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Range Relaxation. III. Variationally Optimal Integral-Transform Wave Functions

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A general and formally exact class of *integral-transform* electronic wave functions may be defined in terms of a distortion operator. This operator, which depends on one or more running parameters, maps some zero-order approximate wave function onto any part of a Hilbert space. The set of all such distorted functions may then completely span the space. The most effective discrete set of n configurations for the approximation of the exact integral transform is considered from the standpoint of a numerical analysis. It is taken to be the set which permits the most accurate n-point evaluation of an integral expression for the expectation value of the energy. In practice, the diophantine integration scheme may be used to provide such a set of configurations. The value of the optimal transform weighting function for ground and excited states at each of the n points can be inferred back at the end via the solution to a conventional linear matrix eigenvalue equation. Preliminary applications are made to the calculation of the radial correlation limits for the helium, lithium, and beryllium atoms.

I. INTEGRAL APPROACH TO THE CALCULATION OF WAVE FUNCTIONS

Efficient general methods for evaluating a definite integral of some function $F(\vec{x})$ as a sum of values of the integrand at a set of points $(i, j, k, \ldots, m)$ are afforded by numerical analysis[1]:

$$\int_b^a F(\vec{x})\, d\vec{x} \simeq \sum_i \sum_j \sum_k \cdots \sum_m A(i, j, k, \ldots, m) \times F(i, j, k, \ldots, m) \, . \qquad (1)$$

The expected error is minimized with respect to the choice of weights $A(i, j, k, \ldots, m)$ and points. The relative efficiency with which a function can be integrated over a given range, besides that with which the same function can be interpolated, can be made to increase very rapidly with the number of dimensions over which the function is defined. The electronic wave function Ψ of an atomic or molecular system is a many-dimensional function. Moreover, it normally appears during its calculation within the usual integral expression for the expectation value of the energy E:

$$E = \int \Psi^* H \Psi \, d\tau \Big/ \int \Psi^* \Psi \, d\tau \ . \qquad (2)$$

It is the purpose of this paper to suggest a method in which the error analysis implicit in numerical integration methods can be used directly to fix, in an effective rational way, certain features in the construction of a wave function, such as the choice of basis functions, which are normally settled on arbitrary grounds. The wave function is expressed as an integral transform, which can formally be regarded as having a variationally optimal weighting function. This can be reduced, using the numerical approximation which can be evaluated separately, to the established framework of configuration interaction. Each configuration ϕ_i represents effectively a point in a many-dimensional surface, and the expansion of the wave function

$$\Psi = \sum c_i \phi_i \qquad (3)$$

is to be regarded then not as an interpolation formula but as a provider of a set of weights and points for an integration formula. It can be reasoned that the use of the conventional approach in which all the configurations from a given one-electron basis are used for configuration interaction is analogous to the process of making a numerical integration using a hyperrectangular grid of points. Far more efficient integration schemes have been devised, particularly when a large number of points can be used.

II. DISTORTION OPERATOR

A functional form for the exact solution to the Schrödinger equation is indicated. To construct the wave function, a complete set of functions is specified, whose members are distinguished by a vector varying continuously between defined limits. The free-particle eigenfunctions

$$\psi(\vec{k}) = e^{i\vec{k}\cdot\vec{r}}$$

provide one well-known example. For bound-state problems, basis functions extending to infinity are not convenient, since the energy eigenfunctions have effectively a finite extent. There is no complete orthogonal set of energy eigenfunctions of some other convenient Hamiltonian similarly indexed by a continously varying parameter. We are forced to use a nonorthogonal set.

In a formal way, the "many-dimensional" infinity of configurations which are needed to expand an arbitrary function in Hilbert space may be described by defining a distortion operator

$$D(\alpha_1, \alpha_2, \ldots, \alpha_n) = D(\vec{\alpha}) \ .$$

This operator maps some arbitrary zero-order generating function ϕ_0 onto any other member ϕ_i of the basis set for the space,[2]

$$D(\vec{\alpha})\phi_0 = \phi_i \quad . \tag{4}$$

In this way, each configuration ϕ_i is indexed by a point or vector $\vec{\alpha}$. One particular point $\vec{\alpha}^0$ may define an identity operation

$$D(\vec{\alpha}^0)\phi_0 = \phi_0 \quad . \tag{5}$$

Since there is a one-to-one correspondence between members of the basis set and points $\vec{\alpha}$, it is convenient to describe the basis set by the running index $\vec{\alpha}$. Equation (4) may be rewritten as

$$\phi(\vec{\alpha}) = D(\vec{\alpha})\phi(\vec{\alpha}^0) \ . \tag{6}$$

The distortion operator is defined here to act only on the generating function $\phi_0 \equiv \phi(\vec{\alpha}^0)$.

To take a specific example, a one-parameter distortion operator $D(\alpha)$ might be defined to act on a $1s$-type Gaussian orbital of unit exponent centered at a particular point in space by the equation

$$D(\alpha)e^{-r^2} = e^{-\alpha r^2}, \quad 0 \leqslant \alpha \leqslant \infty \ . \tag{7}$$

$D(1)$ applies the identity operation. The operator D thus generates every other possible Gaussian orbital centered at the same point. The set of all possible $1s$ functions centered at a point constitutes a complete set for the expansion of any spherically symmetrical radial function.[3] Equation (6) is then just a many-dimensional extension of the same concept. D may be defined to apply distortions to one-, two-, or many-electron parts of electronic wave functions. The definition of a complete set (or subset) of functions thus requires the definition of a suitable distortion operator $D(\vec{\alpha})$, a range of application for the components α_j of $\vec{\alpha}$: $\alpha_j^i \leqslant \alpha_j \leqslant \alpha_j^f$, and a generating function $\phi(\vec{\alpha}^0)$.

Considerable care is needed in formal manipulations with such a set, since it is not orthogonal and is likely to be overcomplete. The former attribute occasions little practical restriction, at least with small systems, and most of the difficulties introduced by the latter are removed in practice by the numerical approximation.

Other definitions of a zero-order function and distortion operator are feasible. The present definition is convenient because it provides a basis $D(\vec{\alpha})\phi(\vec{\alpha}^0)$, whose members each satisfy the appropriate boundary and continuity conditions on the solution to Schrödinger's equation.

III. INTEGRAL-TRANSFORM WAVE FUNCTION

Any function ψ which can be expanded in terms of the set $D(\vec{\alpha})\phi(\vec{\alpha}^0)$ may formally be written as an integral transform

$$\psi = \int_{\vec{\alpha}^i}^{\vec{\alpha}^f} C(\vec{\alpha}) D(\vec{\alpha}) \phi(\vec{\alpha}^0)\, d\vec{\alpha}, \tag{8}$$

in terms of some arbitrary function $C(\vec{\alpha})$ of m variables. We may seek, for example, to use the definition of Eq. (7) to investigate the ground-state wave function for the hydrogen atom. Karplus and Shavitt[4] described the transform

$$e^{-r} = (1/2\sqrt{\pi}\,) \int_0^\infty \alpha^{-1.5} e^{-0.25/\alpha} e^{-\alpha r^2} d\alpha \ . \tag{9}$$

In this case then the transform weighting function is the known function

$$C(\alpha) = \alpha^{-1.5} e^{-0.25/\alpha} \ . \tag{10}$$

The exact transform has of course not been given explicitly for any many-electron system.

A form of the variational principle appropriate to this functional type of wave function follows immediately. The function $C(\vec{\alpha})$ associated with the ground-state wave function ψ has a form such that the integral expression

$$E = \int_{\vec{\alpha}^i}^{\vec{\alpha}^f} d\vec{\alpha} \int_{\vec{\alpha}^i}^{\vec{\alpha}^f} d\vec{\alpha}'\, C(\vec{\alpha})\, C(\vec{\alpha}')\, H(\vec{\alpha}, \vec{\alpha}')$$
$$\times \Big[\int_{\vec{\alpha}^i}^{\vec{\alpha}^f} d\vec{\alpha} \int_{\vec{\alpha}^i}^{\vec{\alpha}^f} d\vec{\alpha}'\, C(\vec{\alpha})\, C(\vec{\alpha}') S(\vec{\alpha}, \vec{\alpha}')\Big]^{-1} \tag{11}$$

is stationary and a minimum with respect to its variation. For excited bound states, the expression is stationary and a minimum, subject to the restriction that the wave function is orthogonal to all lower states. Here, we have

$$\begin{aligned} H(\vec{\alpha}, \vec{\alpha}') &= \int d\tau D(\vec{\alpha}) \phi(\vec{\alpha}^0) H D(\vec{\alpha}') \phi(\vec{\alpha}^0), \\ S(\vec{\alpha}, \vec{\alpha}') &= \int d\tau D(\vec{\alpha}) \phi(\vec{\alpha}^0) D(\alpha') \phi(\vec{\alpha}^0); \end{aligned} \tag{12}$$

$d\tau$ refers to all space and spin variables and H is the Hamiltonian operator. A function such as $C(\vec{\alpha})$ or an approximation to it might be described as a "configuration relaxation function" to distinguish it from two relaxation functions previously introduced.[5,6]

The exact solution to the integral variational principle [Eq. (11)] might be approximated in several ways. The most straightforward would be to put in arbitrary functions $C(\vec{\alpha})$ containing adjustable parameters and possibly adjustable limits of integration: then, to carry out the integrations analytically or numerically. Such a procedure has been independently suggested by Somorjai *et al.*[7] The approach raises interesting possibilities and may prove very useful for small systems. There do, however, seem to be serious difficulties in applying it economically to systems of several electrons. The least attractive feature seems to be that a large number of nonlinear parameters would have to be used. Moreover, a considerable degree of intuition is likely to be implicit in the choice of functional forms. Indeed, in this form, application so far has only been made to two-electron systems. The need in the general case for the solutions to be calculated using linear equations is a near-cardinal constraint. An alternative approach based on Eq. (11) and the use of differential equations derived from it is under consideration. The analogous relationship between integral and differential relationship for range and pass relaxation functions is developed in the next paper of this series.[8]

We consider, in what follows, a different scheme, which can be applied to systems of several electrons and might be expected, moreover, to converge in a predictable and rapid way on the energy and wave function for the true configuration relaxation function. Though it avoids some of the problems, particularly the need to vary nonlinear parameters, the scheme in its present form is not itself devoid of difficulties in its application to larger systems. Some of these are pointed out in later sections.

IV. DETERMINATION OF THE CONFIGURATION RELAXATION FUNCTION

The most efficient known method for integrating arbitrary many-dimensional functions such as the components of Eq. (11) is the diophantine technique of Hazlegrove,[9] Conroy,[10] and Boys.[11] With this technique, (or with any comparable numerical method) the function F must be evaluated at a set of points $\{(\vec{\alpha}, \vec{\alpha}\,')_i\}\, i=1, \ldots, n$, and the integral is approximated as a weighted sum of these values;

$$I \approx \sum_{i=1}^{n} F((\vec{\alpha}, \vec{\alpha}\,')_i)\, A((\vec{\alpha}, \vec{\alpha}\,')_i)\ . \qquad (13)$$

$A((\vec{\alpha}, \vec{\alpha}\,')_i)$ is a weighting coefficient determined by the numerical procedure. The integrals of Eq. (11) of course cannot be carried out at this point since we are ignorant of the function $C(\vec{\alpha})$. However, even with the crudest knowledge of its distribution, the numerical method can be used to determine the set of points at which the integrand *would have had* to be evaluated to give the most significant numerical estimate of the integral. This numerical integration would reduce Eq. (11) to the form

$$E \leqslant \sum_{\text{points}\,(\vec{\alpha}, \vec{\alpha}\,')_i} A((\vec{\alpha}, \vec{\alpha}\,')_i)\, C(\vec{\alpha})_i\, C(\vec{\alpha}\,')_i\, H(\vec{\alpha}, \vec{\alpha}\,')_i \times \left[\sum_{\text{points}\,(\vec{\alpha}, \vec{\alpha}\,')_i} A((\vec{\alpha}, \vec{\alpha}\,')_i)\, C(\vec{\alpha})_i\, C(\vec{\alpha}\,')_i\, S(\vec{\alpha}, \vec{\alpha}\,')_i\right]^{-1}, \qquad (14)$$

which may be rewritten as

$$E \leqslant \sum\nolimits_i B(\vec{\alpha}, \vec{\alpha}\,')_i H(\vec{\alpha}, \vec{\alpha}\,')_i \Big/ \sum\nolimits_i B(\vec{\alpha}, \vec{\alpha}\,')_i S(\vec{\alpha}, \vec{\alpha}\,')_i\ . \qquad (15)$$

The coefficients B have absorbed both the weighting coefficients A and the unknown transform weighting function.

This "most significant" n-point integral representation of the expectation value of the energy can be put into a form in which the variational principle can be applied to determine $B(\vec{\alpha}, \vec{\alpha}\,')_i$. This can obviously be done if the set of points $\{(\vec{\alpha}, \vec{\alpha}\,')_i\}$ in $2m$-dimensional space is chosen from all possible products of two m-dimensional sets $\{\vec{\alpha}_i\} \equiv \{\vec{\alpha}\,'_i\}$. Any point $(\vec{\alpha}, \vec{\alpha}\,')_i$ can now be found among the set of m^2 points $(\vec{\alpha}_i, \vec{\alpha}\,'_j)$, $i, j = 1, 2, \ldots, m$. Thus for each coefficient we have

$$B(\vec{\alpha}, \vec{\alpha}\,')_i = b(\vec{\alpha}_j)\, b(\vec{\alpha}\,'_k)\ . \qquad (16)$$

Then Eq. (15) becomes

$$E \leqslant \sum_{\vec{\alpha}_j} \sum_{\vec{\alpha}\,'_k} b(\vec{\alpha}_j)\, b(\vec{\alpha}\,'_k)\, H(\vec{\alpha}_j, \vec{\alpha}\,'_k) \times \left[\sum_{\vec{\alpha}_j} \sum_{\vec{\alpha}\,'_k} b(\vec{\alpha}_j)\, b(\vec{\alpha}\,'_k)\, S(\vec{\alpha}_j, \vec{\alpha}\,'_k)\right]^{-1}, \qquad (17)$$

which, for the discrete set of points $\vec{\alpha}_i$, is just a variational form of the conventional matrix eigenvalue equation

$$\sum_{\vec{\alpha}_j} [H(\vec{\alpha}_j, \vec{\alpha}\,'_k) - ES(\vec{\alpha}_j, \vec{\alpha}\,'_k)]\, b(\vec{\alpha}_j) = 0\ , \qquad (18)$$

where $\vec{\alpha}\,'_k = \vec{\alpha}\,'_1, \vec{\alpha}\,'_2, \ldots, \vec{\alpha}\,'_n$ runs over the full set of points in m dimensions. The solutions of the equation supply, as usual, the energies of both ground and excited states. Actually, the restriction of having two identical sets may be relaxed:

$$\{\vec{\alpha}_i\} \neq \{\vec{\alpha}\,'_i\}\ .$$

The solution of Eq. (18) then still leads to an estimate of E which converges on the true energy.[12] In the specific examples used here, the same set has been used for $\{\vec{\alpha}_i\}$ and $\{\vec{\alpha}\,'_i\}$.

The numerical scheme has allowed a reduction of the many-dimensional variational integral-transform expression to a set of discrete configurations among which interaction is allowed. The information which is lost in going from the exact transform to this approximation to it is supposed to be of the least significance from the standpoint of the evaluation of the expectation value of the energy. The set of points from the numerical integration procedure provides, in this sense, the most efficient set of configurations with which to carry out the m-dimensional integration:

$$\int d\vec{\alpha}\, C(\vec{\alpha})\, H(\vec{\alpha}, \vec{\alpha}\,'), \quad \int d\vec{\alpha}\, C(\vec{\alpha})\, S(\vec{\alpha}, \vec{\alpha}\,') .$$

The method with $\{\vec{\alpha}_i\} \equiv \{\vec{\alpha}_i'\}$ yields an upper bound to the energy. Moreover, *the energy is the lowest which could have been obtained with any function* $C(\vec{\alpha})$ *which might have been inserted in Eq.* (11) *using the same set of points to approximate the integral with the best possible set of weights.* This is important, since the approach is not now confined to an integral transform of any particular type. The method, in contrast to that of Ref. 7, yields the optimal transform (within an n-point approximation). The inefficiency inherent in the transfer of functional forms from fragments to aggregates is thus excluded from the start.

The value of the optimal transform weighting function $C(\vec{\alpha})$ at the integration points can be determined at the end if necessary, since the weighting coefficients are given and $b(\vec{\alpha}_i)$ are known from the solution of Eq. (18). They might be used as the basis for an interpolation if the function were desired.

Conroy[10] has indicated that his diophantine integration scheme might be used to evaluate integrals over 12-dimensional functions, for example, with errors of the order of parts per million using about 6000 points. Conventional secular equations of over twice this size have been routinely solved.[13] However, the application of the variational principle allows the use, with impunity, of very sparse grids of points, which would be totally unreliable for numerical integration.

V. POINT DISTRIBUTION FUNCTION

An effective way to carry out a Monte Carlo oriented integration involves the use of a function whose derivative varies approximately as the integrand.[14,15] This is used to weight the distribution of points most heavily in the most important parts of space. Each integral might then be considered a special case. However, although the over-all character of such a function significantly affects the convergence, the details are unimportant. The rough form may be based on the zero-order function $\phi(\vec{\alpha}^0)$ or on any other convenient crude approximation to the wave function. In common with the aims of the two previous papers, semitheoretical arguments may conveniently be introduced to give rough forms to certain functions which may be expected to help speed convergence. This is valid when there is a defined limit which readily can be attained for small problems and which is independent of such props. The point distribution function can clearly be handled in this way. With a sufficiently great number of points, the results are independent of the function. Moreover, when a rather smaller set is used, the results are anticipated to be insensitive to crudities in its form.

In the following simple applications to approximate the radial-limit wave functions for some small atoms, the function $\epsilon(\eta, r > r')$ has been used. ϵ is defined as the integral of the electron density of a normalized Slater-type orbital $\chi(\eta, r)$ of exponent η outside a radius r'. In spherical polar coordinates, we have

$$\epsilon(\eta, r > r') = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{r'}^{\infty} \chi(\eta, r)\, dr \;, \tag{19}$$

$$\epsilon(\eta, r > r') = \epsilon(1, r > \eta r') \quad . \tag{20}$$

It is a function varying smoothly and monotonically with r' between one and zero, whose derivative with respect to r' represents an approximate measure of the relative importance of the integrand

$$\chi(\eta, r')\, \chi(\eta, r') \approx E^{-1} \chi(\eta, r') \times H_{\text{effective}}\, \chi(\eta, r') \;.$$

Analytical expressions for ϵ for Slater orbitals have been given previously.[2]

The maximum radial density of an orbital,

$$r^{n-1} e^{-\xi r^m} F(\theta, \phi)$$

(Slater or Gaussian), which is a product of radial and angular functions, with an exponent ξ and principle quantum number n, is a distance r from the orgin:

$$r = (n/m\xi)^{1/m} \quad . \tag{21}$$

A distribution function was chosen to weight the basis orbitals with maximum radial density at r' in proportion to the derivative of the curve of r' against $\epsilon(\eta, r > r')$. Thus (where η is the orbital exponent of the corresponding orbital in the generating function), we have

$$D(\epsilon)\, r^{n-1} e^{-\eta r} = e^{-\gamma r m}, \quad 0 \leqslant \epsilon \leqslant 1 \tag{22}$$

where $\epsilon(\eta, r > r')$ has been inverted to give r' as a function of ϵ :

$$r' = \sigma(\eta, \epsilon) \quad \text{and} \quad \gamma = n/m r'^m \quad . \tag{23}$$

The point distribution function for $m = 1$ (Slater basis) or $m = 2$ (Gaussian basis) to represent the integral transform of a function which is a 1s orbital of exponent η in zero order is

$$d(\xi) = (n/m\xi)^{(2n+1)/m}(1/m\xi)\exp[-2\eta(n/m\xi)^{1/m}]. \tag{24}$$

This particular distribution function is not intended to be represented here as having anything better than a crude, but convenient, form.

The point distribution is itself a "relaxation function" whose form might be determined by the condition that the expectation value of the energy be stationary with respect to its variation. Thus, even for a meager grid of points there is recourse to an objective criterion which might override any intuitive form. General variations are nonlinear operations, and thus unsatisfactory for the present purpose. There is, however, one particular variation, a uniform scaling of the distribution, which can at least for atoms be optimized with recourse to the solution of linear equations alone. At any rate, for fairly small changes of scale, the effect of such a scaling is entirely equivalent to that of applying the same radial scaling[16] to each of the configurations ϕ_i. The whole calculation does not have to be repeated for a succession of trial values of the scaling factor. It is, however, necessary to determine how the transform weighting functions $C(\vec{\alpha})_i$, at the points where the function is evaluated, relax with change in scale factor to keep the energy expectation value at a minumum for all values of the scale factor. Linear perturbation variation equations which may sometimes be used for carrying out the appropriate reduction are proposed in Paper IV.[8] This rescaling transformation requires no new matrix elements.

The curve for a Slater orbital basis has its maximum at 0.5 (that is, half the exponent of the generating orbital), and the numbers of basis orbitals are distributed equally about 0.75. This *ad hoc* distribution function may thus appear to be far from perfect. Gross imperfections in the weight of the distribution can, however, be eliminated by applying the optimum uniform scaling to it, to bring the maximum into a more favorable position. The rescaled results quoted later may be taken then merely to illustrate the effect of altering the point distribution functions in a computationally simple way to one of the same over-all form but a more favorable general position. When a sufficiently large basis can be used, such refinements should become unnecessary.

Since the configurations are essentially random, any other arbitrary configuration [$\phi(\vec{\alpha}^0)$ for example] can be included with the set.

VI. RADIAL-LIMIT CALCULATIONS FOR He; Li AND Be

Preliminary applications were made to approximate the radial limit of the helium atom. The Eckart function[17]

$$\phi(\vec{\alpha}^{\,0}) = \phi(\alpha_1^0, \alpha_2^0) = (e^{-1.19 r_1} e^{-2.18 r_2} - e^{-2.18 r_1} \times e^{-1.19 r_2})\, \chi_{\text{part}}^{\text{spin}} = \phi(1.19, 2.18) \tag{25}$$

was used for the generating function. The distortion operator was defined to act according to the equation

$$D(\vec{\alpha})\,\phi(\vec{\alpha}^{\,0}) = D(\alpha_1, \alpha_2)\,\phi(1.19, 2.18) = (e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} - e^{-\alpha_2 r_1} e^{-\alpha_1 r_2})\, \chi_{\text{part}}^{\text{spin}} . \tag{26}$$

Using the pseudorandom numbers of the numerical integration procedure and the point distribution function, sets of 26 configurations of the form of Eq. (26) were generated using Hazlegrove's[9] method and Conroy's[10] method. The tendency towards near-linear dependencies among the matrix elements, characteristic of overcompleteness, indicates a need for special methods in the solution of the secular equations (18). A convenient method is discussed elsewhere.[18]

In the first three rows of Table I are compared

TABLE I. Radial limit of the helium atom.[a]

	26-point configuration interaction (CI) treatment	Slater or Gaussian transform	Energy (a.u.)
1	Hazlegrove[b]	S	− 2.878 59
2	Conroy, case 1[c]	S	− 2.878 61
3	Conroy, case 2	S	− 2.878 55
4	Hazlegrove, random number generator reversed	S	− 2.878 44
5	Hazlegrove, row 1 rescaled	S	− 2.878 98
6	Conroy, case 1, row 2 rescaled	S	− 2.878 96
7	Conroy, case 2, row 3 rescaled	S	− 2.878 96
8	Conroy, case 1[c]	G	− 2.866 76
9	Conroy, case 1, row 8 rescaled	G	− 2.873 30
10	Conroy, case 2,[d] $\phi(\vec{\alpha}^0) = 1s^2$	S	− 2.878 68

[a] Exact energy = 2.879 03 from C. Schwartz, Phys. Rev. 126, 1015 (1962); C. Bunge, *ibid.* 168, 92 (1968).

[b] All, except the tenth treatment, use as a generating function the Eckart function (Ref. 17) $E(\phi(\vec{\alpha}^0)) = -2.8757$. In no case was $\phi(\vec{\alpha}^0)$ included with the set of configurations.

[c] The point at the origin was arbitrarily approximated as $(10^{-7}, 10^{-7})$.

[d] $\phi(\vec{\alpha}^0) = -2.847\,65$.

three methods of generating the pseudorandom configurations. (The case numbers indicated are Conroy's designation.) There seem to be no significant differences. The inaccuracy appears in each case in the fifth significant figure. This is at least as good as would be expected for an integration using such a sparse set of points.[10] In the fourth row is shown the application of the distortion operator Eq. (26) to a generating function $\phi(2.18, 1.19)$ [where the orbitals have been reversed as compared to Eq. (25)]. As expected, there is no significant difference.

The results obtained by rescaling[8] the first three treatments (rows 5–7) show a narrowing of the energy deficit. (The scale change to correct the distribution function optimally is close to 2, which shows how poor the original distribution function actually was).

Using a Gaussian transform [row 8, $m = 2$ in Eqs. (22) and (24)] gives a substantially less accurate 26-configuration function, though some improvement is obtained by rescaling (row 9). (There is in practice no weight in this distribution function for orbitals of exponent greater than 10, so the electron density in energetically important regions close to the nuclei cannot be represented properly.)

The expected insensitivity of the method to the generating function $\phi(\vec{\alpha}^{\,0})$ is confirmed for this system by the results in row 10. In this case, $\phi(\vec{\alpha}^{\,0})$ was a function in which both electrons were confined to a single Slater orbital of exponent 1.6875.

In the case of lithium, the exact radial limit is not known, though it is close to -7.448.[19] Four treatments were carried through, using in each case Clementi's minimal Slater-type orbital wave function[20] as the generating function. In the first row of Table II, the point distribution function Eq. (24) was used. Rescaling (row 2) produces a significant improvement. In row 3, the reasonable improvement of making the distribution function for the 1s electrons peak at the exponent of the corresponding orbital in $\phi(\vec{\alpha}^{\,0})$ was effected. The last row indicates that this result is, as expected, less sensitive to rescaling of the point distribution function.

TABLE II. Radial limit of lithium atom.[a] Slater transform used throughout. $\phi(\vec{\alpha}^{\,0})$ energy -7.418. See Ref. 20. In no case was $\phi(\vec{\alpha}^{\,0})$ actually included in the set.

	26-point treatment	Energy (a.u.)
1	Conroy, case 2	−7.446 79
2	Conroy, case 2, row 1 rescaled	−7.447 35
3	Conroy, case 2, 1s point distribution function shifted to have maximum at exponent of $\phi(\vec{\alpha}^{\,0})$	−7.447 17
4	Conroy, case 2, row 3 rescaled	−7.447 54

[a] Cf. values −7.447 56, Ref. 19; −7.447 20, A. W. Weiss, Phys. Rev. 122, 1826 (1961); −7.447 71, S. Hameed, S. Seung Hui, J. I. Musher, And J. M. Schulman, J. Chem Phys. 51, 502 (1969); −7.447 33, L. G. Heikes and G. A. Gallup, J. Chem. Phys. 52, 888 (1970).

TABLE III. Radial limit of beryllium atom. (Hartree-Fock energy: −14.573[a]; S-limit energies: −14.5920,[b] −14.5865,[c] −14.5895,[d] −14.5911,[e] −14.5883,[f] −14.5900.[g])

	Treatment	Energy (a.u.)
1	30 point, Hazlegrove[h]	−14.581 20
2	30 point, row 1 rescaled, point distribution function	−14.585 75
3	19 point, Hazlegrove[i]	−14.562 94
4	19 point, row 1 rescaled, point distribution function	−14.585 45

[a] E. Clementi, IBM J. Res. Develop. Suppl. 9, 2 (1965).

[b] C. Bunge, Phys. Rev. 168, 92 (1968).

[c] R. E. Watson, Phys. Rev. 119, 170 (1960).

[d] U. Kaldor and F. E. Harris, Phys. Rev. 183, 1 (1969).

[e] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[f] J. S. Sims and S. Hagstrom, (unpublished), (22 configurations with optimization of some nonlinear exponents).

[g] L. G. Heikes and G. A. Gallup, J. Chem. Phys. 52, 888 (1970).

[h] $E(\phi(\vec{\alpha}^{\,0}))$ −14.557, Ref. a.

[i] $E(\phi(\vec{\alpha}^{\,0}))$ −14.528, Ref. 21, and Eq. (27).

The results of four treatments of the radial limit of beryllium are shown in Tables III and IV. In the first calculation, 30 points were generated using Hazlegrove's scheme. The point distribution function Eq. (24) for the 1s orbitals was scaled by a factor of 2, and the generating function $\phi(\vec{\alpha}^{\,0})$ was taken to be Clementi's optimized $1s^2 2s^2$ Slater orbital based function.[20] Even for this extremely sparse 30-point grid, the error appears in the fourth significant figure and can be reduced to the fifth by rescaling the point distribution function.

An alternative generating function was formed from four 1s Slater orbitals of different orbital exponents, the two inner and two outer orbitals being paired as a singlet. In conventional notation, we have

$$\phi(\vec{\alpha}^{\,0}) = \left|\underset{\underline{\alpha}}{1s}\;\underset{\underline{\beta}}{1s'}\;\underset{\underline{\alpha}}{1s''}\;\underset{\underline{\beta}}{1s'''}\right| + \left|\underset{\underline{\beta}}{1s}\;\underset{\underline{\alpha}}{1s'}\;\underset{\underline{\beta}}{1s''}\;\underset{\underline{\alpha}}{1s'''}\right|$$

TABLE IV. Exponents and coefficients for 30-point Be wave function (Table III, row 1).

	$D(\vec{\alpha}_i)\ \phi\ (\vec{\alpha}^0)$				
	exponents				coefficients
1	4.581 42	19.459 02	0.832 29	1.096 64	−0.000 192
2	3.742 86	14.527 44	0.380 88	0.778 25	−0.004 573
3	11.899 67	12.098 27	0.779 55	0.555 36	−0.001 249
4	5.556 68	10.543 53	1.867 94	0.466 00	−0.009 068
5	2.903 33	9.421 13	0.890 18	0.697 72	−0.059 665
6	8.387 14	8.551 65	0.462 76	0.960 68	0.005 640
7	6.833 85	7.845 81	0.730 44	1.596 62	0.032 880
8	1.770 29	7.253 22	1.506 43	1.295 08	−0.054 634
9	6.591 10	6.742 77	0.955 31	0.868 94	−0.038 468
10	8.789 68	6.294 00	0.519 49	0.632 47	−0.012 003
11	3.051 10	5.892 69	0.683 72	0.314 62	0.006 562
12	5.380 44	5.528 56	1.310 83	0.621 63	−0.037 802
13	12.933 40	5.193 84	1.030 70	0.855 06	0.009 571
14	3.877 12	4.882 42	0.568 58	1.260 33	0.221 006
15	4.436 85	4.589 33	0.638 25	1.676 07	−0.155 871
16	25.357 63	4.310 27	1.177 24	0.977 84	−0.001 133
17	4.729 64	4.041 27	1.121 35	0.708 86	0.220 878
18	3.608 89	3.778 37	0.614 67	0.480 53	0.069 530
19	11.066 20	3.517 17	0.592 78	0.543 75	0.046 960
20	5.740 78	3.252 04	1.075 56	0.766 24	−0.312 922
21	2.746 91	2.974 50	1.236 10	1.074 44	0.067 344
22	8.023 73	2.668 78	0.659 97	2.762 26	0.010 428
23	7.093 60	2.293 98	0.545 61	1.120 03	0.290 338
24	2.136 17	1.542 18	0.993 02	0.790 47	−0.010 369
25	6.363 17	2.204 87	1.393 64	0.566 75	−0.248 991
26	9.240 18	2.604 53	0.705 90	0.450 38	−0.049 438
27	3.193 10	2.918 83	0.493 73	0.686 68	0.107 157
28	5.211 20	3.200 19	0.923 02	0.944 11	0.518 701
29	14.274 44	3.466 91	1.644 83	1.529 26	0.002 485
30	4.012 30	3.728 37	0.753 61	1.332 91	−0.444 247

$$- \left|\begin{array}{cccc} 1s & 1s' & 1s'' & 1s''' \\ \underline{\alpha} & \underline{\beta} & \underline{\beta} & \underline{\alpha} \end{array}\right| - \left|\begin{array}{cccc} 1s & 1s' & 1s'' & 1s''' \\ \underline{\beta} & \underline{\alpha} & \underline{\alpha} & \underline{\beta} \end{array}\right| , \tag{27}$$

where $\underline{\alpha}$, $\underline{\beta}$ refer to the spin function, and $|\ |$ refers to a determinantal product. The four exponents had been approximately optimized.[21] For the last two calculations, only 19 points were used.

VII. DISCUSSION

One significant distinction between the form of configuration interaction advocated here and that conventionally used is that each separate configuration is on the same footing as all the others; there is no distinguishable ground-state configuration. It may not be desirable to order them in some hierarchy according to the sizes of their coefficients in the expansion [Eq. (3)] or in terms of their contribution to a perturbation sum. If any one of them is extracted from a more or less complete set, compensating changes run all through the remaining members. The pseudorandom nature of the configurations is illustrated in Table IV by the set of orbital exponents which define the configurations for one particular treatment of Be (each orbital appears in only one configuration). It is not to be expected that the removal of any one of these configurations would alter the energy in a dramatically more extreme way than the removal of any other, if the set were more or less complete.

There are advantages in this simplicity. When a large set of points is used, for example, it is not obvious that a basis of Gaussian orbitals would be any less satisfactory than one of Slater orbitals. There are no nonlinear operations, and "correlation" is built in from the start.

There is considerable divergence of opinion as to the accuracy which is possible using diophantine integration. For these particular very simple and naive applications, the accuracy which might have been expected of a diophantine integration scheme[10] was indeed attained. However, even if the method in the context of certain integrations is less accurate than might be expected, there is considerably greater hope for accuracy in the present application, since the result is pinned by a variational upper bound. In a loose sense, one might visualize the coefficients arising from the variational minimization of the energy as corresponding to some optimal regression or progressive procedure.[22] In any case, the approach is not tied to a particular integration procedure, and others may give advantages in different contexts. The calculations themselves are intended to be mainly of pedagogical and exploratory interest. Monte Carlo oriented techniques only become relatively efficient for problems of high dimensionality; four or five dimensions has been quoted as the break-even point. The technique is likely then to be of more use for calculations of greater scope. It should be possible to extend considerably the number of configurations used without great difficulty.

As convergence towards a radial (or any other) limit is pursued, the problem of overcompleteness will become more and more pressing. It is inherent in the randomness with which the configurations are selected. Techniques other than direct solution of a matrix eigenvalue equation may have to be followed.

The most serious difficulty with systems of many more electrons will probably be the large number of two-electron integrals which must be calculated; even though only a very small portion of the total number implicit in the basis are actually required. New, perhaps statistical, methods for their generation and use may be indicated.

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Radiative Lifetimes for the $2p\pi\,^3\Pi_u$ State of the Hydrogen Molecule*

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A calculation is made of the radiative electric dipole transition probabilities coupling the vibrational levels of the $2p\pi\,^3\Pi_u$ and the $2s\sigma\,^3\Sigma_g$ electronic states of hydrogen. The radiative lifetimes for those vibrational levels lying above the ground state are found to be approximately 100 μsec. The lifetime of the ground vibrational level, decaying by magnetic dipole and electric quadrupole emissions, is estimated to be 1 msec. Finally, a calculation is made of the dependence of the radiative lifetimes upon an external electric field.

I. INTRODUCTION

The $2p\pi\,^3\Pi_u$ electronic state of the hydrogen molecule is especially interesting because the radiative lifetimes for this state are three to four orders of magnitude longer than the radiative lifetimes for neighboring electronic states. The reasons for these long lifetimes are threefold: The lowest vibrational level of the $^3\Pi_u$ state lies lower than any *g* (*gerade*) level of the triplet spectrum and radiative dipole transitions from this vibrational level are forbidden[1]; for the higher vibrational levels, dipole transitions can occur to the $2s\sigma^3\Sigma_g$ state, but here the transition probabilities are relatively small, in part due to the small energy differences and in part to large scale cancellations in the Frank-Condon factors.

The lowest vibrational level of the $^3\Pi_u$ electronic state can undergo radiative decay to the $^3\Sigma_u$ state through a combination of magnetic dipole and electric quadrupole emissions and with a lifetime estimated to be approximately 1 msec. This level is also susceptible to spontaneous predissociation into two ground-state atoms arising from perturbations coupling the $2p\pi\ ^3\Pi_u$ and $2p\sigma\ ^3\Sigma_u$ states. For the "allowed predissociations," induced by rotational-electronic perturbations,[2] the Kronig selection rules[3] allow for predissociation of the $^3\Pi_u$ vi-