

A multiconfiguration self-consistent-field group function method for problems with repeating potentials

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An implementation of a conceptual scheme for performing a finite-cluster electronic structure calculation so as to simulate, within the finite cluster, an extended periodic continuation of the cluster is reported. The implementation extends a scheme used previously at a single-determinant wave function level of approximation to a multiconfiguration self-consistent-field (MCSCF) level. The total wave function has the form of McWeeny's group functions. The MCSCF working equations are cast in the exponential- i -lambda language (EIL) and the energy expressions are cast in notation of the graphical unitary group approach (GUGA). The modifications to the MCSCF working equations necessary to do group function calculations are also developed in the GUGA-EIL notation. A procedure for wave function transfer from one unit of the cluster to another is described. All of this conceptual scheme has been put together in working computer algorithms and applied to two informative, illustrative systems, Be_2 , and finite hydrogen chains. The results of our computations, while not being definitive, are interesting in being among the first correlated calculations for extended periodic problems.

I. INTRODUCTION

Problems of electronic structure calculation for systems involving extended and periodic or nearly periodic potentials have represented a difficult and continuing challenge to theoreticians. Conventional quantum chemical methods, while they have been capable of achieving highly accurate results including electron correlation effects for small molecules, have thus far had to neglect or severely approximate long range interactions when applied to problems involving extended or periodic potentials. These conventional approaches are also prone to cluster termination effects. Alternatively, conventional solid state methods, while they have been enormously successful in describing properties of bulk solids, because of the assumption of translational invariance, have reduced ability to handle problems where interruption of the translational invariance is an essential feature of the problem. Moreover, to date little *ab initio* work has been done at a correlated level using explicit treatment of translational symmetry. The work presented here proceeds from a conventional quantum chemistry approach utilizing a finite cluster, but modifies the conventional formalism and procedures so as to admit, within the finite cluster, the possibility of achieving a representation of the extended system.

The dominant influence of cluster termination (or edge) effects is the first important deficiency that a finite cluster, conventional quantum chemistry approach has in simulating an extended system. It is primarily this deficiency that we seek to address and thus it is worthwhile recapitulating how other workers have addressed it. The most obvious solution is to make the cluster sufficiently large that the number of terminal sites is small compared with the number of sites experiencing a continued potential. Because computational effort scales nonlinearly with the number of sites included in the computa-

tion, this approach has been successful only for methods that require a very small amount of computation per site such as semiempirical methods¹⁻⁹ or the $MSX\alpha$ methods.¹⁰⁻¹⁴ There have been a few *ab initio* calculations that have attempted this solution to reduce edge effects¹⁵⁻¹⁸; the computational labor involved in *ab initio* calculations is too great for frequent application to increasingly large clusters. Some workers have used high-spin unrestricted Hartree-Fock calculations on clusters to reduce edge effects,^{19,20} thereby simulating the presence of half an electron pair bond around the periphery of the cluster. Surrounding the cluster with hydrogen atoms to saturate "dangling bonds"²¹⁻²⁴ has also been used to offset cluster termination effects. Kunz²⁵⁻²⁷ has exploited the Adams-Gilbert theorem,²⁸⁻³⁰ which casts the Hartree-Fock problem into a localized set of equations, in order to reduce the infinite problem to a localized cluster. All of these approaches recognize the serious disturbances of electronic structure introduced by cluster termination and have sought to diminish them.

One of us (WHF) has exploited an iterative definition of frozen peripheral clusters (analogous to a frozen core) at the single-configuration wave function level of approximation³¹⁻³⁴ in order to simulate extended systems with finite clusters. The present work represents the first extension of the method to admit a correlated wave function treatment. The underlying concept for the approach may be seen by considering a hypothetical problem of determining the electronic structure of a two-dimensional array tiled with identical triangles as depicted in Fig. 1. Each triangle could represent, for example, three atoms in the (111) plane of a close-packed solid, although in that case the specific tiling pattern of Fig. 1 would not apply directly. The successively distant triangles from the representative central unit (*A*) are lettered (*B*), then (*C*), etc. If the true potential experienced by the

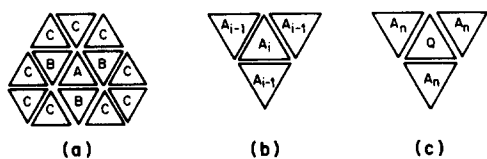


FIG. 1. A schematic representation of a two-dimensional electronic structure problem. (a) An infinite plane tiled with triangles. (b) A portion cut from (a) retaining neighbor interactions. (c) A local disturbance affecting the central representative triangle.

electrons within (A) were known, a single solution for the electronic structure of (A) (e.g. orbitals and configuration mixing amplitudes) would suffice because the solution could then be repeated by translation to all other triangles in the plane. Regrettably, the true potential is not known for (A) so that some approximation for it also becomes essential for any method of solution.

One successive approximation scheme that simultaneously solves for both the potential and the electronic wave function within (A) can be described by reference to Fig. 1(b). Figure 1(b) represents a minimal slice from the infinite plane that still retains an essential feature of the continuing potential, interactions among neighboring triangles. Consider now a solution procedure in which the electronic characteristics of the peripheral triangles are frozen in the form obtained from an energy optimization on the central triangle in a previous iteration. Reoptimization of the electronic wave function and energy of this central triangle in the presence of the frozen periphery then generates new orbitals and configuration mixing coefficients for the central triangle which can be used to define a *new* frozen periphery. When the electronic characteristics of both the central and the peripheral units obtained via this iterative process do not change from one iteration to the next, a solution approximating that for the entire infinite plane will have been reached. Notice that because the electronic characteristics of the peripheral triangles are determined by those of the solution for the central one, which includes interactions with the surrounding triangles, the peripheral triangles will bear electronic characteristics as if they too had a full complement of surrounding structures. Hence, the iterative process described here is not merely a calculation on a cluster with four triangular units, rather it is designed to simulate the local electronic characteristics of the entire infinite plane. While this discussion has proceeded as if the peripheral units contained only a single structure mimicking that of the central unit, it would also be possible to have the peripheral units composed of several structures like that of the central unit if multiple layers of periphery were desired or required.

Furthermore, local disturbances (e.g., chemisorption, defect structure, color center) to a triangle in the infinite plane may be treated as in Fig. 1(c) by fixing the electronic characteristics of the peripheral units with the characteristics of the solution obtained from the iterative process described for Fig. 1(b) in the absence of any disturbances, and then solving for the electronic

wave function of the central triangle, now in the presence of the local disturbance.

Implementation of these concepts within the approximation of a single-determinant wave function has met with reasonable success³¹⁻³⁴ suggesting that the iterative cycles can be effective in reducing cluster termination effects. However, the same deficiencies that the single-determinant approximation has for molecular systems are also deficiencies for modeling extended systems. The most serious deficiencies are frequent failure to describe the energetics at large values of internuclear separations and the omission of electron correlation effects. The latter may be of particular importance for treating problems of local aberrations such as chemisorption.

We report here an extension of these cluster concepts involving the implementation of a many-body wave function treatment within the framework of the graphical unitary group, which provides for spin adaptation of the wave function. As will be made clearer in Sec. II, expressing the problem in the graphical unitary group representation serves both to emphasize the nature of the interactions included in the treatment and to provide a formulation suggesting an efficient computational scheme. Because the systems to which application is ultimately foreseen are large, we have chosen a multi-configuration self-consistent-field formulation of the problem; MCSCF being, in our opinion, the most compact correlated wave function form which removes the essential deficiencies of the single-determinant SCF wave function, while still retaining a simplicity amenable to intuitive understanding.

In implementing the above outlined iterative cluster method at the SCF or MCSCF level, one is faced with an additional problem which requires clarification and elaboration. When the MCSCF wave function for triangle (A) is obtained at the end of a given cycle, some physically meaningful and computationally feasible means of transferring the electronic characteristics of this solution to the peripheral triangles must be available to begin the next cycle. Figure 2 symbolically represents the orbital-transfer component of this wave function transfer process. The schematic depiction of Fig. 2(a) represents an orbital optimized for the electronic wave function of the central triangle (A) in the presence of the peripheral triangles. The optimization for the orbital may or may not have explicitly included basis functions centered on nuclei in the peripheral triangles, however the orbital orthogonality requirement at least will have introduced small contributions from basis functions on nuclei outside the central triangle. Because the peripheral triangles do not have still other triangles outside them, these contributions must be removed before the orbitals can be transferred. Reference 32 defines an orbital projection procedure which achieves this removal by retaining maximum overlap with the original orbital under a reduction of the expansion set to include only basis functions centered on nuclei within the central triangle. Once these outside contributions have been removed, the projected orbital may be translocated to each of the peripheral units as in Fig. 2(c); the trans-

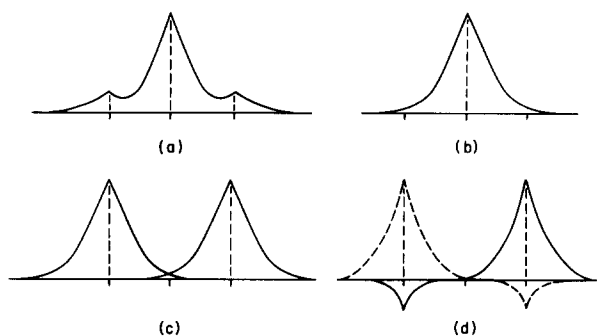


FIG. 2. A schematic representation of the orbital transfer process from central to peripheral units. (a) The central unit optimized orbital has tails in the peripheral units. (b) The tails of (a) have been removed by projection onto the basis functions centered on nuclei in the central unit. (c) The orbital of (b) has been translocated to the peripheral units. (d) The orbitals of (c) have been symmetrically orthogonalized.

located orbitals may then be symmetrically orthogonalized as in Fig. 2(d), and finally, the central unit's variational space may be Gramm-Schmidt orthogonalized to the orbitals on the peripheral triangles so that they are unchanged and frozen through the next cycle. In the single-determinant wave function implementation of these concepts, orbitals are the only electronic characteristics that need be transferred. For the MCSCF implementation, there are configuration mixing coefficients as well. We have adopted the simple direct transfer of the coefficients obtained in the central unit to the analogous configurations in the periphery. While more sophisticated considerations of possible simultaneous readjustment of both orbitals and configuration mixing coefficients can be entertained, we have felt that such considerations introduce more technical complication than is justified at this time since the configuration mixing coefficients are not explicit functions of coordinates whereas the orbitals are.

The concepts described above are very similar to the imbedded cluster approach³⁵ but we do not use a Green's function formalism for this implementation. By utilizing these concepts within an MCSCF formalism, we hope to exploit the accumulated experience obtained from such calculations on molecular systems. Very closely allied to the present approach is that of Whitten, and Whitten and Pakkanen³⁶ who imbed a local correlated function in a substrate potential arising from an RHF or UHF calculation for the substrate. Kirtman and deMelo³⁷ have also presented a closely allied treatment in a density matrix formalism. We turn now to give a detailed exposition of the formal development we have made to permit this first implementation of a correlated (MCSCF) iterative cluster technique. In so doing we also point out the relationship of our work to other recent developments.

II. DEVELOPMENT OF WORKING MCSCF-CLUSTER EQUATIONS

A. The ansatz wave function

We consider a wave function of a generalized antisymmetrized product form

$$\psi = \prod_{\alpha=1}^R \psi_{\alpha}, \quad (1)$$

where the product runs over each unit (e.g., the triangles of Sec. I) in the total cluster. The wave function for each unit α is given as a superposition of configurations $\{|I_{\alpha}\rangle\}$

$$\psi_{\alpha} = \sum_{I_{\alpha}=1}^{m_{\alpha}} C_{I_{\alpha}} |I_{\alpha}\rangle. \quad (2)$$

The configurations consist of products of orthogonal spin orbitals generated by $\{a_{r\alpha}^{\dagger}\}$ that are localized on unit α in a sense to be described later.

$$|I_{\alpha}\rangle = \left(\prod_{r \in I_{\alpha}}^{n_{\alpha}} a_{r\alpha}^{\dagger} \right) |vac\rangle_{\alpha}, \quad (3)$$

$$\langle \psi_{\alpha} | \psi_{\beta} \rangle = \delta_{\alpha\beta}. \quad (4)$$

There are n_{α} electrons identified with unit α ; m_{α} configurations are included in the wave function for unit α and therefore $\prod_{\alpha=1}^R m_{\alpha}$ configurations for the total system. The configurations $\{|I_{\alpha}\rangle\}$ are localized on unit α in the sense that the creation operators defining the configurations for unit α select one particle functions only from the subset associated with unit α , and no other unit uses any of the one-particle functions associated with unit α in defining its configurations. McWeeny^{38,39} has called the individual terms of Eq. (3) appearing in the product function of Eq. (1) group functions. We note that because the antisymmetry of Eq. (1) is carried by the anticommutation relations of the creation operators, no explicit notation to indicate antisymmetrization among the group functions is necessary.

There are a number of remarks about a wave function as in Eq. (1) which should be made. It is, first of all, not designed for achieving an exact solution for any system to which it is applied because the entire class of configurations involving excitations out of one unit and into another has been excluded by construction. However, in implementing the conceptual scheme discussed in Sec. I, we do not seek an exact solution for the cluster under consideration but rather to use that cluster to represent an extended system. Consideration must be given to choosing the units of the calculation not only so that they represent by continuation the extended system, but also so that this neglected class of interunit-excitation configurations may be expected to contribute little. In a somewhat different vein, the description of the regional division given above is somewhat more general than is needed to implement the conceptual solution procedure described in Sec. I. If all regions are identical the n_{α} and m_{α} will be the same numbers for each α . Further, when the self-consistent cluster wave function is found, the $\{C_{I_{\alpha}}\}$ will be independent of α and the $\{a_{r\alpha}^{\dagger}\}$ for all peripheral α will be identical and will differ from those of the central region only as required by the transfer and orthogonalization procedure described in Sec. I.

B. Equations for MCSCF optimization

Let us now write the Hamiltonian in its usual second-quantization form⁴⁰

$$H = \sum_{i,j} h_{ij} a_i^{\dagger} a_j + \frac{1}{2} \sum_{i,j} \sum_{k,l} (ij|kl) a_i^{\dagger} a_k^{\dagger} a_l a_j. \quad (5)$$

Here Mulliken notation has been used for the two-electron integrals, and the h_{ij} integrals contain the usual kinetic and nuclear attraction terms. Thus far the indices i, j, k , and l can label any of the spin orbitals from any of the cluster regions. If we now proceed to evaluate the expectation value of this Hamiltonian over the product form of Eq. (1), we find that a separation of terms into intraregional interactions and interregional interactions is possible. Further, the interregional interactions occur only as products of interactions of pairs within one region with pairs in other regions. Spin adaptation of the wave function of Eq. (1) using the graphical unitary group approach (GUGA),⁴¹⁻⁴⁴ and restricting the wave function to contain only one nonsinglet unit permits the energy to be written in the form

$$\langle H \rangle = \sum_{\alpha=1}^R \langle H_{\alpha} \rangle - \sum_{\alpha=1}^{R-1} \sum_{\beta=\alpha+1}^R \sum_{\substack{i,j \\ \epsilon(r_{\alpha})}} \sum_{\substack{k,l \\ \epsilon(r_{\beta})}} [(ij|kl) - \frac{1}{2}(il|kj)] \times \langle e_{kl} \rangle_{\beta} \langle e_{ij} \rangle_{\alpha}, \quad (6)$$

where

$$\langle H_{\alpha} \rangle = \sum_{\substack{i,j \\ \epsilon(r_{\alpha})}} (h_{ij} + V_{ij}) \langle e_{ij} \rangle_{\alpha} + \frac{1}{2} \sum_{\substack{i,j,k,l \\ \epsilon(r_{\alpha})}} (ij|kl) \langle e_{ij,kl} \rangle_{\alpha}, \quad (7)$$

$$V_{ij} = \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^R \sum_{\substack{k,l \\ \epsilon(r_{\beta})}} [(ij|kl) - \frac{1}{2}(il|kj)] \langle e_{kl} \rangle_{\beta}, \quad (8)$$

$$\langle e_{kl} \rangle_{\alpha} = \sum_{I_{\alpha}} \sum_{J_{\alpha}} C_{I_{\alpha}} C_{J_{\alpha}} \langle I_{\alpha} | e_{kl} | J_{\alpha} \rangle, \quad (9)$$

$$e_{ij,kl} = e_{ij} e_{kl} - \delta_{kj} e_{il}, \quad (10)$$

and

$$e_{ij} = a_{i1/2}^* a_{j1/2}^* + a_{i-1/2}^* a_{j-1/2}^*. \quad (11)$$

All indices in Eqs. (6)–(10) now refer only to spatial orbitals as the spin index has been summed over in Eq. (11).

The total energy expression of Eq. (6) consists of a part that is variationally active for region A plus a part that is constant as far as the variation procedure is concerned. This latter part expresses the “bare” energies of all the surrounding sites as well as the energies of interactions among these peripheral sites (but not including interactions with the variationally active site). Notice that the only true two-electron density matrix elements appearing in Eq. (6) involve all indices exclusively within the active region; interactions of the active region with the others involve products of one electron density matrices for the two separate regions.

In evaluating the final converged MCSCF total energy, one is faced with one difficulty which merits mention. Because of the truncation process (Sec. I) which is used in translocating the MCSCF orbitals of unit A to the peripheral units, the final charge density character of the peripheral units is not identical to that of the central unit. As a result, the “base” energies Eq. (7) and the interaction energies among the peripheral units will

not be the same as the base energy of the central unit and the central unit to peripheral unit interaction energy, respectively. At present we do not know of a reasonable, computationally tractable alternative to simply choosing to accept this charge asymmetry as a slightly disturbing aspect of the proposed procedure.

The equations for the MCSCF wave function of the one active region [involving the H_{α} of Eq. (7)] can be efficiently written using the exponential- i -lambda (EIL) method⁴⁵⁻⁴⁷ for wave function optimization and the graphical unitary group approach⁴¹⁻⁴⁴ for the one- and two-particle density matrix elements⁴⁴ (UEIL). The additional terms due to interaction with the peripheral units in the UEIL equations enter only through addition of the effective one-electron potential of Eq. (8). That this effective operator will contribute the only additional terms in the commutators of the UEIL equations⁴⁴ follows because the excitation operators involved in these commutators will retain the basic wave function form shown in Eq. (1); i.e., the orbital rotation excitation operators will involve indices only from the variational region and therefore the only nonvanishing density matrix elements for interregional interactions appearing in the commutator expressions will involve only pairs of indices between interacting regions.

The economy of effort in determining an MCSCF wave function of the type in Eq. (1) compared with a completely general MCSCF solution for the system may most easily be appreciated by considering the number of electron repulsion integrals required in Eq. (7) compared with the total integral list length. In making this comparison it should be kept in mind that these integrals refer to the MCSCF molecular orbitals (MO) rather than to the atomic basis orbitals. As is well known, the step of computing such MO integrals in terms of atomic-orbital integrals is the slow step in most *ab initio* computations including electron correlation. Therefore it is important to minimize the need for such MO integrals. To illustrate the magnitude of labor that can be saved, consider a calculation for a system divided into two equal units containing n MO's per unit. The number of integrals in the full list of all interactions between the MO's is given by

$$N_T = \frac{1}{2} \left[\frac{2n(2n+1)}{2} \right] \left[\frac{2n(2n+1)}{2} + 1 \right],$$

$$N_T = 2n^4 + 2n^3 + \frac{3}{2}n^2 + \frac{1}{2}n.$$

If i, j, k , and l denote indices from one region while a, b, c , and d denote indices from the other region, the partial list required for calculation of the energy expression of Eq. (6) includes integrals only of the type $(ij|kl)$, $(ab|cd)$, $(ij|ab)$, $(ia|jb)$. The number of integrals in this partial list is given by

$$N_p = n^4 + n^3 + \frac{3}{2}n^2 + \frac{1}{2}n.$$

The ratio of the leading term in N_p to the leading term in N_T is $\frac{1}{2}$. As the size of the problem increases one-half the labor is required for integral processing when a wave function of the form of Eq. (1) is used, and this ratio will decrease with the number of regions. While rigorous implementation of the group-function UEIL ap-

proach still requires calculation of a full integral list over the atomic orbital basis functions, the smaller number of integrals which must be transformed in each iterative cycle reduces the time and space needs in construction of the MCSCF working equations. Further, optimization only within region α in a given step does not require integrals of type $(ab|cd)$ (with all indices in one or more different regions). These more general integrals are only required for a calculation of the total cluster energy and can be delayed until convergence is achieved.

III. ILLUSTRATIVE CALCULATIONS

The development described above has been implemented and applied to calculations on a homonuclear diatomic molecule, Be_2 , and to finite chains of hydrogen atoms. We omit a detailed report of the Be_2 in the interest of brevity and because the calculations served more a pedagogical function than a contribution to the imbedding problem which was the main motivation for us.

A homonuclear diatomic molecule is the simplest example of a system that contains a repeated electronic structure. In the case of Be_2 one Be atom may be treated variationally while the other simply presents a potential as an image atom. Both atoms may be treated as single wave functions to produce the $^1\Sigma$ ground state. Calculations for both a simple single configuration formed as a product of single configuration atomic wave functions and a 25 configuration formed as a product of five configuration atomic wave functions were performed as a function of internuclear separation. The 25 configuration calculation represents a full atomic valence CI. Satisfactory results were obtained, total energies were comparable to the analogous fully variational calculations and as one would expect, the calculations yielded the same total energies at large values of internuclear separation as the fully variational ones. No van der Waals minima were found in these calculations for Be_2 .

Treatment of chains of hydrogen atoms of both finite length⁴⁸⁻⁵⁴ and infinite length⁵⁵⁻⁶³ have a rich *ab initio* theory literature. Their importance as simple model solids, as model aromatic compounds, and as a possible component of the geometry of metallic hydrogen is sufficient alone for the interest displayed in them. For our purposes they are ideal as simple, controlled demonstration systems on which to exercise the MCSCF group function approach. Most of the previous literature, with the exception of the CI calculation of Mattheis^{48,49} a single-geometry calculation by Liskow *et al.*,⁵³ and the recently reported CI calculations of Seel, Bagus, and Ladik⁵⁴ has concerned itself with either restricted-Hartree-Fock (RHF) or unrestricted-Hartree-Fock (UHF) treatments. The interest and novelty which the MCSCF group function approach can bring to the literature is a more general pure spin state treatment which allows the inclusion of electron correlation, and therefore the attendant ability to separate upon geometrical deformation to proper asymptotic states for both spin and space variables. All calculations reported

used the MOLECULE integral program⁶⁴ for atomic orbital integrals and the GRNFNC program⁶⁵ for Hartree-Fock SCF molecular orbitals and energies.

To treat the linear hydrogen chain with the MCSCF group function techniques, one central variational region is chosen and two peripheral frozen regions, one on either end of the central region, are included in the finite cluster. The peripheral regions, by having their electronic structure frozen in the form obtained from the previous iteration, will simulate connection of the central region to a continuous infinite chain. Since the formalism of the UEIL group function method within which we are working permits only the central region to be nonsinglet, and all three regions must be similar, we are obliged to consider multiples of even numbers of hydrogen atoms for our regions. We report results here for two different basis sets on the simplest such cluster system consisting of two hydrogen atoms per region, as well as a preliminary result for the system involving four hydrogen atoms per region. In describing the wave function forms employed, we use orbital and term symbol notation strictly appropriate only for the central region, which contains the center of inversion. Of course when these forms are translocated to the periphery, the (u, g) designation serves only as a local label.

The specific wave function forms used in the group function must now be described. The single configuration description of each two-hydrogen-atom region is $1\sigma_g^2$, whereas that for the four-hydrogen-atom region is $1\sigma_g^2 1\sigma_u^2$. Note that in this latter case, both $1\sigma_g$ and $1\sigma_u$ are bonding orbitals of the H_4 moiety. The group function formalism itself assures proper energetic behavior as the individual regions are separated (e.g., $\text{H}_8 \rightarrow 3\text{H}_2$). However, for arbitrary kinds of separations that destroy the integrity of the group (e.g., $\text{H}_8 \rightarrow 6\text{H}$), a careful selection of multiconfiguration wave functions within each region or group is required to guarantee proper energetic behavior at the asymptotes of the separation. For the two-hydrogen-atom region the two configurations $1\sigma_g^2$ and $1\sigma_u^2$ are required to permit proper separation to individual ground state atoms. These then are the three types of group function calculations we have undertaken: A one-configuration, six-hydrogen atom calculation; a one-configuration, 12-hydrogen atom calculation; and a two-configuration, six-hydrogen atom calculation. In all of these calculations, the step in our MCSCF procedure in which the molecular orbitals (MO's) of the active unit are optimized involves orbital rotations which include the virtual orbitals of the peripheral units. That is, modification of the MO's of the active unit can involve mixing in virtual orbitals on the periphery. In the earlier Be_2 calculations, we restricted the orbital optimization of the central unit to involve only MO's belonging to that unit.

In order to compare our results directly with those of crystal orbital calculations for the infinite chain, for some of our calculations, we used the same minimal basis set, the STO 4G function,⁶⁶ as Kertesz, Koller, and Azman.⁵⁸⁻⁶⁰ Because of the known sensitivity of optimum nuclear geometry to the choice of minimal-

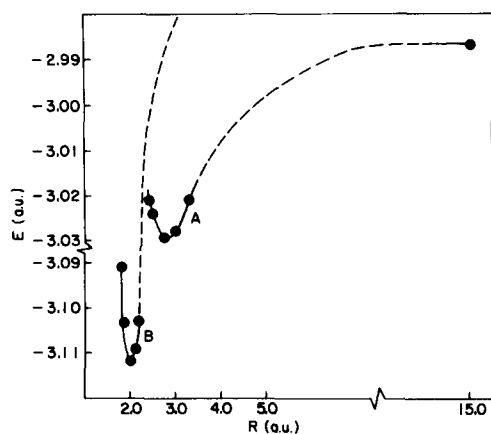


FIG. 3. Calculated energies of H_6 as a function of an equidistant internuclear separation. (A) Two-configurations in each regional wave function. (B) One-configuration in each regional wave function. Energies are in Hartree and distances are in bohr.

basis scale factor,⁶¹⁻⁶³ a double-zeta type 4-31G basis with standard hydrogen parameters⁶⁷ was also used.

Most of the calculations were performed for nuclear geometries in the neighborhood of the metastable point of the potential energy surface involving equidistant hydrogen atoms. Kertesz, Koller, and Azman⁵⁹ (for the infinite hydrogen chain) and Benard and Paldus⁵² (for finite hydrogen rings) have shown the equidistant geometry to be unstable with respect to dissociation to isolated hydrogen molecules. By way of checking the asymptotes of our group function calculations we were able to verify this for the one configuration two hydrogen atoms per region case using the STO 4-31G basis. The energy for a nuclear geometry of 10 a.u. between region centers and 1.88 a.u. between hydrogen atoms within each region is -3.278356 . Three times the energy of an H_2 molecule with 1.88 a.u. between hydrogen atoms and using the same basis set gives -3.278313 . The difference between these two energies is of no physical importance, thereby verifying the group function's ability to properly describe this dissociation. This energy is 0.1 Hartree lower than the energy calculated for the equilibrium geometry of the equidistant chain (which has a separation of 1.88 a.u. between neighboring H atoms). Of course, the energy of three H_2 molecules each 10 a.u. from one another and each with a H-H distance of 1.4 a.u. would be even lower.

Figure 3 displays energy calculated with the STO 4-31G basis for the six hydrogen chain as a function of equidistant internuclear separation for both the one- and two-configuration wave functions. Several aspects of these results are worth noting. First, although the vertical grid spacing is the same for both curves, a break in the vertical axis has been introduced in order to present both curves in the same figure. There is also a break in the horizontal axis in order that the calculated asymptotic point at 15 a.u. can be displayed for the two-configuration calculation.

Table I presents a summary of our results for nuclear

geometry optimization and force constants from the interpolating polynomials. Also included are selected values for the same parameters that were obtained from calculations by other workers on the equidistant hydrogen chain. The data for the group function calculations presented in Table I were obtained by calculating the energy at five points closely surrounding the equilibrium geometry and fitting a polynomial of degree three or four in the internuclear separation to these points. The values of the internuclear separation (R_e) and the second derivative (k) at the minimum of these polynomials are presented in Table I.

Referring first to Fig. 3, we note that the asymptote to which the two-configuration calculation tends as the equidistant internuclear separation is increased, is the energy of six hydrogen atoms in this basis (-2.986876 Hartree at 15.0 a.u.). Our one-configuration calculation at an equidistant internuclear separation of 15.0 a.u. gives an energy of -2.183273 hartree, so far above the correct asymptote that even with the break in the vertical scale, it cannot be depicted in Fig. 3. Proper inclusion of electron correlation by the two-configuration group function calculation has cured this serious deficiency of the one-configuration calculation.

The correct asymptotic behavior of the two-configuration calculation is gratifying and some of the changes seen in passing from the one- to the two-configuration calculation are similar to effects of correlation seen in molecular systems generally, a move to larger values of internuclear separation and a softening of the molecular potential curvature at the equilibrium position. However, the differences between the uncorrelated and correlated results are more dramatic than commonly observed in molecular systems.

Further, that the one-configuration result lies at a lower absolute energy than the two-configuration result at first thought is startling. The possibility of basis set superposition error artificially lowering the one-con-

TABLE I. Equilibrium internuclear separations and harmonic force constants for an equidistant linear hydrogen chain.

No. of atoms	Basis	Calculation	R_e^a	k^b
6	4G	1 cf GF ^c	1.79	17
6	4-31G	1 cf GF ^c	2.03	12
12	4G	1 cf GF ^e	1.87	46
∞	4G	RHF ^f	1.88	
∞	4G	UHF ^f	1.95	
∞	extended	RHF ^g	1.839	2.48
6	4-31G	2 cf GF ^d	2.82	0.8

^aBohr = 52.9177 pm.

^bm dyn/ \AA = Hn/m.

^cThis work, one configuration (σ_g^2) for each of the three regions containing two hydrogen atoms per region.

^dThis work, two configurations (σ_g^2, σ_u^2) for each of the three regions containing two hydrogen atoms per region.

^eThis work, one configuration (σ_g^2, σ_u^2) for each of the three regions containing four hydrogen atoms per region.

^fReference 59.

^gReference 63.

figuration calculation can be dismissed. Calculation of an H_2 unit at 1.88 a.u. with phantom functions on either side of the hydrogens gives a lower energy than without the phantom functions by only 0.0038 hartree. Thus, an overestimate of basis set superposition error is only 0.01 hartree. Rather, the major reason for the two-configuration calculation to lie at a higher absolute energy is that it simply has a smaller variational space available to it. With two basis functions per atom and six hydrogen atoms in the cluster, there are a total of 12 basis functions. In the one-configuration calculation, two of these degrees of freedom are removed to fix the $1\sigma_g$ orbital on either side of the central unit leaving a ten parameter variational problem. In the two-configuration calculation, four of the orbitals are removed to fix both $1\sigma_g$ and $1\sigma_u$ on either side of the central unit leaving an eight parameter variational problem. With fewer variational parameters, the two-configuration calculation yields a higher absolute energy than does the one-configuration calculation. A conventional (one configuration and 12 orbital parameters) restricted Hartree-Fock calculation on the full six hydrogen chain would give a curve still lower in absolute energy, but that would not represent the ends of the H_6 chain in a manner similar to the continuing infinite chain. It is precisely these termination influences that we are attempting to remove and one consequence is that the absolute energy is no longer an infallible guide to wave function quality.

The overdramatic changes in the potential curve shapes between the uncorrelated and correlated calculations, however, are of greater importance and may be related to the discussion in Sec. I regarding the charge asymmetry introduced as a requirement of orbital orthogonality. The energies for both curves in Fig. 3 and all the data presented in Table I were obtained from the energy expression of Eq. (6). As was pointed out in Sec. I, the requirement of orbital orthogonality, at least, results in orbitals on the two ends of the six hydrogen chain being different from the final variational orbitals of the central hydrogens. This constraint of the formalism will be more severe the more complex the wave functions within each region become, and will possibly produce the result that the wave function for the system as a whole becomes more asymmetric. It is possible that some of the dramatic differences between the correlated and uncorrelated results of Fig. 3 and Table I have their origin in these asymmetries. We have considered possibilities for a total energy more representative of the full symmetry of the system, but have not yet found anything more satisfactory than Eq. (6). However, it is also worth pointing out in this connection as McWeeny^{38,39} has previously, that Eq. (6) does admit the major class of interunit correlations that are responsible for van der Waals interactions, namely configurations involving simultaneous single excitations within the individual interacting regions.

IV. CONCLUSIONS

We have presented a formal development of a conceptual scheme for solution of the electronic structure

problem for systems involving repeating potentials. This development admits the inclusion of general, correlated electron, many-body wave functions and exploits the group function approximation first suggested by McWeeny^{38,39} and previously used by one of us (WHF) in a single-determinant approximation. The addition of an external iterative cycle to the group function procedure seeks to minimize edge effects for a given cluster size simulation of an extended chain, surface, or three-dimensional solid. The equations for the additional terms to be included in an MCSCF implementation of the scheme have been presented in the notation of the graphical unitary group approach. This notation aids in the design of efficient algorithms for carrying out the computations. Results of calculations on finite chains of hydrogen atoms have explored the capabilities, disadvantages, and highlights of the scheme.

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