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The factorized wave function

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The consequences of factorizing an exact wave function into the product of an antisymmetric part and an exponential part are discussed. The exponent is taken as a symmetric real function and satisfies the equations of infinite-order perturbation theory. Practical calculations to determine both factors are performed by minimizing two functionals and the roles these play are analyzed. The relation between this procedure and that suggested by Boys and Handy for the transcorrelated wave function is pointed out. Illustrative calculations on helium show that good wave functions are obtained by both procedures.

I. INTRODUCTION

In contemporary research on the calculation of accurate wave functions for electronic systems, "the correlation problem," there is a growing emphasis on the use of operator techniques. The recent reviews by McWeeny[1] and Schaefer[2] illustrate this and give detailed references. These techniques enable certain perturbation-theory ideas to be implemented, but they have the disadvantage of making the wave function very abstract so that an intuitive appreciation of its significance is very difficult to achieve.

The possibilities of solving the correlation problem using wave functions which are just functions of the coordinates have not yet been exhausted, however, and can be extended by incorporating ideas more typical of the operator approach. One example of this is described in a recent publication[3] where the exact wave function for the closed-shell ground state of an atom or molecule is expressed in the factorized form

$$\psi = e^{L}\varphi \tag{1}$$

and equations are derived for φ, the orbital determinant, and L, the multielectron correlation function. This wave function is based on an orbital approach and consequently is easily interpreted, but it has the exponential factor typical of operator wave functions. It also has very close connections with the Boys-Handy theory of transcorrelated wave functions.[4]

In this paper a more general factorization of the wave functions is proposed in Sec. II. This permits φ to be an open-shell wave function or to be a combination of several determinants so that the earlier constraint to a single determinant can be dropped. It allows φ and L to be determined by minimizing functionals in which the balance of effort between the two remains flexible. In Sec. III the significance of optimizing a parameter in the wave function is examined in more detail.

The relation between this treatment of correlation and other treatments, including that of Boys and Handy, is investigated further in Secs. IV and V using various simple wave functions for the helium atom. In certain circumstances this treatment may be identical with the transcorrelated treatment.

II. FORMULATION

The Schrödinger equation for an atom or the Born-Oppenheimer equation for the electronic motion in a molecule is written

$$H\psi = W\psi \ , \tag{2}$$

where H is the electronic Hamiltonian and ψ the electronic wave function. This wave function is now written in the factorized form (1). The factor φ is an antisymmetric function of the electrons and has the spatial and spin symmetry of the ground state. A single determinant is usually the simplest form of wave function to satisfy these requirements, but more elaborate functions are permitted. This function satisfies trivially the eigenvalue equation

$$H_0\varphi = w_0\varphi \ , \tag{3}$$

where $H_0 = w_0 |\varphi \times \varphi|$, $w_0 = \langle \varphi, H\varphi\rangle$ and $\langle \varphi, \varphi\rangle = 1$.

The correlation function L is symmetric to electron exchange and to any spatial symmetry. It is here taken as a real function. By substituting the product (1) into Eq. (2) it follows that

$$e^{-L}He^{L}\varphi \equiv (H + [HL] + \tfrac{1}{2}[[HL]L])\varphi = W\varphi \ , \tag{4}$$

which is the transcorrelated form[4] of the Schrödinger equation. The commutator expansion here terminates because L is a function and H involves no more than the second derivative. The corresponding operator equation has an infinite expansion. When φ is fixed, Eq. (4) determines L. Its nature becomes more clear if a perturbation potential is defined by

$$V=H+\tfrac{1}{2}[[HL]L]-H_0 \ . \tag{5}$$

The mean value of V is then

$$w_1=\langle\varphi, V\varphi\rangle/\langle\varphi,\varphi\rangle=W-w_0 \tag{6}$$

and the equation for L becomes

$$[HL]\varphi=(w_1-V)\varphi \ . \tag{7}$$

This has exactly the form of the equation for the first-order perturbed wave function in the Dalgarno-Lewis-Schwartz formalism.[5] It does have one feature, however, which alters its nature, namely, that V which is regarded as fixed in (7) depends on L through its definition in (5) and has to be made consistent with both equations. This feature is typical of infinite-order perturbation theory.[6] Thus, in general, there will be an iteration between L and V. The convergence of this iteration has to be established in each instance, but the discussion given by Armour[7] makes this plausible when $[[HL]L]$ is bounded. In some circumstances the constraint that L is real may prevent convergence but this does not seem to arise for ground states in the absence of magnetic fields.

The differential equation (7) for L cannot usually be solved exactly. During the first iteration, when φ is an orbital wave function and L is zero in V, it can be shown, by methods analogous to those of Sinanoğlu,[8] that L is a sum of two-electron functions, each dependent on two orbitals and approximate forms for these can be found. This geminal form of L is likely to represent a very good wave function. When the iteration is continued by inserting this L into V the new solution must also have three- and four-electron functions and so eventually L involves functions of all the electrons simultaneously. This differential-equation approach is feasible for atoms since (7) does not contain any of the integral operators of H_{HF} and consequently is easier to solve than Sinanoğlu's perturbation equation.

An alternative and more practical method[5] is to incorporate suitable parameters into a trial function for L and to minimize the Hermitian functional

$$\mathfrak{F}(L)=\langle\varphi,\{L(V-\omega_1)+(V-\omega_1)L-\tfrac{1}{2}[[HL]L]\}\varphi\rangle \ , \tag{8}$$

where V is not varied during the optimization but is defined using (5) with the best previous estimate of L. By modifying V it is possible to find consistent values for these parameters.

Although L is defined as the solution of (7), subject to (5), for *any* given φ it will generally be more efficient to devote effort to the improvement of φ rather than to the refinement of L. One reason for this is that the iteration involved in finding L may not converge until φ itself is sufficiently close to ψ. Another reason is that the techniques of improving φ are more familiar. This improvement can be effected by introducing parameters into φ and minimizing the functional

$$\mathcal{E}(\varphi)=\langle\varphi,(H+\tfrac{1}{2}[[HL]L])\varphi\rangle/\langle\varphi,\varphi\rangle \ , \tag{9}$$

where L is kept fixed during the optimizing. If L is a sum of geminals the extra term in $\mathcal{E}$ involves three-electron integrals and the evaluation of these becomes the limiting factor in the calculation. $\mathfrak{F}$ also involves three-electron integrals. Practical considerations must play the major role in deciding whether to introduce flexibility into φ or L. This double optimizing procedure[3] has the advantage of retaining the maximum degree of choice.

III. SIGNIFICANCE OF PARAMETER OPTIMIZATION

The use of functionals to optimize approximate wave functions may disguise the underlying processes of solving the equations so it is useful to investigate in more detail the significance of the various stages in the calculation.

If $\mathcal{E}(\varphi)$ is optimized without any constraint on φ, then the optimum φ will satisfy the eigenvalue equation

$$(H+\tfrac{1}{2}[[HL]L])\varphi=W\varphi \tag{10}$$

or, because of (3),

$$V\varphi=w_1\varphi \ . \tag{11}$$

Thus the best φ will be an eigenfunction of the Hermitian part of the transcorrelated equation.[7] If a trial φ contains a parameter λ whose best value λ_0 is fixed by minimizing $\mathcal{E}$, then the result is equivalent to the replacement of φ in $\mathcal{E}$ by its linear variation around λ_0

$$\varphi:=\varphi(\lambda_0)+(\lambda-\lambda_0)\frac{\partial\varphi}{\partial\lambda_0} \ . \tag{12}$$

The stationary condition on $\mathcal{E}$ then becomes the equation for λ_0

$$\left\langle\frac{\partial\varphi}{\partial\lambda_0}, (H+\tfrac{1}{2}[[HL]L]-W)\varphi\right\rangle=0 \tag{13}$$

or

$$\left\langle\frac{\partial\varphi}{\partial\lambda_0}, (V-w_1)\varphi\right\rangle=0 \ . \tag{14}$$

Thus, optimization with respect to λ is the same as diagonalization of V in the subspace spanned by φ and $\partial\varphi/\partial\lambda_0$. An alternative interpretation of this process is that φ is varied to minimize the mean value of V, i.e.,

$$\frac{\partial}{\partial\lambda}\frac{\langle\varphi, V\varphi\rangle}{\langle\varphi,\varphi\rangle}=0 \ . \tag{15}$$

Thus the more φ is optimized the smaller becomes the right-hand side of (7) until in the limit this equation becomes homogeneous.

The introduction of a parameter μ into a trial L can be examined in a similar way. The replacement

$$L := L(\mu_0) + (\mu - \mu_0)\frac{\partial L}{\partial \mu_0} \tag{16}$$

in $\mathfrak{F}$ leads to the equation for μ_0, the optimum μ,

$$\left\langle \varphi \frac{\partial L}{\partial \mu_0}, (V - w_1 + [HL])\varphi \right\rangle \;, \tag{17}$$

which is one component of the differential equation (7) satisfied by the best L. Increasing the number of parameters extends the space of functions within which this equation is satisfied.

Boys and Handy have drawn special attention to the problem of redundancy that arises when parameters are optimized in each factor of a product wave function. Unless countermeasures are taken, a modification of L may so influence the optimization of φ that the entire process becomes unstable. One way of achieving stability is to introduce into L a linear parameter μ such that

$$\frac{\partial L}{\partial \mu} = \frac{1}{\varphi}\frac{\partial \varphi}{\partial \lambda_0} \;, \tag{18}$$

where λ_0 is the value of one of the parameters in φ optimized using L_0 where

$$L = L_0 + \mu\left(\frac{\partial L}{\partial \mu}\right) . \tag{19}$$

$\mathfrak{F}$ is then optimized with respect to μ. From (17) the equation for μ is

$$\left\langle \varphi \frac{\partial L}{\partial \mu}, (V - w_1 + [HL])\varphi \right\rangle = 0 \tag{20}$$

while, from (14), λ_0 is determined by

$$\left\langle \frac{\partial \varphi}{\partial \lambda_0}, (V - w_1)\varphi \right\rangle = 0 \; . \tag{21}$$

Thus, using (18)

$$\left\langle \varphi \frac{\partial L}{\partial \mu}, [HL]\varphi \right\rangle = \left\langle \frac{\partial \varphi}{\partial \lambda_0}, [HL]\varphi \right\rangle = 0 \; . \tag{22}$$

It is now possible to evaluate $\mathcal{E}$ with this modified L as

$$\begin{aligned}\mathcal{E} &= \Big\{\langle \varphi, V\varphi\rangle + \left\langle \varphi, \left[[HL_0]\frac{\partial L}{\partial \mu}\right]\varphi \right\rangle \mu \\ &\quad + \tfrac{1}{2}\left\langle \varphi, \left[\left[H\frac{\partial L}{\partial \mu}\right]\frac{\partial L}{\partial \mu}\right]\varphi \right\rangle \mu^2 \Big\}\Big/\langle \varphi, \varphi\rangle \\ &= \Big\{\langle \varphi, V\varphi\rangle + \left\langle \varphi, \left[[HL]\frac{\partial L}{\partial \mu}\right]\varphi \right\rangle \mu \\ &\quad - \tfrac{1}{2}\left\langle \varphi, \left[\left[H\frac{\partial L}{\partial \mu}\right]\frac{\partial L}{\partial \mu}\right]\varphi \right\rangle \mu^2 \Big\}\Big/\langle \varphi, \varphi\rangle\end{aligned} \tag{23}$$

but

$$\begin{aligned}&\left\langle \varphi, \left\{[HL_0]\frac{\partial L}{\partial \mu} - \frac{\partial L}{\partial \mu}[HL_0]\right\}\varphi \right\rangle \\ &\qquad = -2\left\langle \varphi \frac{\partial L}{\partial \mu}, [HL_0]\varphi \right\rangle = 0,\end{aligned} \tag{24}$$

so that $\mathcal{E}$ becomes independent of μ to first order,

$$\frac{\partial \mathcal{E}}{\partial \mu} = 0 \; . \tag{25}$$

It follows from this that the optimization of $\mathcal{E}$ with respect to λ will not be disturbed to first order by a change in μ, i.e.,

$$\frac{\partial^2 \mathcal{E}}{\partial \lambda \partial \mu} = 0 \; . \tag{26}$$

In principle, a redundant parameter like μ is needed in L corresponding to each parameter λ in φ, but in practice, it is likely that a smaller number will suffice to produce numerical stability.

When L contains redundant parameters the equations of this theory become very similar to those of the Boys-Handy theory.[4] Thus (13) and (22) are the Hermitian and anti-Hermitian parts of their orbital equation

$$\left\langle \frac{\partial \varphi}{\partial \lambda}, (H + [HL] + \tfrac{1}{2}[[HL]L] - W)\varphi \right\rangle = 0 \tag{27}$$

and (17) can be rewritten as the correlation equation

$$\left\langle \varphi \frac{\partial L}{\partial \mu}, (H + [HL] + \tfrac{1}{2}[[HL]L] - W)\varphi \right\rangle = 0 \; . \tag{28}$$

The contraction equation, to fix a redundant parameter μ, is not unique in this theory. One equation which they use is

$$\left\langle \varphi \frac{\partial L}{\partial \mu}, [HL]\varphi \right\rangle = 0 \tag{29}$$

and this is exactly (22). Another of their contraction equations is exactly (25), but in the circumstances here, when (18) is satisfied, (25) and (29) become equivalent.

The Boys-Handy theory has been applied to Ne and to LiH with remarkably good results that demonstrate clearly the potential of this approach. In these calculations L was expressed as a sum of two-electron functions of the form

$$g_{ij} = r_{ij}/(a + r_{ij}) \; . \tag{30}$$

This form is chosen in order to introduce an interelectronic cusp into the wave function without disrupting the long-range behavior of the orbital factor in the wave function. For this reason it is given the same form for all electrons. The orbitals are involved in L only through the redundant functions which are added to this g_{ij} to enable the contraction equations to be satisfied. Unfortunately, this form leads to integrals which cannot be evaluated in terms of simple functions and Boys and Handy resorted to numerical quadrature to complete their calculation. Since it has proved difficult to adapt and extend these numerical procedures, few attempts have been made to follow up their lead.

An alternative solution to this practical problem is to restrict the functional forms so that analytic integration is possible. One such choice uses for L the sum of two-electron functions such as

$$g_{ij} = e^{-Ar_{ij}^2} \ , \tag{31}$$

since this Gaussian form, together with Gaussian forms for the orbitals, gives integrals which can be entirely evaluated using the familiar F_n functions related to the error function. Calculations on He using correlation functions having one or two Gaussians of this type and with orbitals having two or three Gaussians, have been reported by Handy.[9] These calculations have been repeated here and reproduce Handy's results apart from a mislabeling of the wave functions in one of his tables. Thus the analytic variant of this method is unambiguous and reliable. The calculations have also been extended to include five Gaussians in the representation of the orbital and the change in the correlation energy is generally less than 10^{-4} hartree, showing that the results have become stable to small changes in the orbitals.

In a practical calculation using the functionals $\mathcal{E}$ and $\mathfrak{F}$ it is proposed that L should be expressed as a sum over Gaussians using at least two different exponents and with redundant functions around each nucleus. Experience from the He calculation suggests that this is an adequate representation of the interelectronic cusp. The entire Boys-Handy experience suggests that this direct approach to L will be more efficient than the indirect approach through pair functions. The computing cost of manipulating the three-electron integrals is expected to be high, but against it has to be set the compact form of the wave function and the greatly increased possibility of interpreting its parts physically.

IV. HELIUM-ATOM EXAMPLE

One possible reason for the obvious delay in the appreciation of the Boys-Handy theory is that the examples they gave seemed so complicated that the equations themselves were not illuminated. In this section a calculation for He is presented which is simple enough to be checked quickly but can be used to illustrate the various equations of the Boys-Handy theory and also of the alternative approach suggested here. In its simplest form this wave function is

$$\psi = \exp[-a(r_1+r_2)+br_{12}] \ . \tag{32}$$

The mean energy of helium with this ψ is

$$\begin{aligned}\langle H\rangle &\equiv \langle\psi, H\psi\rangle/\langle\psi,\psi\rangle \\ &= (8a^4 - 15a^3b + 11a^2b^2 - 5ab^3 + b^4 - 27a^3 \\ &\quad + 31a^2b - 3ab^2 - b^3)/\ (8a^2 - 5ab + b^2) \ . \end{aligned} \tag{33}$$

If a and b are determined by minimizing $\langle H\rangle$ the results reproduce those originally found by Hylleraas.[10] This calculation is labeled B in Tables I and II, while the simpler calculation in which $b = 0$ is A. It is also possible to determine a and b by minimizing the energy variance. This optimization was performed numerically and is denoted by C.

In the Boys-Handy theory this function (32) is written

$$\varphi = e^{-a(r_1+r_2)} \ , \quad L = br_{12} - c(r_1+r_2) \ . \tag{34}$$

The transcorrelated energy is then

$$\begin{aligned} W_{\text{TC}} &= \langle\varphi,\ e^{-L}He^{L}\varphi\rangle/\langle\varphi,\varphi\rangle = \mathcal{E}(\varphi) \\ &= a^2 - \tfrac{27}{8}a - b^2 - c^2 + \tfrac{5}{4}bc \ . \end{aligned} \tag{35}$$

TABLE I. Wave functions for He using various criteria.

Function criteria	a	b	c	$a+c$	$-W_{\text{TC}}$	$-\langle H\rangle$	Variation	Deviation ϵ
A min$\langle H\rangle$	1.6875	0	0	1.6875	⋯	2.8477	0.897	0.0137
B min$\langle H\rangle$	1.8580	0.2547	0	1.8580	⋯	2.8896	0.171	0.0053
C min Var	1.9651	0.3265	0	1.9651	⋯	2.8835	0.104	0.0101
D trans	1.8638	0.2821	0	1.8638	2.8961	2.8890	0.157	0.0050
E trans	1.6595	0.2683	0.1956	1.8551	2.8997	2.8893	0.168	0.0049
$F\left\{\begin{matrix}\text{trans}\\ \text{min } \mathcal{E},\mathfrak{F}\end{matrix}\right\}$	1.6875	0.2703	0.1689	1.8564	2.8922	2.8893	0.167	0.0049
G min $\mathcal{E},\mathfrak{F}$	1.6875	0.1719	0	1.6875	2.8772	2.8726	0.474	0.0065
H min $\mathfrak{F}$	2	0.3672	0	2	2.8848	2.8786	0.115	0.0114

TABLE II. Mean values of operators.

Function	r^{-1}	r	r^2	r_{12}^{-1}	r_{12}	$-\vec{r}_1\cdot\vec{r}_2$	Ranks
A	3.375	1.778	2.107	1.0550	1.296	0	62
B	3.378	1.805	2.195	0.9774	1.386	0.1010	32
C	3.491	1.753	2.075	0.9934	1.361	0.1163	52
D	3.351	1.823	2.241	0.9617	1.407	0.1141	26
E	3.353	1.820	2.233	0.9659	1.402	0.1086	26
F	3.353	1.820	2.234	0.9653	1.402	0.1094	24
G	3.151	1.926	2.494	0.9300	1.460	0.0848	40
H	3.503	1.751	2.075	0.9865	1.368	0.1288	56
Exact (Ref. 10)	3.377	1.859	2.387	0.9458	1.422	0.0647	

The parameter c may be fixed using the contraction equation (25), i.e.,

$$\frac{\partial W_{\mathrm{TC}}}{\partial c}=0, \tag{36}$$

which yields $c=\frac{5}{8}b$, while a is fixed using the orbital equation

$$\frac{\partial W_{\mathrm{TC}}}{\partial a}=0, \tag{37}$$

which yields $a=\frac{27}{16}$. This value of a is exactly that obtained when $b=0$ so that the orbital and correlation equations have been effectively separated. The correlation equation to fix b is

$$\langle[r_{12}-\tfrac{5}{8}(r_1+r_2)]\varphi,\,(e^{-L}He^{L}-W_{\mathrm{TC}})\varphi\rangle=0 \tag{38}$$

which reduces to

$$\tfrac{170}{1024}b^2+\tfrac{39}{64}ab-\tfrac{5}{8}a^2+\tfrac{113}{128}a=0\,. \tag{39}$$

The numerical solution of this is shown under F in the tables. A less flexible wave function D in which $c=0$ and the orbital and contraction equations are

$$16a-10b=27\,,\quad 80a-128b=113\,. \tag{40}$$

is also shown.

An alternative contraction equation used by Boys and Handy can be expressed as

$$\frac{\partial}{\partial c}\langle\varphi,L^2\varphi\rangle=0 \tag{41}$$

and this leads to a slightly different relation for c:

$$c=\tfrac{35}{48}b\,. \tag{42}$$

This calculation E makes clear that the contraction equation (41) is not equivalent to the earlier one (36) though the numerical differences are not very significant.

The theory of this paper can be applied to (34) with $c=0$. The energy functional becomes

$$\mathcal{E}(a)=a^2-\tfrac{27}{8}a-b^2\,. \tag{43}$$

The potential V can be evaluated in convenient form as the function

$$V=(a-2)/r_1+(a-2)/r_2+1/r_{12}-b^2\,, \tag{44}$$

where the final term arises from L. Since this term is a constant, no iteration between φ and V is required. The second functional also can be evaluated simply:

$$\mathcal{F}(b)=b^2+b\left(\tfrac{113}{64}-\tfrac{5}{4}a\right). \tag{45}$$

The optimal values for a and b must satisfy

$$\frac{\partial\mathcal{E}}{\partial a}=0\,,\quad\frac{\partial\mathcal{F}}{\partial b}=0 \tag{46}$$

and are shown as G in the tables. Since $a=2$ reduces V to a form without singularities at the nuclei, it is of some interest to include a calculation H in which φ is fixed and only b is optimized.

When all three parameters in (34) are included, these results become modified. The expression for $\mathcal{E}$ becomes identical with that in (35) so that the orbital parameter is $a=\frac{27}{16}$. The optimization of $\mathcal{F}$ with respect to b and c yields the equations

$$c=\tfrac{5}{8}b+\tfrac{27}{16}-a\,, \tag{47}$$

$$2ab+\tfrac{17}{32}bc-\tfrac{5}{4}ac-\tfrac{5}{4}a^2+\tfrac{113}{64}a=0\,, \tag{48}$$

and, although these equations are different, their solution is identical with the transcorrelated calculation F. This is to be expected from the discussion of Sec. III since

$$\frac{1}{\varphi}\frac{\partial\varphi}{\partial a}=-(r_1+r_2)=\frac{\partial L}{\partial c}\,, \tag{49}$$

so that c is a redundant parameter in the sense used there.

V. NUMERICAL RESULTS

The results of these calculations of the wave function and the energy are summarized in Table I. To facilitate comparisons of the full wave function the value of $a+c$ is included. A parameter which is not optimized is shown with the value zero.

The accuracy of an approximate wave function may be assessed by various criteria. The most familiar is that the corresponding value of the mean energy $\langle H\rangle$ should be as low as possible. The table shows a steady decline in $\langle H\rangle$ as the number of parameters increases with the wave function E and F approaching closely the minimum value of wave function B. Another criterion of accuracy is the magnitude of the variance. It is noteworthy that all the functions except A and G have variances between that of the minimum variance function C and the minimum energy function B. As may be expected, the difference between W_{TC} and $\langle H\rangle$ is roughly correlated with the variance. By this criterion F is superior to E, the function which it most nearly resembles. A third criterion is the deviation ϵ of the functions from a good approximation[11] to the exact wave function

$$\epsilon = |\psi - \psi_{\text{exact}}|^2 . \tag{50}$$

By this criterion D, E, and F are seen to be superior even to B.

These comparisons suggest the conclusion that these nonconventional methods of calculating a wave function give results which improve as the number of parameters is increased and become close to the minimum energy results. Further evidence for this conclusion is shown in Table II which lists the mean values of various operators along with the Pekeris values (Ref. 12). In each column the value closest to the exact one has been underlined. For each property the wave functions were ranked according to their closeness to its true value. The final column in Table II shows the sum of these ranks for the six properties in that table and the three in Table I. The best overall agreement is obtained with F, though D, E, and B are not much poorer.

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