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Lower-Bound Method for Atomic Calculations*

L. J. Kijewski
Physics Department, Monmouth College, West Long Branch, New Jersey
and
J. K. Percus
Courant Institute of Mathematical Sciences and Physics Department, New York University, New York, New York 10012
(Received 9 July 1970)

In the reduced-density-matrix variational method, a trial density matrix $\Gamma_t^{(2)}$ is varied subject to physical realizability conditions in order to calculate the ground-state energy $E_0 = \frac{1}{2}N \min \mathrm{Tr} H^{(2)}\Gamma_t^{(2)}$. Here we expand $\Gamma_t^{(2)}$ in a finite basis of Hartree-Fock geminals and apply a number of equalities to reduce the parameter space of $\Gamma_t^{(2)}$. The method is completely general, but application is made only to the C^{++} ion, where a six-geminal expansion coupled with positivity of $\Gamma_t^{(2)}$ recovers the Hartree-Fock result.

I. INTRODUCTION

It is known that the ground-state energy $E_0(N)$ for a system of electrons with Hamiltonian

$$H = \sum_{i=1}^{N} T(i) + \sum_{i<j} V(i,j) \tag{1.1}$$

can be written in terms of a two-body reduced density matrix

$$\Gamma^{(2)}(\vec{x}_1', \vec{x}_2' | \vec{x}_1, \vec{x}_2) \equiv \int \cdots \int dx_3 \cdots dx_N \sum_\alpha C_\alpha \times \psi_\alpha(\vec{x}_1, \vec{x}_2', \vec{x}_3, \ldots, \vec{x}_N) \psi_\alpha(\vec{x}_1, \ldots, \vec{x}_N),$$

where

$$\sum_\alpha C_\alpha = 1, \quad C_\alpha \geq 0 \tag{1.2}$$

via the relation

$$E_0(H) = \min_{\text{all } \Gamma^{(2)}} \tfrac{1}{2}N \mathrm{Tr} H^{(2)}\Gamma^{(2)}, \tag{1.3}$$

where

$$H^{(2)} \equiv T(1) + T(2) + (N-1)V(1,2). \tag{1.4}$$

The mechanics of carrying out the minimization required for (1.3) is, however, far from trivial.

There are a number of obvious necessary conditions which $\Gamma^{(2)}$ must satisfy – normalization, positive definiteness, antisymmetry – and a number of less obvious ones which have gradually come to light.[1] If the $\Gamma^{(2)}$ in (1.3) are taken as the set of all trial densities $\Gamma_t^{(2)}$ consistent with these conditions, without assuring that each comes from the right-hand side of (1.2) – is N realizable – then one obtains a lower bound to the energy $E_0(H)$. A lower bound is of course guaranteed only if one varies over *all* $\Gamma_t^{(2)}$; any representation of the trial $\Gamma_t^{(2)}$ by a finite expansion will result in an upper bound to the lower bound, a fact which must be borne in mind when any claims of accuracy are made.

In previous papers,[2] it was shown how an expansion of $\Gamma^{(2)}$ in terms of the lowest states of helium results in a one-particle density matrix for a series of partially ionized atoms which does not satisfy the Pauli principle, a fair indication that the restrictions employed were not very efficient. The purpose of this paper is to report on still another necessary symmetry condition for N real-

izability of $\Gamma^{(2)}$, and to use it for an improved trial density matrix for the atom C^{++} which does satisfy the Pauli principle. A companion purpose is that of replacing the helium geminal expansion functions used when somewhat naive ideas of the structure of $\Gamma^{(2)}$ were adequate by a systematic expansion in simpler Hartree-Fock geminals – i.e., an orbital expansion. The computed energy resulting from the severely truncated basis set of this initial investigation is very good indeed – precisely the Hartree-Fock energy – and one may anticipate rapid improvement as further orbitals are appended.

II. CATALOG OF CONDITIONS

Accurate lower bounds to energy levels are usually more difficult to obtain than upper bounds. Our aim is to rectify this situation, if possible, and the reduced-density-matrix technique for a many-body system has the advantage of working with quite simple quantities. In particular, as we have pointed out, a lower bound to the ground-state energy $E_0(H)$ of a system with Hamiltonian of the form (1.1) is obtained if $\frac{1}{2}N\,\mathrm{Tr}H^{(2)}\Gamma^{(2)}$ is minimized over all positive definite functions of four arguments $\Gamma^{(2)}(\vec{x}_1', \vec{x}_2'|\vec{x}_1, \vec{x}_2)$, antisymmetric in each pair of arguments ($\vec{x}$ denotes space and spin), with $\mathrm{Tr}\Gamma^{(2)} = 1$. This lower bound is, however, typically so low as to be useless. The art in the field consists of finding appropriate further restrictions on $\Gamma^{(2)}$ required by its construction [see (1.2)] from an ensemble of N-particle wave functions. These restrictions fall into two classes, inequalities and equalities. The former are in principle sufficent to obtain exact results but are hard to apply in practice. The latter are presumably insufficient, but their power has only come to be realized of late, and they are extremely easy to use in practice. In fact, our intention is to use equality conditions as extensively as possible, reserving the inequalities for crucial points to keep the computation honest.

Equalities satisfied by $\Gamma^{(2)}$ are of two basic types, Hamiltonian dependent and symmetry dependent. The first arises from the observation that for the ground-state wave function $|\psi_0\rangle$ satisfying $H|\psi_0\rangle = E_0|\psi_0\rangle$, we have $[H, |\psi_0\rangle\langle\psi_0|] = 0$. Thus $\mathrm{Tr}\{\sum Q(i) \times [H, |\psi_0\rangle\langle\psi_0|]\} = 0$ for any one body Q, integrating down to[2, 3]

$$\mathrm{Tr}[Q(1)+Q(2)][H^{(2)}, \Gamma^{(2)}] = 0 \tag{2.1a}$$

or

$$\mathrm{Tr}[Q(1)+Q(2), H^{(2)}]\Gamma^{(2)} = 0. \tag{2.1b}$$

Of course these remain true for a $\Gamma^{(2)}$ constructed from any eigenfunction of H. An important example of (2.1b), especially for Coulomb interactions, is the virial theorem obtained by setting $Q = (i\hbar)^{-1}\vec{r}\cdot\vec{p}$. For a nonrelativistic atom,

$$T = p^2/2m - Ze^2/r, \quad V(1,2) = e^2/r_{12}, \tag{2.2}$$

and (2.1b) becomes the standard

$$\mathrm{Tr}[H^{(2)} + (p_1^2+p_2^2)/2m]\Gamma^{(2)} = 0. \tag{2.3}$$

More generally, if $\Gamma^{(2)}$ is expanded in a set of orbitals $\{\phi_\alpha(\vec{x})\}$, it is appropriate to choose $Q = |\phi_\gamma\rangle\langle\phi_{\gamma'}|$. Since $[H^{(2)}, \Gamma^{(2)}]$ is symmetric in particles 1 and 2 anyway, (2.1a) then yields

$$\langle\phi_\gamma(1)|\mathrm{Tr}_2[H^{(2)}, \Gamma^{(2)}]|\phi_{\gamma'}(1)\rangle = 0. \tag{2.4}$$

The symmetries we have in mind are of the form

$$[\sum_1^N Q(i), H] = 0 \tag{2.5}$$

for Hermitian Q, so that the ground state may be taken to satisfy

$$\sum Q(i)\psi_0 = q\psi_0\,. \tag{2.6}$$

It follows then that

$$|\psi_0\rangle\langle\psi_0|\sum Q(i) = \sum Q(i)|\psi_0\rangle\langle\psi_0| = q|\psi_0\rangle\langle\psi_0|\,. \tag{2.7}$$

Applying the trace over particles $3, \ldots, N$ to the left-hand equation of (2.7), we obtain

$$[Q(1)+Q(2), \Gamma^{(2)}(1,2)] = 0\,, \tag{2.8}$$

which has been used before. Applying the same operation to the right-hand equation yields instead[4]

$$Q(1)\Gamma^{(1)}(1) + (N-1)\,\mathrm{Tr}_2 Q(2)\,\Gamma^{(2)}(1,2) = q\Gamma^{(1)}(1), \tag{2.9}$$

where

$$\Gamma^{(1)}(\vec{x}_1'|\vec{x}_1) = \int d\vec{x}_2\,\Gamma^{(2)}(\vec{x}_1', \vec{x}_2|\vec{x}_1, \vec{x}_2) \tag{2.10}$$

is the one-particle reduced density matrix. The new restriction (2.9) in fact implies (2.8). In this paper we shall not be concerned with symmetries involving two-body sums; instead it will suffice to note that (2.9) remains true if Q is a non-Hermitian operator for which (2.6) holds.

Proceeding to the well-tilled field of restrictions in the form of inequalities, we have already commented on the positive definiteness of $\Gamma^{(2)}$ as a matrix; it follows that $\Gamma^{(1)}$ is positive definite (more precisely, both are positive semidefinite). But the eigenvalues of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are bounded from above as well. The relevant theorems are

$$0 \le \lambda(\Gamma^{(1)}) \le 1/N\,, \tag{2.11a}$$

$$0 \le \lambda(\Gamma^{(2)}) \le 1/(N-1)\,, \quad N \text{ even}$$
$$\le 1/N\,, \quad N \text{ odd}. \tag{2.11b}$$

Eq. (2.11a) is the justly famed Pauli exclusion principle, which says that at most one of the N electrons can occupy a given orbital; the corresponding principle for $\Gamma^{(2)}$ is also very well known in the density-matrix lore but has proved relatively ineffective. A considerably stronger relation

$$\lambda(\Gamma^{(2)}) \geq \frac{2}{N(N-1)} + \frac{N-2}{N-1}\,\mathrm{Tr}\Gamma^{(1)}\left(\frac{1}{N} - \Gamma^{(1)}\right) \tag{2.12}$$

has been suggested (for even N) but this remains conjectural. An enormous number of more detailed inequalities exist, upon which the ultimate success of the reduced-density-matrix program undoubtedly rests, but we shall not discuss these here.

III. EXPLICIT FORM FOR $L=0$, $S=0$ STATE

In order to deal with $\Gamma^{(2)}$ in practice, it is convenient to operate in some definite representation. If the $\{u_{\alpha\beta}(1, 2)\}$ are a complete orthonormal set of (antisymmetric) geminals, we can of course expand as

$$\Gamma^{(2)}(1', 2'|1, 2) = \sum_{\alpha\beta\alpha'\beta'} A_{\alpha'\beta'\alpha\beta} u_{\alpha'\beta'}(1', 2') u^*_{\alpha\beta}(1, 2). \tag{3.1}$$

Here A must be Hermitian, $\mathrm{Tr}A = \sum A_{\alpha\beta\alpha\beta} = 1$, and the eigenvalues of A satisfy (2.11b). In Ref. 2, a trial $\Gamma^{(2)}_t$ for the ion C^{++} was constructed by restricting the $u_{\alpha\beta}$ to the first 14 states of helium (unitarily equivalent to $H^{(2)}$ for C^{++}), i.e., 1^1S 2^3S (three states), 2^1S, and 2^3P (nine states). Application of a number of restrictions to this trial function resulted in an excessively low computed energy, with the Pauli principle not being automatically satisfied. There was the strong suggestion that the higher autoionizing (doubly excited) states would be required for improvement.

Here, we initiate a more systematic development by basing the expansion upon a truncated set of orbitals $\{\phi_\alpha(1)\}$ and therefore choosing the geminal basis as

$$u_{\alpha\beta}(1, 2) = (1/\sqrt{2})[\phi_\alpha(1)\phi_\beta(2) - \phi_\beta(1)\phi_\alpha(2)], \tag{3.2}$$

with redundancy allowed in that $u_{\beta\alpha} = -u_{\alpha\beta}$. To handle rotational invariance most efficiently, we select the ϕ_α as appropriate orthonormal eigenstates

$$\phi_\alpha(\vec{r}, \sigma) = \phi_{n_\alpha l_\alpha}(r) Y^{m_\alpha}_{l_\alpha}(\hat{r}) \chi_{s_\alpha}(\sigma) \ . \tag{3.3}$$

We also combine the geminals (3.2) into simultaneous eigenfunctions of L^2, L_z, S^2, S_z:

$$u^{LS}_{\alpha\beta m_L m_S}(1, 2) = \sum_{\substack{m_\alpha + m_\beta = m_L \\ s_\alpha + s_\beta = m_S}} C(\alpha\beta L) C_S(\alpha\beta S)\, u_{\alpha\beta}(1, 2), \tag{3.4}$$

where the $C(\alpha\beta L)$ are the standard Clebsch-Gordan coefficients[5]

$$C(\alpha\beta L) = C(l_\alpha, l_\beta, L;\ m_\alpha, m_\beta) \ , \tag{3.5}$$

and similarly for spin. For a state of zero total angular momentum and zero spin, it has been shown[2] [by using $Q = L_x \pm i L_y$, $S_x \pm i S_y$, L_z, S_z in (2.8)] that only geminal pairs of identical L, S, m_L, m_S occur in the geminal expansion of $\Gamma^{(2)}$, and in fact with equal weight. Thus we may write

$$\Gamma^{(2)} = \sum A(\alpha'\beta'\alpha\beta LS)\Delta(\alpha'\beta'\alpha\beta)\, |u^{LS}_{\alpha'\beta' m_L m_S}(1, 2)\rangle \times \langle u^{LS}_{\alpha\beta m_L m_S}(1, 2)|, \tag{3.6}$$

where A is independent of $m_\alpha, m_{\alpha'}, \ldots, s_\beta, s_{\beta'}$ and $\Delta = 1$ only if $m_\alpha + m_\beta = m_{\alpha'} + m_{\beta'}$, $s_\alpha + s_\beta = s_{\alpha'} + s_{\beta'}$, otherwise $\Delta = 0$. In detail, then,

$$\Gamma^{(2)} = \sum A(\alpha'\beta'\alpha\beta LS)\Delta(\alpha'\beta'\alpha\beta) C(\alpha'\beta' L) C^*(\alpha\beta L) \times C_S(\alpha'\beta' S) C^*_S(\alpha\beta S) |u_{\alpha'\beta'}(1, 2)\rangle \langle u_{\alpha\beta}(1, 2)| \ . \tag{3.7}$$

The pair density $\Gamma^{(2)}$ will enter our computations only in certain specific forms. Let us consider these. First there is the reduced one-body density $\Gamma^{(1)}$ obtained by taking the trace over particle 2. Using the orthonormality of the orbital basis $\{\phi_\alpha\}$, and the symmetry of the Clebsch-Gordan coefficients[5] in the form

$$C(\beta\alpha L) = (-1)^{l_\alpha + l_\beta - L} C(\alpha\beta L) \ , \tag{3.8}$$

it follows that

$$\Gamma^{(1)} = \sum [A(\alpha'\beta\alpha\beta LS) + (-1)^{l_\alpha + l_\beta}(-1)^{L+S} \times A(\alpha'\beta\beta\alpha LS)]\, \Delta(\alpha'\beta\alpha\beta) C(\alpha'\beta L) C^*(\alpha\beta L) \times C_S(\alpha'\beta S) C^*_S(\alpha\beta S) |\phi_{\alpha'}(1)\rangle \langle \phi_\alpha(1)| . \tag{3.9}$$

Applying the orthogonality condition[5]

$$\sum_{m_\beta} C(l_\alpha l_\beta L;\ m_\alpha m_\beta) C^*(l_{\alpha'} l_\beta L;\ m_\alpha m_\beta) = \frac{2L+1}{2l_\alpha + 1}\, \delta_{l_\alpha, l_{\alpha'}} \ , \tag{3.10}$$

we then readily find

$$\Gamma^{(1)}(1'|1) = \sum_{\alpha\alpha'\beta L S} [A(\alpha'\beta\alpha\beta LS) + (-1)^{l_\alpha + l_\beta}(-1)^{L+S} A(\alpha'\beta\beta\alpha LS)]\, \delta_{l_\alpha, l_{\alpha'}} \times \left(\frac{2L+1}{2l_\alpha + 1}\right)\left(\frac{2S+1}{2}\right) \phi_{n_{\alpha'} l_\alpha}(r'_1) \phi^*_{n_\alpha l_\alpha}(r_1) \Lambda_{l_\alpha}(\hat{r}'_1, \hat{r}_1) \ , \tag{3.11}$$

where Λ_{l_α} is the projection onto $l=l_\alpha$:

$$\Lambda_l(\hat{r}_1', \hat{r}_1)=\sum_m Y_l^m(\hat{r}_1')\,Y_l^m(\hat{r}_1)^* = \frac{2l+1}{2\pi}\,P_l(\hat{r}_1'\cdot\hat{r}_1)\ . \tag{3.12}$$

We will also need (2.9) for $Q=S_z$. The required evaluation is very similar except for the additional sum

$$\sum_{s_{\alpha'}s_\beta} C(\tfrac{1}{2}\tfrac{1}{2}S;\, s_\alpha s_\beta)\,C^*(\tfrac{1}{2}\tfrac{1}{2}S;\, s_\alpha s_\beta)\,s_\beta\chi_{s_\alpha}(\sigma')\,\chi^*_{s_\alpha}(\sigma) = \tfrac{1}{2}(S-1)\sum s\,\chi_s(\sigma')\,\chi_s^*(\sigma) \tag{3.13}$$

most easily obtained by direct substitution. Instead of (3.11), then

$$\mathrm{Tr}_2 S_z(2)\Gamma^{(2)}(1,2)=\sum_{\alpha\alpha'\beta LS}\ [A(\alpha'\beta\alpha\beta LS) + (-1)^{l_\alpha+l_\beta}(-1)^{L+S}A(\alpha'\beta\beta\alpha\,LS)]\delta_{l_{\alpha'},l_\alpha} \times\left(\frac{2L+1}{2l_\alpha+1}\right)\left(\frac{S-1}{2}\right)\phi_{n_{\alpha'}l_\alpha}(r_1')\phi^*_{n_\alpha l_\alpha}(r_1) \times\Lambda_{l_\alpha}(\hat{r}_1', \hat{r}_1)S_z(1)\ . \tag{3.14}$$

For a spinless ground state, then $q=0$ in (2.9) and on substituting (3.11) and (3.14) we have the useful

$$\sum_{\beta LS}(2L+1)\delta_{l_\alpha,\,l_{\alpha'}}[A(\alpha'\beta\alpha\beta LS)+(-1)^{l_\alpha+l_\beta}(-1)^{L+S} \times A(\alpha'\beta\beta\alpha\,LS)]\,[(1-S)N-S-2]=0. \tag{3.15}$$

Next, we have the very extensive set (2.4). It is only necessary to observe that

$$\mathrm{Tr}\,H^{(2)}(1,2)\,|u_{\alpha'\beta'}(1,2)\rangle\langle u_{\alpha\beta}(1,2)|\,[\,|\phi_{\gamma'}(1)\rangle \times\langle\phi_\gamma(1)| + |\phi_{\gamma'}(2)\rangle\langle\phi_\gamma(2)|\,] = \delta_{\alpha\gamma'}\langle u_{\gamma\beta}|H^{(2)}|u_{\alpha'\beta'}\rangle + \delta_{\beta\gamma'}\langle u_{\alpha\gamma}|H^{(2)}|u_{\alpha'\beta'}\rangle$$

and similarly

$$\mathrm{Tr}\,|u_{\alpha'\beta'}(1,2)\rangle\langle u_{\alpha\beta}(1,2)|H^{(2)}(1,2)[\,|\phi_{\gamma'}(1)\rangle\langle\phi_\gamma(1)| + |\phi_{\gamma'}(2)\rangle\langle\phi_\gamma(2)|\,] = \delta_{\alpha'\gamma}\langle u_{\alpha\beta}|H^{(2)}|u_{\gamma'\beta'}\rangle + \delta_{\beta'\gamma}\langle u_{\alpha\beta}|H^{(2)}|u_{\alpha'\gamma'}\rangle\ .$$

Since $\mathrm{Tr}_2[H^{(2)}(1,2),\ \Gamma^{(2)}(1,2)]$ is diagonal in spin, we lose no information by setting $m_\gamma=m_{\gamma'}$ and summing over m_γ. Combining (2.4) and (3.7), we find

$$\begin{aligned}\sum_{\alpha'\beta'\beta LS}&[A(\alpha'\beta'\gamma'\beta LS)+(-1)^{l_\beta+l_{\gamma'}}(-1)^{L+S}A(\alpha'\beta'\beta\gamma' LS)]\Delta(\alpha'\beta'\gamma'\beta)(2S+1)\\ &\times C(\alpha'\beta' L)\,C^*(\gamma'\beta L)[\langle\overline{\phi}_\gamma\overline{\phi}_\beta|H^{(2)}|\overline{\phi}_{\alpha'}\overline{\phi}_{\beta'}\rangle+(-1)^S\langle\overline{\phi}_\beta\overline{\phi}_\gamma|H^{(2)}|\overline{\phi}_{\alpha'}\overline{\phi}_{\beta'}\rangle]\\ =\sum_{\alpha\beta\beta' LS}&[A(\gamma\beta'\alpha\beta LS)+(-1)^{l_{\gamma'}+l_{\beta'}}(-1)^{L+S}A(\beta'\gamma\alpha\beta LS)]\Delta(\gamma\beta'\alpha\beta)(2S+1)\\ &\times C(\gamma\beta' L)\,C^*(\alpha\beta L)[\langle\overline{\phi}_\alpha\overline{\phi}_\beta|H^{(2)}|\overline{\phi}_{\gamma'}\overline{\phi}_{\beta'}\rangle+(-1)^S\langle\overline{\phi}_\beta\overline{\phi}_\alpha|H^{(2)}|\overline{\phi}_{\gamma'}\overline{\phi}_{\beta'}\rangle]\,,\end{aligned} \tag{3.16}$$

where $\overline{\phi}_\alpha$ indicates that the spin factor is removed from ϕ_α. The ubiquitous combination of A's occurring in (3.11), (3.15), (3.16) is of course due to our use of $u_{\alpha\beta}$ and $u_{\beta\alpha}$ independently in the geminal expansion. Since $u_{\beta\alpha}=-u_{\alpha\beta}$, we can without loss of generality define

$$A(\beta'\alpha'\alpha\beta LS)=(-1)^{l_{\alpha'}+l_{\beta'}}(-1)^{L+S}A(\alpha'\beta'\alpha\beta\ LS)\ , \tag{3.17}$$

$$A(\alpha'\beta'\beta\alpha LS)=(-1)^{l_\alpha+l_\beta}(-1)^{L+S}A(\alpha'\beta'\alpha\beta LS)$$

and so reduce the combination to a single term.

Finally, we complete our enumeration of the quantities required for the general $L=S=0$ ground state by observing that for the energy itself

$$E_0=\tfrac{1}{2}N\sum A(\alpha'\beta'\alpha\beta LS)\,\Delta(\alpha'\beta'\alpha\beta)\,C(\alpha'\beta' L)\,C^*(\alpha\beta L) \times C_S(\alpha'\beta' S)\,C_S^*(\alpha\beta S)\,\langle u_{\alpha\beta}|H^{(2)}|u_{\alpha'\beta'}\rangle\ . \tag{3.18}$$

IV. APPLICATION TO C^{++}

As a primitive first step in assessing the utility of the technique we have discussed, we reconsider $C^{++}(N=4, Z=6)$, the first $N>2$ atomic ground state with $L=S=0$. The smallest number of orbitals we can use is clearly just four, and four are sufficient to construct a Hartree-Fock state, a not unreasonable approximation at this primitive stage. Our question then is whether we have enough restrictions to at least reproduce the Hartree-Fock energy and perhaps density matrix, noting of course that the Hartree-Fock $\Gamma^{(2)}$ must be consistent with any N-realizability condition we impose. If this is the case, we can hope to achieve rapid convergence as further orbitals and appropriate restrictions are added.

As our four-orbital basis, we shall take[6]

$$\phi_{10s}=\phi_1(r)\chi_s(\sigma),\quad \phi_1(r)=(\mu^3a^3/\pi)^{1/2}e^{-\mu ar}, \tag{4.1}$$

$$\phi_{20s} = \phi_2(r)\chi_s(\sigma), \quad \phi_2(r) = (\mu^5/3\pi N)^{1/2}[re^{-\mu r} - (3A/\mu)e^{-\mu br}],$$

with the parameters $\mu a = 5.74$, $\mu b = 4.82$, $a = 3.14$, $A = (a+b)^3/(1+a)^4$, $N = 1 - 48A(1+b)^4 + 3A^2/b^3$. These are fairly good simple approximations to the 1s and 2s Hartree-Fock orbitals of C^{++}, yielding a ground-state energy of $-36.38e^2/a_0$ compared to experimental $-36.59e^2/a_0$, and we certainly shall not need greater accuracy at this stage of development. The four orbitals then combine to six geminals: three singlets,

$$|1'S\rangle \equiv 1s^2, \quad |2'S\rangle \equiv (1s\,2s)_{S=0}, \quad |ae\rangle \equiv 2s^2,$$

and one triplet,

$$|0\rangle, \ |+1\rangle, \ |-1\rangle \equiv (1s\,2s)_{S=1},$$

with S_z explicitly indicated. Hence our trial density matrix in the form (3.7), assumed real, can be expressed as

$$\begin{aligned}\Gamma_t^{(2)} = {} & A|1'S\rangle\langle 1'S| + Y_1|1'S\rangle\langle 2'S| + Y_1|2'S\rangle\langle 1'S| \\ & + B|2'S\rangle\langle 2'S| + P|ae\rangle\langle ae| + Y_2|1'S\rangle\langle ae| \\ & + Y_2|ae\rangle\langle 1'S| + C|+1\rangle\langle +1| + C|0\rangle\langle 0| + C| \\ & -1\rangle\langle -1| + Y_3|2'S\rangle\langle ae| + Y_3|ae\rangle\langle 2'S| \ . \end{aligned} \tag{4.2}$$

Equation (4.2) reduces to simple Hartree-Fock when $A = B = C = P = \frac{1}{6}$, $Y_1 = Y_2 = Y_3 = 0$. Let us now see to what extent this is preordained.

Since all orbital angular momenta are zero, only the one-body symmetry associated with spin is available. There are now three independent conditions [(2.9), (3.15)]; combined with normalization, $\mathrm{Tr}\Gamma^{(2)} = 1$, they yield immediately

$$A = P, \quad B = \tfrac{1}{2} - 2P, \quad C = \tfrac{1}{6}, \quad Y_3 = -Y_1 \ . \tag{4.3}$$

Only one independent restriction [(2.4), (3.16)] now exists, e.g., $\langle \phi_{10\,1/2}|\mathrm{Tr}_2[H^{(2)}, \Gamma^{(2)}]|\phi_{20\,1/2}\rangle = 0$, as well as the virial theorem (2.3), and these can be used to express Y_1 and Y_2 numerically in terms of P (see Table I). The next step would normally be to write the energy expectation in terms of the free parameter P and minimize with respect to P. However, in the present case of (4.2), (4.3), $\Gamma_t^{(1)}$ reduces to

$$\begin{aligned}\Gamma_t^{(1)} = {} & \tfrac{1}{4}|\phi_{10\,1/2}\rangle\langle\phi_{10\,1/2}| + \tfrac{1}{4}|\phi_{10\text{-}1/2}\rangle\langle\phi_{10\text{-}1/2}| \\ & + \tfrac{1}{4}|\phi_{20\,1/2}\rangle\langle\phi_{20\,1/2}| + \tfrac{1}{4}|\phi_{20\text{-}1/2}\rangle\langle\phi_{20\text{-}1/2}| , \end{aligned} \tag{4.4}$$

TABLE I. Eigenvalues of $\Gamma^{(2)}$ for allowed range of P.

P	Y_1	Y_2	λ_1	λ_2	λ_3
3/36	−0.5573	−2.9989	3.2922	0.1234	−2.9156
4/36	−0.3715	−1.9993	2.2503	0.1378	−1.8882
5/36	−0.1858	−0.9996	1.2085	0.1522	−0.8607
6/36	0.0000	0.0000	0.1667	0.1667	0.1667
7/36	0.1858	0.9996	1.1941	0.1811	−0.8752
8/36	0.3715	1.9993	2.2215	0.1955	−1.9170
9/36	0.5573	2.9989	3.2489	0.2100	−2.9589

independent of P. Thus the kinetic energy, and the total energy by virtue of the virial theorem, is independent of P, taking on precisely its Hartree-Fock value. Only the eigenvalues of the singlet part of $\Gamma^{(2)}$ are listed, since for our trial $\Gamma^{(2)}$, the triplet eigenvalues are $\frac{1}{6}$. For this table, $\mu = 1.8272175$.

The more profound question, as an indication of the convergence of the procedure of which we exhibit only the first step, is whether subtle and extensive restrictions are required to force $\Gamma_t^{(2)}$ to its Hartree-Fock form. Since $\Gamma_t^{(1)}$ is already in this form, the Pauli principle is no help. As Table I indicates, the corresponding $\Gamma^{(2)}$ condition (2.11b) that all eigenvalues be bounded by $\frac{1}{3}$ renders substantial assistance: $\lambda_1 \leq \frac{1}{3}$ requires that P lie in the range $\frac{1}{6} \pm \frac{1}{450}$, very close to Hartree-Fock. However, as Table I also indicates, the much more basic restriction that $\Gamma_t^{(2)}$ be positive semidefinite, i.e., that $\lambda_3 \geq 0$, results in precisely the same bound, $P = \frac{1}{6} \pm \frac{1}{450}$. Thus an inequality which is neither subtle nor extensive proves sufficient.

V. CONCLUSION

With the systematic use of equality conditions on $\Gamma^{(2)}$, one can carry through the minimization of $\mathrm{Tr}H^{(2)}\Gamma^{(2)}$ with a small amount of labor for truncated $\Gamma^{(2)}$ expansions. The method is general and so can be applied to any atomic system, the number of available conditions increasing as the expansion of $\Gamma^{(2)}$ is given new orbitals. For example, the commutator condition (3.16) contains $\frac{1}{2}n(n-1)$ independent relations for n spin-free orbitals, and the one-body symmetry restrictions increase similarly with n. For the very primitive expansion used here, the positivity of $\Gamma^{(2)}$ was nearly sufficient to specify the form of $\Gamma^{(2)}$ uniquely, but it is anticipated that a more powerful inequality will prove necessary when the orbital basis is further expanded. We intend to report in a later paper how effective the "G-matrix" condition[1] is in this regard.

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[1]See C. Garrod and J. K. Percus [J. Math. Phys. 5, 1756 (1964)] for an early survey.

[2]L. J. Kijewski and J. K. Percus, Phys. Rev. 179,

45 (1969); L. J. Kijewski, J. K. Percus, I. H. Pratt, and J. P. Tranchina, Phys. Rev. A 2, 310 (1970).
[3]M. Rosina, J. K. Percus, L. J. Kijewski, and G. Garrod, J. Math. Phys. 10, 1761 (1969).
[4]This is equivalent to the G-matrix symmetry condition of C. Garrod and M. Rosina, J. Math. Phys. 10, 1855 (1969).
[5]See, e.g., M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
[6]P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. 48, 948 (1935).

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Exchange Symmetry of Many-Particle State Functions*

W.R. Salzman
Department of Chemistry, University of Arizona, Tucson, Arizona 85721
(Received 17 October 1969; revised manuscript received 15 June 1970)

A formal operator definition of indistinguishability of identical particles alternative to permutation invariance of configuration probabilities is presented. The exchange-symmetry properties of many-particle wave functions are shown to follow simply and directly from the new definition.

INTRODUCTION

The requirement that state functions for systems of identical particles be either totally symmetric or totally antisymmetric under interchange of the coordinates[1] of two of the particles is so well established experimentally that it is often presented as a fundamental postulate of quantum mechanics (the symmetrization postulate).[2-4] Upon agreement that particles with totally symmetric states are called bosons and particles with totally antisymmetric states are called fermions, the symmetrization postulate may be stated: *All particles are either fermions or bosons*. States with other symmetries are conceivable but particles have not been found in nature to fit them.

The relatively late introduction of the symmetrization postulate into the logical scheme of quantum mechanics contributes to the feeling that it is an *ad hoc* assertion introduced at the last minute to make the theory fit experiment. It would be more pleasing to derive the symmetrization postulate from general principles and the indistinguishability of identical particles. Accordingly, a number of workers have attempted to reduce the symmetrization postulate to a theorem,[5-11] but most attempts so far have either been based on assumptions which are not generally true or have placed seemingly unnecessary restrictions on the type of physical systems to which they apply. Girardeau,[9] after pointing out the deficiencies of previous arguments, presented a proof of the symmetrization postulate which depends in an essential way on the topology of the configuration space of the particles (in particular the argument depends on the connectedness of the configuration space). Since there exists an interesting class of systems[12] for which the topological requirements do not hold, the proof seemed to be unnecessarily restricted. The connectedness restriction on configuration space was lifted by Flicker and Leff[10] for the case of particles with no internal degrees of freedom, and then for the general case by Giradeau.[11] These more recent proofs are still topological in nature and use the permutation invariance of configurational probabilities (stated variously as $|\underline{P}\Psi|^2 = |\Psi|^2$ or $\underline{P}|\Psi|^2 = |\Psi|^2$ for every Ψ) as the fundamental definition of particle indistinguishability. They thus are very strongly tied to a particular representation of quantum mechanics, namely, the configuration-space representation.

In the present paper we offer an alternative definition of particle indistinguishability which, although more formal and lacking the lucid pictorialization of permutation invariance, characterizes the indistinguishability of identical particles realistically. In particular, we show that the statement "the exchange of two identical (indistinguishable) particles is not observable" leads directly and unambiguously to the result "identical particles are either fermions or bosons." The first statement implicitly defines identical particles as those whose interchange is not observable.

We first establish that this definition is reasonable and has precedent and then show that it leads directly and simply to the desired result.

PERMUTATIONS OF INDISTINGUISHABLE PARTICLES

The set of $N!$ operations which produce all possible permutations of the coordinates of N particles form the group S_N, the symmetric group of order