined. The diagonal pair Fock operators, F_{PP}, are used to select different sets of external orbitals for each internal pair. Sets of doubles iterations are performed with each iteration requiring the construction of the generalized external exchange operators, $K(\underline{C}_p)$. Improvement of the wavefunction is made by first-order perturbation and is performed for all substitutions from one pair at a time. Finally, the singly substituted configurations are included in the wavefunction. If desired the orbitals can be modified and the cycle repeated. Figure 3 is an outline of the method.

Figure 3.

The SCEP method involves several steps of constructing operators used to determine the wavefunction. At two points, the list of two-electron integrals is used to calculate some of the operators. Iterations are preformed for the doubly substituted configurations, following which the singles are included. The calculation can then be terminated, the "fixed-ψ_0" treatment, or the orbitals can be improved or otherwise modified and the procedure repeated.

SCEP



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The Density Matrix and Density Function

Calculation of one-electron properties,[5] such as the dipole moment or net atomic charges, is done with the first order reduced density matrix. In this section, some considerations of the general density function and density matrices of correlated wavefunctions are given along with expressions for the first order reduced density matrix in the SCEP formalism.

The density function, ρ, is defined in the following way

$$\rho = \psi\psi^* = |\psi|^2 = |\psi\rangle\langle\psi| \tag{117}$$

If ψ is given as a linear combination of some basis functions, Φ_i,

$$\psi = \sum_i C_i \Phi_i \tag{118}$$

then one may define a density matrix, D, as a representation of the density function in the following way:

$$\rho = (\sum_i C_i \Phi_i)(\sum_j C_j^* \Phi_j^*) \tag{119}$$

$$= \sum_{ij} C_i C_j^* \Phi_i \Phi_j^* \tag{120}$$

$$= \sum_{ij} D_{ij} \Phi_i \Phi_j^* \qquad \text{where } D_{ij} = C_i C_j^* \tag{121}$$

At this point, no information contained in the original wavefunction ψ has been lost in the density matrix because the N expansion coefficients, C_i, could easily be obtained from the N^2 elements of D in about the same

way CI-like expansion coefficients are obtained from an external pair coefficient matrix (57).

In a CI wavefunction (118) is the expansion over determinants so that the density matrix defined by (121) is also over determinants. The Slater determinants are products of orthonormal orbitals, ϕ_i, so that we could write

$$\rho = \sum_{ij} D_{ij} \rho_{ij} \tag{122}$$

$$\rho_{ij} = \Phi_i \Phi_j^* \tag{123}$$

We could then try to find a density matrix representation for (123); however, the product nature of each Φ_i means that such a density matrix will have 2N dimensions and N^{2N} elements where N is the number of occupied spin orbitals in the determinant. If we did find such matrices, which would be difficult but straightforward, the total density function, ρ, could be given directly in terms of orbitals, though the representation matrix would be quite large. One could continue and perform a simpler step of transforming this representation into the basis of the set of functions used to construct the orbitals. The point of this discussion is that we can represent the density function in a variety of bases and at no point is any information contained in ψ lost by the manipulations.

The density function and matrices considered above would be useful if there were some operator of interest which corresponded to an interaction among all particles in the system. Fortunately, most properties of interest involve interactions of one particle with another. Even the total energy involves interaction between no more than two

electrons with two other electrons. We thus seek to reduce the density function and density matrix by asking what is the probability function, not for N electrons as was done in (117), but for M electrons where M is less than N. The answer is to integrate over the coordinates of the N-M electrons[6] which reduces the dimensionality of the density matrix to 2(N-M). Each integration necessarily loses some of the information contained in the original ρ; that is, it is not possible to map unambiguously the reduced density function onto the wavefunction space.

For the first order reduced density matrix, ρ^1, N - M = 1. Since a Slater determinant is a sum of products, several integrations are necessary for all the cross products between the terms in the sum when calculating ρ^1. Fortunately, Slater-Condon rules can be applied yielding[10]

$$D^1_{ij} = 0 \quad \text{if } \Phi_i \text{ and } \Phi_j \text{ differ by more than one spin-orbital} \tag{124}$$

$$[D^1_{ij}]_{\alpha\beta} = \delta_{\alpha\beta}\,\delta_{ij} + \delta_{\alpha k}\,\delta_{\beta\ell}\,(1 - \delta_{ij}) \tag{125}$$

where D^1_{ij} is defined by the reduction to first order of (123):

$$\rho^1_{ij} = \sum_{\alpha\beta} \phi_\alpha\,\phi^*_\beta\,[D^1_{ij}]_{\alpha\beta} \tag{126}$$

This leaves

$$\rho^1 = \sum_{ij} D_{ij} \sum_{\alpha\beta} [D^1_{ij}]_{\alpha\beta}\,\phi_\alpha\,\phi^*_\beta \tag{127}$$

A useful simplification is to work in terms of orbitals (since we know the overall spin of the state) instead of spin-orbitals. Thus,

integrating over spins and labeling row and column indices by orbitals gives[10]

$$[D^1_{ij}]_{\alpha\beta} = 2\delta_{\alpha\beta}\,\delta_{ij} + (1 - \delta_{ij})\delta_{\alpha k}\,\delta_{\beta\ell} \tag{128}$$

If desired, we can define ρ^1 directly in terms of the basis functions used to construct the orbitals. Using (12)

$$\phi_\alpha\,\phi^*_\beta = \sum_r \sum_s W_{r\alpha}\,W_{s\beta}\,\chi_r\,\chi^*_s \tag{129}$$

$$= \sum_r \sum_s [D^{\alpha\beta,\chi}]_{rs}\,\chi_r\,\chi^*_s \tag{130}$$

where

$$[D^{\alpha\beta,\chi}]_{rs} = W_{r\alpha}\,W^*_{s\beta} \tag{131}$$

The final density matrix now becomes

$$\rho^1 = \sum_{ij} \sum_{\alpha\beta} \sum_{rs} D_{ij}\,[D^1_{ij}]_{\alpha\beta}\,[D^{\alpha\beta,\chi}]_{rs}\,\chi_r\,\chi^*_s \tag{132}$$

If the wavefunction were restricted to one closed shell determinant, an SCF wavefunction, expression (132) reduces to

$$\rho^1 = \sum_{rs} [D_o]_{rs}\,\chi_r\,\chi^*_s \tag{133}$$

where D_o was previously given by (21).

In SCEP, the wavefunction is given directly in terms of basis functions so we will be most interested in density matrices given in

terms of the basis functions. All that is necessary is to use (55) and rearrange the summation in (132) so that it is over electron pairs:

$$D = D_o + \sum_P \{\underline{D}_{PP} - \sum_Q D_{QP} \langle \underline{D}_{PQ} S \rangle / 2\} / \langle \psi | \psi \rangle \tag{134}$$

when only doubles are included in the wavefunction. $\underline{D}_{QP}$ is defined analogous to (70).

$$\underline{D}_{QP} = 2\, \underline{C}_Q\, S\, \underline{C}_P^{\dagger} \tag{135}$$

With singles included in the wavefunction, the first order reduced density matrix is:[28]

$$D_S = D + \sqrt{2}\,(D_1 + D_1^{\dagger}) + D_1^{\dagger} S D_1 - D_1 S D_1^{\dagger} + \sum_P [C_P^{\dagger} S D_1 S \underline{C}_P + \underline{C}_P^{\dagger} S D_1^{\dagger} S C_P] \tag{136}$$

where

$$D_1 \equiv \sum_{i,a} C_i^a\, |i\rangle \langle a|$$

The actual calculation of an SCEP first order density matrix is simple involving several matrix multiplications. Furthermore, as already mentioned and as will be discussed more fully in Section III, D_{QP} will always reduce to one or two terms. This and other reductions make the calculation of D or D_S quite fast computationally.

Computational Aspects

An important feature of any new calculational method is its dependence on the size of the problem. One might conceivably formulate some approach which is particularly fast for small systems but is limited in application because of the increase in effort with an increase in the size of the problem. In this section, a comparison will be made with conventional CI in order to demonstrate that SCEP is a generally efficient scheme but becomes even more advantageous than CI in larger problems.

There are two main types of operations in an SCEP calculation. The first is the processing of the two-electron integrals in setting up generalized Coulomb and exchange operators while the second is the collection of all matrix operations. If there are K basis functions in some given calculation there will be $I \leq K^4$ two-electron integrals. If there are N occupied orbitals, and $M = N^2$ electron pairs, then there will be M of the $K(\underline{C}_p)$ operators (on each iteration), $N(N + 1)/2$ of the K^{ij} operators and $N(N + 1)/2$ of the J^{ij} operators to construct. Since the external operators are either symmetric ($p = 1$) or antisymmetric ($p = -1$) then determining $K(\underline{C}_p)$ for $P=(ij,1)$ and $K(\underline{C}_Q)$ for $Q=(ij,-1)$ requires no more work than calculating one square exchange operator; since $\underline{C}_p$ and $\underline{C}_Q$, and the corresponding exchange operators, together have only K^2 unique elements. Therefore, only $N(N + 1)/2$ external exchange operators need to formed on each doubles iteration. We can now count the construction of K^{ij} and J^{ij} as an additional iteration since it has the same dependence

for integrals processing. Assuming a constant iteration number since we are always able to achieve convergence in seven iterations, we are left with an $I[N(N + 1)/2]$ dependence for operations involving the two-electron integrals. The analagous step in CI is transforming the integrals over basis functions to integrals over orbitals. The transformation is given by (30) which, if performed directly, requires K^8 multiplications. Of course, this transformation is normally done in steps, called quarter-transformations, which overall require about K^5 multiplications.[29]

As discussed in Section II, the SCEP calculation is performed one pair at a time; that is, G_p is set up for one pair and ψ_p is improved and then processing of the next pair begins. As a result, much of the computational effort is matrix multiplication, matrix addition, multiplication of a matrix by a constant and inputting and outputting a matrix to external storage. These processes are, respectively, K^3, K^2, K^2 and constant dependent processes and the number of times each process is performed increases with the number of pairs, M. In constructing G_p, there is an additional dependence on M because of inclusion of the F_{QP} operator sum. Hence, the dominant dependence from the matrix manipulations is as much as M^2K^3.

The M^2K^3 dependence can be reduced by looking at the individual F_{QP} operators and realizing that there are three possibilities: F_{QP} has all unique elements, or it is equal to a constant times the overlap matrix, or it is zero. Only in the first of these three cases is it necessary to perform a matrix multiplication in forming G_p. To see the non-trivial

types of F_{QP} operators we consider the D_{QP} matrices, for by (69) if $D_{QP} = 0$, F_{QP} will be one of the last two of the three possible cases, i.e. trivial. Expression (71) shows that D_{QP} will always be zero if P has no orbitals in common with Q. Table I provides reductions of (71) for all other cases and it can be seen that ~~for~~ all D_{QP}'s have two or fewer terms. ~~two additional cases D_{QP} is again zero~~. In Table I, it has been assumed that $P \leq Q$ since the D_{PQ} matrices from (70) are

$$D_{PQ} = pqD_{QP}^{\dagger} \tag{137}$$

With N as the number of occupied orbitals, a given orbital will occur in 2N-1 pairs. Hence, with the ij pair of electrons there can be no more than 4N-2 pairs which have less than two orbitals in common with ij. Thus, the method's dependence due to F_{QP} multiplications is not M^2K^3 but somewhat less than $4N(MK^3) = 4N^3K^3$. If one rigorously adds up all the multiplications which are required the result is:

$$R = (N^4 - N^2)/2 + N - \sum_{J=2}^{N-1}(2J^3 - 3J^2) \tag{138}$$

The summation in (138) cancels the N^4 dependence and Table II shows the reduction in effort implied by (138) for selected values of N. Large values of N are given to show that the N^3 dependence dominates, though slowly.

For comparison with CI we first count up the number of configurations. For K basis functions, there are the following number of configurations

$$N(N + 1)(K - N)(K - N + 1)/4 + N(N - 1)(K - N)(K - N - 1)/4 \tag{139}$$

Table I. D_{QP} Matrices.

$P = (ij,p)$			$\leq$	$Q = (kl,q)$			D_{QP}
$i \leq j$		p		$k \leq l$		q	
i	i	1		i	i	1	$2\,\lvert i\rangle\langle i\rvert$
i	i	1		i	j	1	$\sqrt{2}\,\lvert j\rangle\langle i\rvert$
i	i	1		i	j	-1	$-\sqrt{2}\,\lvert j\rangle\langle i\rvert$
i	j	1		i	j	1	$\lvert i\rangle\langle i\rvert + \lvert j\rangle\langle j\rvert$
i	j	1		i	j	-1	$\lvert i\rangle\langle i\rvert - \lvert j\rangle\langle j\rvert$
i	j	1		j	j	1	$\sqrt{2}\,\lvert j\rangle\langle i\rvert$
i	j	1		j	k	1	$\lvert k\rangle\langle i\rvert$
i	j	1		j	k	-1	$-\lvert k\rangle\langle i\rvert$
i	j	-1		i	j	-1	$\lvert i\rangle\langle i\rvert + \lvert j\rangle\langle j\rvert$
i	j	-1		j	j	1	$\sqrt{2}\,\lvert j\rangle\langle i\rvert$
i	j	-1		j	k	1	$\lvert k\rangle\langle i\rvert$
i	j	-1		j	k	-1	$-\lvert k\rangle\langle i\rvert$

Table II. Numbers of F_{QP} Operators.

Number of Orbitals N	Number of Pairs $M = N^2$	Unique F_{QP} Operators $M(M + 1)/2$	Non-trivial F_{QP} Operators R	R/N^3
1	1	1	1	1.0
2	4	10	8	1.0
3	9	45	35	1.296
4	16	136	93	1.453
5	25	325	194	1.552
6	36	666	350	1.620
7	49	1 225	573	1.671
8	64	2 080	875	1.709
9	81	3 321	1 268	1.739
10	100	5 050	1 764	1.764
12	144	10 440	3 113	1.802
14	196	19 306	5 018	1.829
16	256	32 896	7 575	1.849
18	324	52 650	10 880	1.866
20	400	80 200	15 029	1.879
25	625	195 625	29 724	1.902
30	900	405 450	51 794	1.918
40	1 600	1 280 800	124 059	1.938
50	2 500	3 126 250	243 824	1.951

where the first term is for internal (and external) electrons singlet coupled and the second term is for triplet coupling giving the total number of doubly substituted configurations with a closed shell reference determinant. Expression (139) can be summed to give an approximate number of configurations, $N^2(K-N)^2$. Construction of most of the CI matrix elements involves fetching one or two values from the transformed two-electron integrals list and while constructing some of the elements is more involved, on the average, setting up the CI matrix varies as the number of non-zero elements. Any two configurations which differ by two or fewerorbitals will have non-zero CI matrix elements. Considering the $N^2(K-N)^2$ configurations as $(K-N)^2$ substitutions from each of N^2 internal pairs, each configuration would have a CI matrix element with somewhat more than $(K-N)^2$ other configurations. As a result, the overall dependence is larger than $N^2(K-N)^4$ or roughly N^2K^4. Diagonalization of the CI matrix is at best dependent to the first power on the number of non-zero elements. Therefore, in CI the number of required operations increases as K^5 for the integrals transformation and N^2K^4 for remaining steps.

A comparison of CI and SCEP dependencies is summarized in Table III. To draw some conclusions from this comparison, we consider the increase in the number of operations when the number of electrons in the systems is increased and the number of basis functions increased proportionately to provide an equivalent description, i.e. fixed K to N ratio. From Table III, it can be seen that CI appears to be favored in comparing the dependencies of the increased effort with the larger problem.

Table III. Comparison of SCEP and CI. The dependence on K, the number of basis functions, and N, the number of occupied orbitals, is given using a, b, c, d and e, as constants.

	SCEP	CI	
Coulomb and Exchange Operators	$\frac{1}{2}N(N+1)K^4$	K^5	Integrals Transformation
Process Pairs:			
Multiply F_{QP}'s	N^3K^3	N^2K^4	Construct CI Matrix
Other Multiplies	N^2K^3		
Matrix Addition, etc.	N^2K^2		
Input/Output	N^2		
TOTAL DEPENDENCE			
	$aN^2K^4 + bN^3K^3 + cN^2K^3 + dN^2K^2 + e$	$aK^5 + bN^2K^4$	
FIXED $\frac{K}{N}$ DEPENDENCE			
	aK^6	$aK^5 + bK^6$	
FIXED N DEPENDENCE			
	$aK^4 + bK^3$	$aK^5 + bK^4$	

Alternatively, we could fix the number of electrons and argue that SCEP seems preferable in going to a larger problem, where larger problem now means a bigger basis set. Taken together, these two ways of comparing SCEP and CI indicate that for some given N there will be a cut-off number of basis functions, K_N, at which SCEP will be more efficient for larger basis sets and CI will be more efficient for smaller sets. Our experience with the still preliminary version of the SCEP computer program suggests that for small molecular systems, say N up to 5, K_N seems to be at about double-zeta size and seems more efficient than CI for extended basis sets. K_N will probably increase slowly with N but on the basis of this experience, the SCEP line in Figure 2 was drawn. Whatever the precise cut-offs are, it is clear that at some point SCEP is the desirable approach if one is interested in using larger and larger basis sets to provide increasingly better descriptions of a molecule's electronic structure.

Calculation of the First Order Reduced Density Matrix

Calculation of the density matrices in (134) or (136) involves double summations over electron pairs. Furthermore, the terms in the sums require several matrix multiplications as in (135). Thus, at first glance, calculation of D might appear to be quite time consuming. In fact, though it is not "instantaneous", it can be made reasonable. Looking at (134) specifically, we use Table I to remove all zero-valued D_{QP}'s and thus, as with the F_{QP} operators reduce the effort by a factor of N. A reduction by a factor of two can be realized by noting that $< \underline{D}_{PQ}S >$ will be zero if $p \neq q$. For example, with $\underline{C}_p = \underline{C}_p^{ab}$ and $\underline{C}_Q = \underline{C}_Q^{cd}$, (135) gives

$$\underline{D}_{QP} = [(1+\delta_{ab})(1+\delta_{cd})]^{-\frac{1}{2}}[|c><d|+q|d><c|]\ S \qquad (140)$$

$$[p|a><b|+|b><a|]$$

$$< \underline{D}_{QP}S> = [(1+\delta_{ab})(1+\delta_{cd})]^{-\frac{1}{2}}\ [p\ <d|S|a><b|S|c>+q<d|S|a><b|S|c>$$

$$+pq<c|S|a><b|S|d>+<c|S|a><b|S|d>\ ]$$

$$= [(1+\delta_{ab})(1+\delta_{cd})]^{-\frac{1}{2}}[(p+q)<d|S|a><b|S|c> \qquad (141)$$

$$+p(p+q)<c|S|a><b|S|d>]$$

$$= 0 \quad \text{if} \quad p+q = 0.$$

The next step is to take the list of external pair coefficient matrices, $\underline{C}_p$, and multiply each times the overlap matrix and store the result. This requires $M\ K^3$ operations. However, when this is done,

calculation of the non-zero $< \underline{D}_{QP} S >$ is just a K^2 process which is relatively unimportant. All the remaining operations consist of matrix addition or multiplying a matrix by a constant, again both K^2 processes. Thus, $M K^3$ is the dominant dependence in determining D with some additional effort required to find D_S. This reduction in effort is quite nice, since brute force application of (134) would give an M^2K^3 dependence and the calculation of D could easily approach an iteration time.

Selected Chemical Applications

Small systems with less than ten basis functions were typically used in testing the SCEP computer program as it was being developed, but when the program appeared to working reasonably well at all stages, the interest turned to testing the method both with respect to the quality of the wavefunction and the computational features of the method, such as speed and size limits. Two cases used to test the method were water and methylene and results are given in Tables IV and V.

In comparison with CI results, the water calculations using a 35 function basis set were within 4×10^{-5} au of the CI results. This small difference, again, is due to the effect of the singles on the doubles which are not relaxed when the singles are included in the wavefunction. The same value could be achieved by diagonalizing a CI matrix which includes the reference configuration and double substitutions and then diagonalizing a smaller CI matrix which includes the total wavefunction from the first diagonalization and the singly substituted configurations. Measured as a percentage of the correlation energy, this neglected effect is very small.

Several methylene calculations were performed with basis sets up to 42 functions. The set of methylene calculations with different basis sets gave some interesting comparisons in pair correlation energies.[22] The reason for this seems to be that the improvement in using larger basis sets can give a relatively better improvement in the correlated description of one pair of electrons over another. This suggests that examination of pair correlation energies could well be

Table IV. Fixed-ψ_0 Water Molecule Calculations.

	Energy (CI)	Energy (SCEP)	Correlation Energy Difference[a]	Configurations[b] C_{2v}	Configurations[b] C_1	Percent of Correlation[c] Valence	Percent of Correlation[c] Total
14 Functions, Frozen Core[d]	-	-76.135 310	-	224	703	41.2	
14 Functions[d]	-	-76.148 067	-	451	1081		37.5
35 Functions, Frozen Core[c]	-76.278 910	-76.278 870	0.018%	2032	7381	74.6	
35 Functions[c]	-76.297 392	-76.297 354	0.015%	3238	11476		66.7
50 Functions, Frozen Core[c]	-	-76.284 370	-	4631	16471	75.8	

[a] The difference is relative to a conventional CI result and measures the effect of the singly substituted configurations on the doubly substituted configurations. It has been calculated by taking the difference of the CI and SCEP results and giving that as a percentage of the correlation energy obtained in the CI calculation.

[b] The number of configurations is the number required to obtain an equivalent CI result. The

Table IV continued.

C_1 or no symmetry configurations are of interest since the current SCEP program does not take advantage of symmetry.

[c] The CI results for 35 basis functions and the estimates of total and valence correlation energy are from Rosenberg and Shavitt[30] and the same set of functions and molecular geometry were used here. The 35 function set was completely uncontracted to yield the 50 function set. The SCF energy obtained with this basis was -76.052394 compared with the 35 function SCF energy of -76.050698.

[d] A double zeta basis[31] was used with the geometry given by Bender and Schaefer.[32]

Table V. Fixed-ψ_0 Methylene Calculations.

Basis Set[a]-	A	A[b]	B[b]	C[b]
SCF Energy	-38.86153	-38.86153	-38.88979	-38.89239
Sum of Pair Energies	-0.09480	-0.08214	-0.13570	-0.14635
Singles Contribution	-0.00022	-0.00022	-0.00092	-0.00088
Correlation Energy	-0.09502	-0.08237	-0.13661	-0.14723
Total Energy	-38.95655	-38.94390	-39.02640	-39.03962

[a] Set A is a 14 basis function double zeta set of Dunning[31] contracted functions. Set B used a much larger basis set of 32 contracted functions as in the calculations of Bender, Schaefer and McLaughlin.[33] Set C consisted of 42 functions. Huzinaga's[34] (10s 6p) carbon basis and (5s) hydrogen basis were contracted to (6s 4p) and (3s), respectively, using Dunning's scheme.[35] A scale factor of 1.49 was used for hydrogen and a set of hydrogen p functions with exponent 1.0 was added. Carbon d functions with exponents 1.3088 and 0.38768 were included as in the calculations of Bender et al.[36] A 1.11 Å bond length and 102.4° bond angle were used. The last column, to our knowledge, is the largest methylene calculation yet performed and gives a lower energy than the previous best singlet methylene energy of Pakiari et al.[37]

[b] Frozen core ($1a_1$ orbital).

useful in the selection of basis sets. Indeed, if one finds a dominant correlation effect localized in one or two electron pairs, one could justifiably improve the basis set with just a few additional functions selected for the one or two pairs.

Methylene with 42 basis functions represented a fairly large calculation especially considering that it was carried out on a Harris 100 mini-computer with 32K of 48-bit words. This calculation would require that over 2900 configurations be included in an equivalent CI calculation. The out-of-core storage and computer memory for such a CI calculation begin to touch the limits of the system, while SCEP handles the problem routinely. Indeed, remembering that symmetry has not yet been included into the SCEP calculational approach, this methylene calculation really involved over 6000 configurations (C_1 symmetry). To establish further the potential for the new method, the water calculations with the 35 and 50 function sets were performed. Water has two more electrons than methylene and thus, the number of configurations in a singles and doubles configuration expansion is larger for a given size basis set than in methylene. The largest water calculation would require 4631 symmetry adapted configurations and over 16,000 in no symmetry. The apparent practical limits for CI on the Harris 100 are 48 functions and around 9000 configurations or determinants. Furthermore, the water calculation does not represent the SCEP limit, just the largest performed. With the current program version which keeps six square arrays in core at any one time, the basis function limit on the Harris 100 is 56. But the method only requires about 3½ arrays in core for the necessary manipulations and

therefore, the limit could be raised to 67. And of course, with only operators being kept in core, there is no limit on the number of configurations. The computation times for the water calculations with the large basis sets were about 2 hours for the first 35 function calculation, 4 hours for the next, and 6 hours for 50 functions. These were done with a still preliminary program version which had some notable inefficiencies that become important with increasing numbers of electrons. More recently, the 42 function methylene calculation was found to require 75 minutes and the 32 function calculation 35 minutes. Relative to the other steps in the calculation, finding integrals and an SCF wavefunction, obtaining a correlated wavefunction with SCEP in these cases is not too expensive.

Convergence

The efficiency of the method can be completely lost if convergence is poor. As a consequence, test calculations were made on several differing systems to test convergence. The first such system was the diatomic LiH. A basis set of 30 functions was used and it was found that five doubles iterations were required for convergence (to 10^{-6} au) in the fixed-ψ_0 treatment as shown in Table VI. The calculation through this point required under nine minutes of execution time on the Harris 100 which is reasonable in comparison with SCF times (about one-fourth the time for a like number of iterations). Convergence in so few iterations in LiH is the result of the small interaction between pairs of electrons. The structure of the molecule may be described as Li^+H^- which corresponds to two spatially removed pairs. This small interaction means self-consistency is easy to achieve, especially with the optimally selected sets of external orbitals.

Calculations on systems where electron pairs were interacting were not as successful. Simple water calculations required up to nine doubles iterations with any basis set; and double zeta calculations on acetylene and formaldehyde required even more. From this, several refinements in the iteration scheme were developed. The earliest such refinement involved using an estimate for the correlation energy in the (H-E) operator on the second iteration. On each iteration, the pair coefficient matrices are improved, but on the first iteration, the initial matrices are zero-valued so there is no correlation energy calculated in the first iteration. The energy for the wavefunction

Table VI. Convergence of the LiH Calculation.[a] In this calculation, the sets of doubles iterations have each been carried to the same convergence limit to show the nature of the iterative approach. However, the same final result is obtained by using larger limit for all but the last set(s) of iterations. Thus, with a limit of 10^{-3} au for the first set and 10^{-5} for the second set, several iterations can be saved.

Doubles Iteration	Energy	Energy Change	$\langle\psi\|\psi\rangle$	Variance[b]
1[c]	-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	-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	-8.039 459 3	-0.000 016 4		
10	-8.039 457 7	+0.000 001 6	1.024 685	0.000 003 8

Table VI continued.

Doubles Iteration	Energy	Energy Change	$\langle\psi\|\psi\rangle$	Variance
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	-8.039 463 0	-0.000 001 7		
13	-8.039 463 0	0.0	1.025 058	0.0

[a] The LiH basis set consisted of 30 uncontracted function. Huzinaga's[34] Li (10s) and H (5s) sets were used along with a Li (4p) set of Williams[38] and a set of H p functions with exponent of 1.0. The internuclear distance was 3.015 bohrs.

[b] The variance is the sum, for each (P,ab), of the square of T_P^{ab} divided by E_P^{ab}. It represents the sum of the squares of the changes in configuration expansion coefficients.

[c] The first iteration requires substantially less computational effort than following iterations since $\underline{C}_P = 0$ and matrix elements are calculated only with ψ_0. The energy through this iteration is just the SCF energy.

produced in the first iteration is only calculated in the second iteration. However, using the reference determinant's energy, E_0, in constructing (H-E) pair operators would displace the operator by an amount equal to the correlation energy. Not surprisingly, then, it was found that convergence was aided by making a guess of the correlation energy during the first iteration and using this in (H-E) on the second. This guess is the energy improvement according to first order perturbation theory, i.e. the sum of $-(T_p^{ab})^2/E_p^{ab}$. In practice, this estimate is most often too large and thus, is scaled down by a factor of 0.6. It is possible to include such an estimate in later iterations, but this was found to be of little value.

The estimate of the correlation energy for use in the second iteration's set of pair operators could, of course, affect convergence by no more than one iteration, since after the second iteration a true variational correlation energy would have been calculated for use in (H-E). Thus, there were other problems in the iterative scheme and these seemed to be in the choice of the energy denominators, E_p^{ab}. In general, it seemed that these denominators were too small and actual oscillations in the value of $<\psi|\psi>$ could be seen between iterations. Two weighting approaches were tried, the first of which was to multiply the energy denominators by some factor greater than 1.0. However, while this did have an effect, it was not the best approach since some of the E_p^{ab} were already large numbers and making them larger by the same factor as the samll E_p^{ab}'s delayed convergence. Obviously, an additive constant might be more useful. Hence, tests were made where each energy denominator was increased by some constant, say 0.2.

This helped convergence in difficult cases and reduced to seven the number of iterations required for water. But in going from one molecule to another, it seemed that new experience was needed to select the best additive constant.

After quite a few test cases, it became apparent that the best choise of an additive constant was what the final correlation energy turned out to be. Looking at (91) shows that the E_p^{ab}'s change from one iteration to the next only by the calculated correlation energy. Once again, on the first iteration this was zero making the E_p^{ab}'s smaller than their final values. With this realization, the final working scheme is to use an additive constant on the first and second iterations roughly approximating the anticipated correlation energy. Then, on later iterations, this additive constant is scaled down proportionately to the correlation energy which is now being included in each E_p^{ab}. With this technique, we have been able to achieve convergence of the doubles for all test cases in seven or fewer iterations (to 10^{-6} au). The water calculation shown in Table VII, for instance, required seven iterations and the 42 basis function methylene calculation mentioned above required six iterations.

Table VI also shows convergence of the absorbed singles procedure for which LiH is not a very good case. Typically, though, the change in the orbitals in satisfying the Brueckner condition (see appendix) is small. Thus, the pair coefficient matrices are little changed after the orbitals are modified so that only two doubles iterations might then be required. The number of orbital improvements to reduce

Table VII. Convergence in an H_2O Calculation.[a]

Doubles Iteration	Energy	$\langle\psi\|\psi\rangle$	Diagonal Pair Energies[b] $(2a_1\ 2a_1)$	$(1b_2\ 1b_2)$	$(3a_1\ 3a_1)$	$(1b_1\ 1b_1)$
1	-76.050 698 1	1.0	0.0	0.0	0.0	0.0
2	-76.263 503 4	1.080 820	-0.009 732	-0.020 573	-0.019 390	-0.019 205
3	-76.277 002 8	1.051 512	-0.010 364	-0.022 042	-0.020 650	-0.020 458
4	-76.277 607 8	1.057 179	-0.010 306	-0.022 028	-0.020 625	-0.020 449
5	-76.277 681 4	1.055 051	-0.010 342	-0.022 076	-0.020 663	-0.020 482
6	-76.277 686 9	1.055 595	-0.010 335	-0.022 069	-0.020 657	-0.020 476
7	-76.277 687 4	1.055 440	-0.010 338	-0.022 073	-0.020 660	-0.020 478
Singles	-76.278 869 8					

[a] Fixed-ψ_0 calculation as in the third line of Table IV.

[b] The $1a_1$ orbital was frozen to substitution so there were 16 pairs, with the occupancy $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$.

the singles contribution to the total energy to less than 10^{-6} au is usually two, so that three sets of doubles iterations are needed. Realizing that full convergence is not necessary in the first two sets of doubles iterations, a calculation where the singly substituted configurations are fully absorbed should not require more than about twice the amount of computation needed to obtain the fixed-ψ_0 result.

In Table VIII are given the iteration results for a calculation on the BH molecule. Unlike LiH, the electron pairs in BH are interacting so it is interesting to consider not only stability of the energy in the iterative improvement of the wavefunction, but also the stability of the wavefunction itself. The dipole moment provides some measure of the variations of the wavefunction since it is dependent on the first order density matrix. As seen in Table VIII, changes in the dipole moment become small after the fifth iteration as do changes in the energy. Inclusion of the singly substituted configurations, of course, dramatically changes the first order reduced density matrix and thus, can be quite important in one electron properties such as the dipole moment. The important conclusion is that the iterative part of SCEP can converge to stable and hence, accurate properties which is not always the case even in one-configuration SCF.

Table VIII. Convergence in a Fixed-ψ_0 BH Calculation[a]

Doubles Iteration	Energy	Dipole Moment (Debyes)
1[b]	-25.108 641	1.6218
2	-25.201 502	1.6018
3	-25.204 211	1.6195
4	-25.204 298	1.6146
5	-25.204 312	1.6180
6	-25.204 314	1.6173
7	-25.204 315	1.6178
Singles	-25.205 002	1.4425

[a] The internuclear difference was 2.33 bohrs and a basis set of 19 functions[39] was used.

[b] The first itereation energy and dipole moment are the SCF results.

The Be_4 Cluster

The aim of recent studies[40-42] on beryllium atom clusters has been to provide an understanding of catalysis at a molecular level. An important consideration in such studies is the rate at which the properties of the clusters approach those of the bulk metal surface. One measure of how well small clusters model a large surface is the difference between the dissociation energy per atom and the atomic cohesive energy of the bulk. SCF wavefunctions have been used almost exclusively to study the chemisorption of atomic hydrogen on beryllium clusters[42] since correlated wavefunctions for systems up to the largest studied, Be_{36}, would be immensely difficult simply because of the size of the problem. However, it has been predicted[41] that the SCF wavefunctions may be quite reasonable for the properties being studied. In the case of the cluster dissociation energy one might at first expect that correlation effects would increase the dissociation energy since there is greater electron correlation in the cluster than in the separated atoms. However, a one-configuration SCF wavefunction provides a balancing effect since in the dissociated limit it allows only $1s^2 2s^2$ atomic occupancies. In the cluster, p functions contribute substantially yielding roughly sp hybridization. The p orbitals in the Be atom are very near in energy with the valence s orbitals and thus, a two-configuration wavefunction is most appropriate for the atom.[43-44] Restricting the atom's wavefunction to one configuration may balance the neglect of correlation effects in the cluster.

Since Be_4 was previously used to study basis set effects[41] in Be_n

clusters, it was an obvious choice for studying correlation effects with SCEP to check the assertion that SCF wavefunctions adequately, if not fortuitously, can give correct cluster dissociation energies. A contracted basis set (9s/5s) of gaussian functions optimized for the atom by van Duijneveldt[45] was used along with a (4p/2p) basis of Yarkony et al.[46] In Table IX are given the results of the calculations. The internuclear separation was optimized both for SCF and SCEP. In addition to these calculations, SCEP/CEPA-2 calculations were performed. CEPA-2 (Coupled Electron Pair Approximation[47]) is a non-variational treatment which approximately includes effects of triply and quadruply substituted configurations. CEPA-2 calculations using the SCEP method require no more effort than variational SCEP calculations.[48] The results given in Table IX required about seven hours each and are equivalent to CI expansion including up to several thousand configurations. Except for CEPA-2 calculations, convergence was achieved in seven iterations. The SCF dissociation energy is only 1.6 kcals below the SCEP energy and the CEPA-2 results suggest that inclusion of higher order substituted configurations would slightly lower the SCEP result, because of the more accurate description at the dissociation limit, making it even closer to the SCF value.

Given in Table X are selected pair correlation energies for the tetrahedral Be_4 cluster. The interpretative value of pair energies is seen by the change in the correlation contribution of electron pairs including the $2a_1$ electrons. Correlation effects are not quite as important in these orbitals because of the sp hybridization in the

Table IX. Tetrahedral Be_4. Energies are given in au unless otherwise indicated.

Geometry	R_{Be-Be}	E(SCF)	E(SCEP)	Correlation Energy	E(CEPA)
SCF Optimum	2.096 Å	-58.34322	-58.48923	-0.14601	-
SCEP Optimum	2.114 Å	-58.34310	-58.48934	-0.14624	-58.51884
Separated Atoms	∞	-58.28915	-58.43270	-0.14355	-58.46619
ΔE ($Be_4 \rightarrow 4Be$) in kcal/mole		33.9	35.5		33.0

Table X. Pair energies, ε_p, in a.u. for Be_4 at its determined equilibrium geometry and separated atom limit.

Pair = (i j, p)[a]	R = 2.114 Angstroms	R = 100 Bohrs[b]
$2a_1$ $2a_1$ 1	-0.0059	-0.0357
$2a_1$ $2t_2$ 1	-0.0066	0.0
$2a_1$ $2t_2$ -1	-0.0036	0.0
$2t_2$ $2t_2$ 1	-0.0164	-0.0357
Singles Contribution	-0.0021	-0.0009
Total Correlation Energy	-0.1463	-0.1435

[a] These pair energies are the sum over the three components of the degenerate t orbitals divided by three to give the energy per actual pair of electrons, the first pair excepted, of course.

[b] Localized orbitals were used at 100 bohrs (see ref. 48).

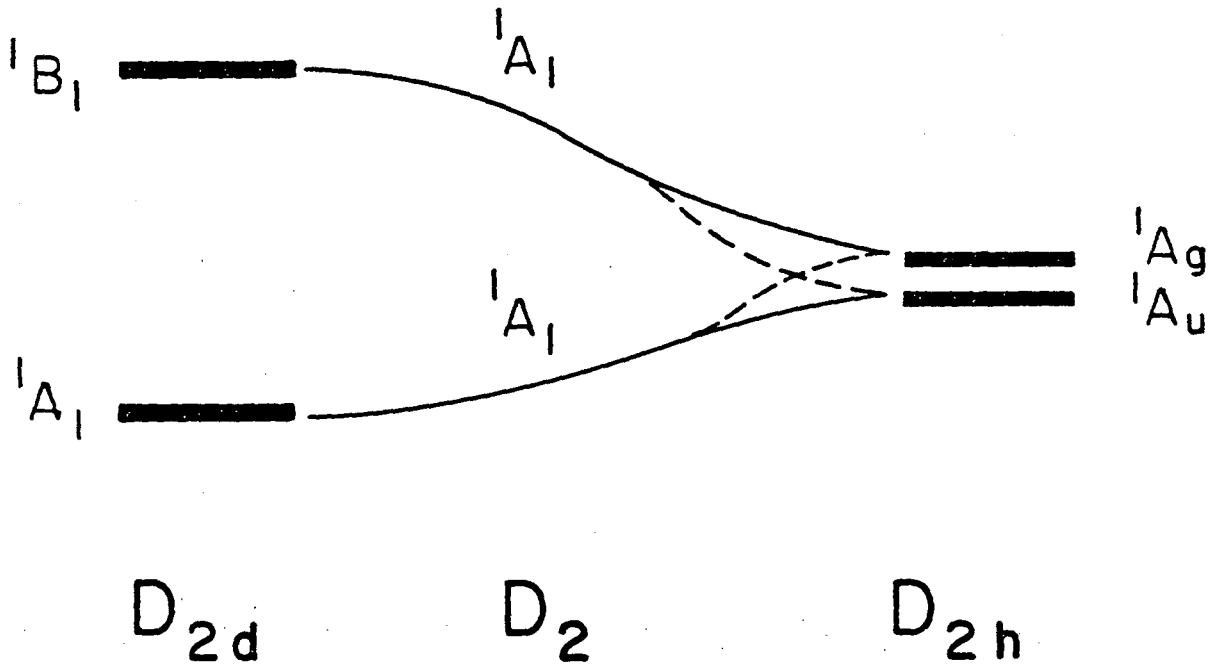
cluster. In the separated atoms, correlation effects from $2a_1$ electrons increase to that of the now degenerate t orbital electrons. Hence the balancing of correlation effects which makes SCF a reasonable way to study the Be_n clusters is seen to be due to a balancing of correlation effects from different electron pairs.

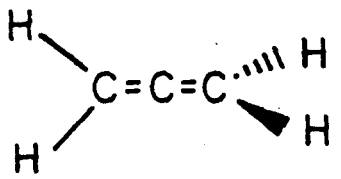
Allene

Allene is somewhat important as a representative calculation for SCEP because it is of the size of other small organic molecules which we have studied[11,49-51] exclusively with SCF methods, but where correlation effects are certainly important in placing excited states energetically accurately and describing them structurally. The problem of interest in allene was the internal rotation potential for the ground state since previous SCF studies[52-53] have predicted that the D_{2d} symmetry closed shell ground state correlates with an open shell D_{2h} planar state and thus that the D_{2h} closed shell is an excited state. A double-zeta basis set of Dunning[31] contracted gaussian functions were used and geometries for closed shell and planar open shell states were optimized with SCF. SCEP calculations were then performed for the planar and non-planar closed shell states. It was thought that correlation effects in the planar form, if greater than the non-planar form, could place the closed shell state as the lowest state (see Figure 4). However, as the results in Table XI show, correlation effects do just the reverse: the separation between the two closed shells is greater than predicted by SCF by up to 10%. To understand this, increasing numbers of lower-lying electrons were frozen to substitution in the calculations in Table XI. Then comparing pair energies shows that the $1b_{3g}$ electrons in the planar form contribute much less correlation energy than the 2e (D_{2d}) electrons. The 2e orbital correlates by symmetry with a $1b_{3g}$ and a $1b_{2u}$ planar orbitals. The $1b_{2u}$ electrons do not change substantially in their

Figure 4.

Qualitative representation of the correlation of the lowest electronic states between the planar (D_{2h}) and non-planar (D_{2d}) structures of allene. The dotted line shows the avoided crossing.





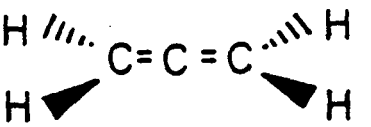


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Table XI. Correlation Effects in Allene Closed Shell States.

	Frozen Orbitals[a]	Electron Pairs[a]	$^1A_1$ Energy (au) D_{2d} - 90°	^1A_g Energy (au) D_{2h} - Planar	Difference (kcal)
SCF			-115.8303	-115.7195	69.5
SCEP	9	4	-115.8884	-115.7651	77.4
SCEP	7	16	-115.9394	-115.8165	77.1
SCEP	6	25	-115.9739	-115.8524	76.2

[a] Orbitals were frozen to substitution in SCEP on the basis of orbital energies. In the D_{2d} structure, the degenerate e orbitals have been counted as two to compare with the D_{2h} wavefunctions where no orbital is occupied by more than two electrons. The number of pairs is the number from which substitutions have been included.

correlation contribution. This probably suggests a more delocalized structure for the $1b_{3g}$ orbital than the 2e or $1b_{2u}$ orbitals.[54]

Summary and Outlook

The method of self-consistent electron pairs represents a new and certainly clever approach to the electron correlation problem. Constructing an operator formalism which makes possible pair by pair improvement in the wavefunction is in itself quite nice. But the SCEP approach seems truly impressive because it produces operators which collect up all the information contained in a variety of types of Hamiltonian matrix elements and is used without relying on any complicated logic scheme to handle all the types of elements. Furthermore, SCEP is general enough to work with non-orthogonal basis sets and even non-orthogonal sets of externals. All this is made possible by restricting the wavefunction to a configuration space of single and double substitutions, but within this restriction, SCEP poses as a radically new concept in electronic structure.

The work described here is primarily implementation of the theory along with some refinements, computational tests using the method and the demonstration of SCEP as a viable approach. What has been presented, then, are the detailed expressions used in actually working with self-consistent electron pairs and, where derivations have not been given, representative examples of how the SCEP operator formalism functions. Finally, a careful breakdown of the operations at a level important to computation was developed, and then calculations on real chemical systems were given. The intended conclusions to be drawn from this are the following advantages and limitations of SCEP.

1. The wavefunction is given directly in terms of basis functions rather than orbitals, as in CI. This has important implications, the most obvious of which is that an explicit transformation of the two-electron integrals from basis functions to orbitals, a potentially expensive operation, is avoided. Furthermore, the representation of the wavefunction by external pair coefficient matrices allows one to improve the orbitals in any desired way, or even go to a different geometry with different orbitals, with less than the expense of a whole new calculation, as would be the case for CI. All that is required is to rotate trivially the coefficient matrices and begin the iterations. The representation also makes calculation of the first order reduced density matrix quite easy, and as Meyer[21] has shown, the second order reduced density matrix can also be obtianed directly. As a result, the highly effective Gradient Method of Pulay[55] which requires the second order density matrix can be applied to a correlated wavefunction.

2. Pair contributions to the total energy are conveniently obtained in SCEP and while this is not unique to SCEP, the pair correlation energies are of definite interpretative value.

3. Different sets of external orbitals can be used for different internal pairs and these externals can be chosen to improve convergence, which is important to any iterative method.

4. The amount of computer core required for an SCEP calculation is

small compared to that required for an equivalent CI calculation. This is, of course, a direct result of the operator formulation of SCEP. At any one time in an SCEP calculation all the required information is contained in a few small arrays, either operators or coefficient matrices. Thus, the basis function limit for a given amount of computer core can be quite large, even approaching the limits of one-configuration SCF calculations (which also require just a few arrays). Quite important is that an explicit configuration list is not used in SCEP; the singly and doubly substituted configurations are implicitly defined by the method. This has an attractive consequence: there is no configuration limit in SCEP. That is, if some number of singles and doubles configurations can be defined for a given system with a certain number of basis functions, then the calculation can be performed spanning the whole space of the set of configurations provided only that the number of basis functions is within the computer core imposed limit. (For the Harris 100 mini-computer, the programs' current basis function limit is 56 with 67 possible. The maximum number of configurations for a given basis set size would occur when the number of occupied orbitals is about half the number of functions. Thus, it would be possible with this small scale computer system to do calculations including over 600,000 configurations with the current function limit and over one million with a function limit of 67. Of course, external storage of operators could at some point limit this.) In general, this can not be said of any CI method.

5. The method shows computational efficiency and the increase in effort for larger basis sets, and hence, more accurate descriptions, is less than conventional CI.

6. The method's notable limitations are that it is defined for singly and doubly substituted configurations and is restricted to systems dominated by a closed shell determinant.

The first five points indicate that SCEP is an important method and that future theoretical work is needed to overcome the limitations in the last point. Features which can be included in the near term are the incorporation of symmetry transformations which would reduce the computational effort in symmetrical systems and integrating the Gradient Method with SCEP. Overcoming SCEP's limitations is far from impossible. All that is needed to describe systems dominated by open-shell configurations is a set of somewhat more complicated operators. One could also extend the operator formalism so as to include single and double substitutions from more than one reference configuration and this would mean that the effects of higher order substituted configurations could be accounted for accurately. Therefore, it seems that SCEP is a highly workable, efficient approach to the correlation problem which has closed shells as its immediate area of application and its extension to a larger class of systems anticipated.

Appendix: Brillouin and Brueckner Conditions

The many-body theory developed by Brueckner[23-26,56-58] leads to a criterion, termed the Brueckner condition, for selecting an orbital basis for a wavefunction expanded over configurations and determined variationally or perturbatively. The Brueckner condition has a very simple form:

$$C_i^a = 0 \tag{A1}$$

where C_i^a is the expansion coefficient of the singly substituted configuration ψ_i^a. The intention of the Brueckner condition is that selecting orbitals where the single substitutions vanish will yield the lowest, or nearly lowest energy. However, Nesbet[59] tends to refute this notion, though isolating cases where using the Brueckner condition can yield the lowest energy wavefunction. But, as Nesbet has carefully demonstrated, the Brueckner condition can not, in general, be proven to be equivalent with the condition for the minimization of the energy of the wavefunction by variation of the orbitals, and therefore, the usefulness of the Brueckner condition may need to be decided rather empirically. Since Nesbet's work there has been no abundance of molecular calculations which sought to determine Brueckner orbitals. Indeed, it is quite likely that work discussed here includes the first calculations where the Brueckner condition was fully satisfied in a molecular system. The ease with which orbitals may be modified in SCEP suggested some examination of the Brueckner condition.

For a given wavefunction ψ the condition for minimization of the

energy is that the change in energy with first order variations in the wavefunction is zero. Let us define an incremental change in the wavefunction using a parameter, ε.

$$\delta\psi = \psi' \, \delta\varepsilon \tag{A2}$$

where ψ' is orthogonal with ψ. Then using the variational energy expression for a normalized wavefunction gives

$$E + \delta E = \langle \psi + \delta\psi | H | \psi + \delta\psi \rangle / \langle \psi + \delta\psi | \psi + \delta\psi \rangle \tag{A3}$$

$$\delta E = 2 \langle \delta\psi | H | \psi \rangle + \langle \delta\psi | H | \delta\psi \rangle - E \langle \delta\psi | \delta\psi \rangle / (1 + \langle \delta\psi | \delta\psi \rangle) \tag{A4}$$

Thus, to minimize the total energy, $dE/d\varepsilon = 0$.

$$dE/d\varepsilon = 2 \langle \psi' | H | \psi \rangle = 0 \tag{A5}$$

An equivalent approach was given in (59) to (62) and the general result where ψ' is not restricted to be orthogonal with ψ is

$$\langle \psi' | H - E | \psi \rangle = 0 \tag{A6}$$

If ψ is a configuration expansion the variations $\delta\psi$ can be variations in the expansion coefficients, as in (59), or variations in the orbitals. Assuming that the expansion coefficients are optimally determined or at least fixed, the variations in the orbitals have the following linked form.

$$\delta\psi: \qquad \delta\phi_i = \phi_a \, \delta\varepsilon \quad \text{and} \quad \delta\phi_a = -\phi_i \, \delta\varepsilon \tag{A7}$$

In each configuration ψ_L we make variations using (A7).

$$\delta\psi_L = \psi_L^{i,a}\ \delta\varepsilon \tag{A8}$$

where $\psi_L^{i,a}$ is the one or two configurations formed by replacing the ith orbital in the configuration with the ath orbital or by replacing the ath with the ith. Simultaneous replacement of two orbitals is discarded as a second order variation.

If the wavefunction under consideration has the trivial form that it is restricted to one configuration, ψ_o, then (A6) with the variations given by (A7) reduces to

$$< \psi_i^a |\ H\ | \psi_o > \ = \ 0 \tag{A9}$$

This is Brillouin's theorem[6] which shows that the Hartree-Fock energy is stable with respect to first order variations in the orbitals.[9] In light of the discussion of SCF in the introduction, this explains why restricting a wavefunction to one configuration is not a completely bad approximation since the best one configuration wavefunction has zero interaction with the first level of substituted configurations. In addition, (A9) points out that as an alternative to solving the Hartree-Fock self-consistent field problem, one could achieve the same result, though with a different set of orbitals, by diagonalizing a CI matrix that included the reference configuration and the single substitutions.

Brueckner theory attempts to perform more ambitiously the same analysis but with a more complex wavefunction, typically, one including double substitutions. Let us take the following general configuration wavefunction,

$$\psi = C_o\psi_o + \sum_L C_L\psi_L \tag{A10}$$

Applying (A6) yields

$$< C_o\psi_i^a + \sum_L C_L\psi_L^{i,a} | H - E | \psi > = 0 \tag{A11}$$

Condition (A11) is a rigorous statement of the condition for the best choice of orbitals in any type of configuration expansion. Brueckner's condition, on the other hand, is that the singly substituted configurations will have a zero Hamiltonian matrix element with the total wavefunction and thus, will have a zero expansion coefficient. But this clearly amounts to approximating the summation term in (A11) as zero. As Nesbet has indicated,[59] this might serve as a reasonable approximation since most of the neglected terms depend quadratically on the C_L coefficients. It should also be noticed that assuming the reference configuration dominates, (A11) will look approximately like the Brillouin condition. Hence, it has been believed that Brueckner orbitals are close to Hartree-Fock orbitals.[60]

Using the absorbed singles treatment of SCEP, the Brueckner orbitals for methylene with the 42 basis function set were found. As shown in Table XII, the Brueckner orbitals give a higher energy result than even Hartree-Fock orbitals. This, of course, is not always the case because the Brueckner orbitals for LiH as shown in Table VI improve the energy relative to using Hartree-Fock orbitals. What is important is that the Brueckner condition seems to be too approximate to apply with certainty. One observation made in looking at Brueckner condition results is that it is a more dependable condition for selecting the orbitals

for an expansion which includes doubles but not the singles. That is, the Brueckner orbital total energy result is often lower than the energy obtained using Hartree-Fock orbitals in an expansion restricted to the reference configuration and double substitutions.

The difficulty with the Brueckner condition is that for molecular systems it can easily become a bad approximation to (A11) since it is not even correct to first order in the C_L coefficients.[61] The correct condition shows that the singles do not vanish independently. As an experiment, the singles were forced to become important using the following condition in the hope of better satisfying the energy stability condition.

$$\langle\psi_i^a|H - E|\psi + C_0\psi_0\rangle = 0 \qquad \text{(A12)}$$

With ψ corresponding to the wavefunction which includes both singly and doubly substituted configurations, the improvement in orbitals indicated by (A12) is

$$\phi_i' = \phi_i + \sqrt{\tfrac{1}{2}} \sum_a \phi_a \, (C_i^a - \langle i|F_0|a\rangle)/E_i^a \qquad \text{(A13)}$$

This can then be used in place of (110). Note that in (A13), C_0 has been approximated as 1 which is reasonable if the reference configuration dominates. Test calculations were performed with this new orbital improvement scheme on water and the results are given in Table XIII. It is found that after a few iterations using (A13), a set of orbitals was found that give a lower energy wavefunction than Brueckner or Hartree-Fock orbitals. Extensive application of this new condition for choosing orbitals is not anticipated since it is a difficult condition to apply. What is interesting is that it suggests

Table XII. Brueckner Orbitals for Methylene. Basis Set C as in Table V was used and the lowest occupied orbital was frozen to substitution.

	Hartree-Fock Orbitals	Brueckner Orbitals
Reference Determinant Energy	-38.892 387	-38.891 365
Sum of Pair Energies	-0.146 353	-0.148 137
Total Energy	-38.039 621	-39.039 501

Table XIII. Improved Orbitals for Water. The 14 function double zeta basis set, as in Table IV results, was used and the lowest occupied orbital was frozen to substitution.

	Hartree-Fock Orbitals	Brueckner Orbitals	Improved Orbitals
Reference Determinant Energy	-76.009 294	-76.008 468	-76.005 460
Sum of Pair Energies	-0.125 228	-0.126 533	-0.122 364
Singles Contribution	-0.000 788	-	-0.009 183
Total Energy	-76.135 310	-76.135 001	-76.135 591

that better approximations to (A11) than the Brueckner condition might be found. Furthermore, in the water calculation, using (A13) caused the singly substituted configurations to become <u>more</u> important in the wavefunction, the opposite of the Breuckner condition's result.

Supplementary Tables

In using or understanding the SCEP computer program, some additional information may be helpful. Specifically, Table XIV gives an integral identifying scheme used in the POLYATOM[62] program package. This scheme, which attaches an extra index to each integral label, has been found to be quite helpful in efficiently processing the two-electron integrals list. Table XV gives a complete breakdown of the construction of F_{QP} operators for all possible cases. This may be useful in some applications where storage of the rather long list of F_{QP} operators is undesirable and one chooses instead to construct each operator every time it is needed.

Table XIV. The MU Indexing Scheme for Two-Electron Integrals.

MU Index	Label		Number of Integrals[a]
1	(ii|ii)		1
2	(ij|ij)	i > j	4
3	(ii|kk)	i > k	2
4	(ii|il)	i > l	4
5	(ii|kl)	i > k > l	4
6	(ij|jj)	i > j	4
7	(ij|kk)	i > j > k	4
8	(ij|kk)	i > k > j	4
9	(ij|jl)	i > j > l	8
10	(ij|il)	i > j > l	8
11	(ij|kj)	i > k > j	8
12	(ij|kl)	i > j > k > l	8
13	(ij|kl)	i > k > j > l	8
14	(ij|kl)	i > k > l > j	8

[a] Since only unique integrals need to be stored, each label represents all integrals which are equivalent by permutation of the indices, e.g. (12|34) = (21|34) = (12|43) = (34|12), etc.

Table XV. Explicit Construction of F_{QP} Operators.

	P	Q	F_{QP}
1	i i 1	i i 1	$F_0 + K^{ii} - 2J^{ii} - S(\langle i\|F_0\|i\rangle - \frac{1}{2}\langle i\|K^{ii}\|i\rangle)$
2	i i 1	i j 1	$2^{-\frac{1}{2}}(K^{ij} - 2J^{ij}) - S(\langle i\|F_0\|j\rangle - 8^{-\frac{1}{2}}\langle i\|K^{ii}\|j\rangle)$
3	i i 1	i j -1	$-(3^{\frac{1}{2}}/2)\ K^{ij}$
4	i i 1	j j 1	$\frac{1}{2}S\langle j\|K^{ii}\|j\rangle$
5	i i 1	j k 1	$S\langle j\|K^{ii}\|k\rangle$
6	i i 1	j k -1	0
7	i j 1	i j 1	$F_0 + \frac{1}{2}(K^{ii}+K^{jj}) - J^{ii} - J^{jj} - S[\langle i\|F_0\|i\rangle + \langle j\|F_0\|j\rangle - \frac{1}{2}(\langle j\|K^{ij}\|i\rangle + \langle i\|K^{ij}\|j\rangle)]$
8	i j 1	i j -1	$(3^{\frac{1}{2}}/2)\ (K^{ii} - K^{jj})$
9	i j 1	i k 1	$\frac{1}{2}K^{jk} - J^{jk} - S[\langle j\|F_0\|k\rangle - \frac{1}{2}(\langle k\|K^{ij}\|i\rangle + \langle i\|K^{ij}\|k\rangle)]$
10	i j 1	i k -1	$-(3^{\frac{1}{2}}/2)\ K^{jk}$

11	i j 1	j k 1		$\frac{1}{2}K^{ik} - J^{ik} - S[\langle i\|F_0\|k\rangle - \frac{1}{2}(\langle k\|K^{ij}\|j\rangle + \langle j\|K^{ij}\|k\rangle)]$
12	i j 1	j k -1		$-(3^{\frac{1}{2}}/2)\ K^{ik}$
13	i j 1	k l 1		$\frac{1}{2}S(\langle l\|K^{ij}\|k\rangle + \langle k\|K^{ij}\|l\rangle)$
14	i j 1	k l -1		0
15	i j -1	i j -1		$F_0 + (3/2)(K^{ii}+K^{jj}) - J^{ii} - J^{jj} - S[\langle i\|F_0\|i\rangle + \langle j\|F_0\|j\rangle - \frac{1}{2}(\langle i\|K^{ij}\|j\rangle - \langle j\|K^{ij}\|i\rangle)]$
16	i j -1	i k -1		$(3/2)K^{jk} - J^{jk} - \frac{1}{2}S(\langle j\|F_0\|k\rangle - \langle i\|K^{ij}\|k\rangle + \langle k\|K^{ij}\|i\rangle)$
17	i j -1	j k -1		$(3/2)K^{ik} + J^{ik} + \frac{1}{2}S(\langle i\|F_0\|k\rangle + \langle k\|K^{ij}\|j\rangle - \langle j\|K^{ij}\|k\rangle)$
18	i j -1	k l -1		$-\frac{1}{2}S(\langle l\|K^{ij}\|k\rangle - \langle k\|K^{ij}\|l\rangle)$
19	i j 1	k j 1		$\frac{1}{2}K^{ik} - J^{ik} - \frac{1}{2}S(\langle i\|F_0\|k\rangle - \langle j\|K^{ij}\|k\rangle - \langle k\|K^{ij}\|k\rangle)$
20	i j 1	k j -1		$(3^{-\frac{1}{2}}/2)\ K^{ik}$
21	i j -1	k j -1		$(3/2)K^{ik} - J^{ik} - \frac{1}{2}S(\langle i\|F_0\|k\rangle - \langle j\|K^{ij}\|k\rangle + \langle k\|K^{ij}\|j\rangle)$

Notation

Wherever possible the following were used as notation conventions.

MATRICES

C	coefficient matrix
D	density matrix
F	Fock or Fock-like operator
G	pair operator
H	Hamiltonian operator
I	the one-electron part of the Hamiltonian operator
J	Coulomb operator
K	exchange operator
R	rotation operator
S	overlap matrix (operator)
T	operator transformed to some final basis
U	unitary transformation
W	orbital eigenvector array
$[A]_{ij}$ or A_{ij}	the ij element of the array A
A^{ij} or A^{P}	the ij or P particular matrix among some set of similar matrices, A

INDICES

i j k l	occupied orbitals; also, specific configurations or determinants
a b c d	virtual or external orbitals
α β γ δ μ ν	basis functions
r s t u v w	summation indices
P Q	electron pairs
p q	spin coupling

NUMBERS

I	the number of two-electron integrals
K	the number of basis functions
L	the number of nuclear centers
M	the number of electron pairs
N	the number of occupied orbitals
n, m	iteration numbers

SYMBOLS

$\|i>$ $\|a>$	orbital coefficient vectors or orbitals
$\|i>_\alpha$	the αth coefficient in the basis set expansion of the ith orbital
$(ij\|kl)$	two-electron integrals in the orbital basis
$(\alpha\beta\|\gamma\delta)$	two-electron integrals over basis functions

ϕ	orbitals (function form)
χ	basis functions
Φ	configurations or determinants
ψ	wavefunction or wavefunction components
$A^{\dagger}$	adjoint of A
$\underline{A}$	refers to external orbitals when A would refer to internal orbitals
ρ	density functions

ENERGY VALUES

E	total energy
E_o	reference configuration energy
ε_p	pair correlation energy

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