Some Restrictions on the Use of Reduced Density Matrices in Atomic Calculations*

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The method of reduced density matrices for obtaining the ground-state energy of an atomic system is developed, making full use of the symmetry relations for orbital and spin angular momentum. These, together with an extensive set of Hamiltonian-dependent identities, serve to decrease the number of parameters which must be varied in the density-matrix variational principle. With only a small number of parameters required, inequalities such as the Pauli restriction can then be enforced. Numerical calculations for C^{++} show the relative ineffectiveness of certain low-lying geminals (in the $\Gamma^{(2)}$ expansion) in reaching the Pauli restriction limit, and thus point the way to significant improvement.

I. INTRODUCTION

There exists a number of methods for obtaining upper and lower bounds to the eigenenergies of the many-electron Schrödinger equation. The use of reduced density matrices is a current method being developed primarily to obtain lower bounds to the ground-state energy. It is based on the fact that for two-body interactions, the standard Rayleigh-Ritz variational principle becomes

$$E_0(H) = \tfrac{1}{2}N \min_{\Gamma^{(2)}} \mathrm{tr} H^{(2)} \Gamma^{(2)} , \qquad (1.1)$$

where if the Hamiltonian is

$$H = \sum_{i=1}^{N} T(i) + \tfrac{1}{2} \sum_{i \neq j=1}^{N} v(i,j) , \qquad (1.2)$$

then $$H^{(2)} = T(1) + T(2) + (N-1)v(1,2) , \qquad (1.3)$$

and

$$\Gamma^{(2)}(\vec{x}_1', \vec{x}_2' | \vec{x}_1, \vec{x}_2) = \int \cdots \int d\vec{x}_3 \cdots d\vec{x}_N \times \sum_\alpha C_\alpha \psi_\alpha(\vec{x}_1' \vec{x}_2' \vec{x}_3 \cdots \vec{x}_N) \psi_\alpha^* (\vec{x}_1 \cdots \vec{x}_N), \qquad (1.4)$$

with $$\sum_\alpha C_\alpha = 1, \quad C_\alpha \geq 0. \qquad (1.5)$$

For a nondegenerate ground state, the minimum is achieved when ψ_0 is the ground state and $C_\alpha = \delta_{\alpha,0}$. If the class of $\Gamma^{(2)}$ is not sufficiently restricted to guarantee that each member be N representable, i.e., be realizable in the form (1.4), then (1.1) results instead in a lower bound to $E_0(H)$.

Bopp[1] was the first to apply the density-matrix technique to atomic systems with more than two electrons, and his calculation merely required a knowledge of the first few energy levels of helium. He first observed that for an atom with $T = p^2/2m - Ze^2/r$, $v(1,2) = e^2/r_{12}$, the scale transformation $\vec{r} = \vec{R}/(N-1)$, $\vec{p} = (N-1)\vec{P}$ converts (1.3) to

$$\frac{H^{(2)}}{(N-1)^2} = \frac{P_1^2 + P_2^2}{2m} - \frac{Ze^2}{N-1}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{e^2}{R_{12}} , \qquad (1.6)$$

a heliumlike Hamiltonian. If $Z = 2(N-1)$, (1.6) represents helium itself, whose properties – and certainly whose energy levels – are well known and tabulated. Thus, for singly ionized beryllium, Bopp's computed ground-state energy differed by about 1% from the experimental value, a relatively good result considering the simple conditions on the two-matrix $\Gamma^{(2)}$ that he used. Since then, many other conditions have been found and are being found, although most tend to be rather impractical.

If we want to improve upon the results obtained by Bopp and others, then more restrictions must be imposed on the class of reduced density matrices over which one varies in the variational principle. The most appropriate restrictions will, of course, depend upon the particular Hamiltonian being considered. Garrod and Percus[2] have obtained an extensive set of restrictions resulting from the positive definiteness of a certain class of operators. Their "G-matrix" conditions give exact

results for the Bogoliubov condensed Bose fluid Hamiltonian, and with an additional weak restriction, for the BCS Hamiltonian. These conditions on the two-matrix are apparently very strong. For practical purposes, however, they cannot stand alone. If one expands out the reduced two-particle density matrix $\Gamma^{(2)}$ in a complete set of two-particle functions (geminals), there are just too many variational parameters floating around. They may nonetheless be reduced to a somewhat manageable size by making use of a number of symmetry properties. These are discussed in Secs. II and III, and generalized in Sec. V.

Possibly the first numerical improvement to Bopp's result appeared in the work of Grimley and Peat,[3] who enforced the spin restrictions

$$\langle\psi_0|[\textstyle\sum_1^N \vec{S}(i)]^2|\psi_0\rangle = S(S+1)\,,$$
$$\langle\psi_0|\textstyle\sum_1^N S_z(i)|\psi_0\rangle = M_S \qquad (1.7)$$

on the two-matrix. In a previous paper, Kijewski and Percus[4] have shown that the two-matrix of Grimley and Peat does not satisfy the Pauli restriction, which requires that the eigenvalues of the one-matrix

$$\Gamma^{(1)}(\vec{x}_1'|\vec{x}_1) = \int d\vec{x}_2\, \Gamma^{(2)}(\vec{x}_1', \vec{x}_2|\vec{x}_1, \vec{x}_2) \qquad (1.8)$$

should not exceed $1/N$. Thus, the Pauli restriction can improve Grimley and Peat's result. (Incidentally, the Pauli restriction comes from the G-matrix condition.) The problem is that of assuring that not too many low-lying geminals $u_\alpha(1,2)$ are permitted in a geminal expansion

$$\Gamma^{(2)} = \sum_{\alpha,\beta} C_{\alpha\beta}|u_\alpha\rangle\langle u_\beta|\,, \quad \sum_\alpha C_{\alpha\alpha} = 1 \qquad (1.9)$$

of $\Gamma^{(2)}$. Indeed the geminals based upon a Hartree-Fock approximation belong mainly to the two-body continuum. In the present paper, we augment the Grimley-Peat geminal basis for the atomic system C^{++} to include the first 14 states of helium. As the computation of Sec. IV shows, the blatant failure of the Pauli principle is unaltered by this expanded basis.

In principle, one should expand the two-matrix for an atomic system in terms of a complete set of helium wave functions, or other complete set s of geminals, and determine the coefficients of the expansion by using a combination of various restrictions and the variational principle. This gives a rigorous lower bound to the ground-state energy. In practice, one must truncate any expansion and be satisfied with a presumably very good upper bound to a poorer lower bound. For this purpose, the helium geminals will not necessarily be optimal, and Sec. VI discusses expansions of $\Gamma^{(2)}$ in terms of nonhelium-type geminals.

II. HELIUM GEMINAL EXPANSION

Bopp originally expanded the two-matrix in terms of helium wave functions [suitably scaled – see (1.6)]. This choice is particularly convenient, since only diagonal elements then enter into (1.1),

$$E_0(H) = \tfrac{1}{2}N(N-1)^2 \min \textstyle\sum C_{\alpha\alpha}\epsilon_\alpha\,, \qquad (2.1)$$

where ϵ_α are the helium levels. Furthermore, the virial theorem is automatically satisfied by even a truncation of (1.9) for this expansion. The discrete and autoionizing spectra of helium are experimentally available, so that *only* the determination of the $C_{\alpha\alpha}$ remains. In Bopp's work, the single effective restriction was that the eigenvalues of $(C_{\alpha\beta})$ were bounded from below by zero and from above by $2/N(N-1)$; it readily followed that $C_{\alpha\alpha} = 2/N(N-1)$ for the $N(N-1)/2$ lowest geminals, all belonging to the discrete spectrum. As has been discussed many times, the upper bound is not rigorous, and a rigorous upper bound yields results for $E_0(H)$ far poorer than those of Bopp for larger atoms. Attempts have been made to recover the Bopp result, e.g., by bounding not the largest but the sum of the highest few[5] eigenvalues of $\Gamma^{(2)}$, but the Bopp result itself is very poor for larger atoms. A $\Gamma^{(2)}$ eigenvalue condition, no matter how stringent, is simply inadequate.

The Pauli principle, which asserts that the eigenvalues of $\Gamma^{(1)}$ lie between 0 and $1/N$, should be a far more severe restriction for atomic states. $\Gamma^{(1)}$ for a Hartree-Fock state – a single configuration – falls right on the boundary of this restriction, and one configuration in a mixed configuration expansion is generally dominant. In Ref. 4, the two-matrix for C^{++} was expanded in the lowest five states of helium and some weak symmetry conditions applied. It was then found impossible to satisfy the Pauli restriction. The purpose of this paper is to effectively preclude the possibility of satisfying the Pauli principle by using only low-lying geminals – those with one electron excited – and thereby to force the inclusion of doubly excited geminals with a corresponding decrease in the 1s occupancy. We therefore include the next set of states in the helium spectrum, the ninefold degenerate 2^3P states, and test the 14 state geminal basis for "Pauliability."

Our trial density matrix now takes the form

$$\Gamma_t^{(2)}(\vec{x}_1', \vec{x}_2'|\vec{x}_1, \vec{x}_2) = c_1(|1'S\rangle\langle 1'S|)$$
$$+ \sum_{S_z, S_z'=-1}^{1} c_2^{S_z S_z'}(|2^3S, S_z\rangle\langle 2^3S, S_z|)$$
$$+ c_3(|2'S\rangle\langle 2'S|) + \sum_{S_z, S_z', m_l, m_l'=-1}^{1} c_4^{S_z m_l S_z' m_l'}$$
$$\times(|2^3P, S_z' m_l'\rangle\langle 2^3P, S_z, m_l|) + \Gamma_{OD}\,, \qquad (2.2)$$

where the Γ_{OD} represents the terms which are off diagonal with respect to energy. An important preliminary reduction (for critical comments, see Sec. VI and Refs. 4 and 6) is obtained by applying the condition

$$\mathrm{tr}_2[H^{(2)}(1,2),\ \Gamma^{(2)}(1,2)]=0\ , \tag{2.3}$$

which for the special form (2.2) insists that $\Gamma_{OD}=0$. Condition (2.3) may be obtained either as the first member of the Bogoliubov hierarchy for density matrices [take $\mathrm{tr}_{2,3\cdots N}$ of the N-body relation $(H,\ |\psi\rangle\langle\psi|)=0$], or from the more general variational restriction

$$\mathrm{tr}(H^{(2)}e^{i\gamma[C(1)+C(2)]}\Gamma^{(2)}e^{-i\gamma[C(1)+C(2)]})\geq \mathrm{tr}(H^{(2)}\Gamma^{(2)}).$$

Even with the elimination of Γ_{OD}, however, numerous parameters remain to be varied. We shall now show how this freedom may be further reduced.

III. SYMMETRY CONDITIONS FOR AN $\vec{L}=0$, $\vec{S}=0$ STATE

Although no set of equalities alone appears likely to permit determination of the two-matrix of a given system, the choice can be narrowed considerably by the use of suitable equalities. Equation (2.3) is the prototype of one class of equalities, occurring whenever the state of the system is also an eigenstate of some two-body operator (assumed Hermitian) other than the energy:

if

$$\sum_{i,j} R(i,j)\psi=r\psi\ ,$$

then

$$\mathrm{tr}_2[(R(1,1)+R(2,2)+2(N-1)R(1,2))\ ,\ \Gamma^{(2)}(1,2)]=0\ , \tag{3.1}$$

$$\mathrm{tr}_{12}(R(1,1)+R(2,2)+2(N-1)R(1,2))\,\Gamma^{(2)}(1,2)=2r/N\ .$$

Equation (3.1) results immediately from successive traces of $\sum R|\psi\rangle\langle\psi|=|\psi\rangle\langle\psi|\sum R=r|\psi\rangle\langle\psi|$. It is not too valuable in an $H^{(2)}$ representation for (1.9) unless the u_α are also eigenfunctions of $R(1,1)+R(2,2)+2(N-1)R(1,2)$. For example, if for a spin-independent Hamiltonian,

$$\sum R=[\sum\vec{S}(i)]^2=\sum\vec{S}(i)\cdot\vec{S}(j)\ ,$$

then

$$\begin{aligned}R(1,1)+R(2,2)+2(N-1)R(1,2)&=S(1)^2+S(2)^2+(N-1)\,2\vec{S}(1)\cdot\vec{S}(2)\\&=(N-1)\{[S(\vec{1})+S(\vec{2})]^2-S(1)^2-S(2)^2\}+S(1)^2+S(2)^2\\&=(N-1)[\vec{S}(1)+\vec{S}(2)]^2-\tfrac{3}{2}(N-2),\end{aligned}$$

and (3.1) becomes

$$\mathrm{tr}_2[(\vec{S}(1)+\vec{S}(2))^2,\ \Gamma^{(2)}(1,2)]=0\ ,$$

$$\mathrm{tr}_{12}[\vec{S}(1)+\vec{S}(2)]^2\,\Gamma^{(2)}(1,2)=\tfrac{3}{2}(N-2)/(N-1)+2S(S+1)/(N-1)N\ . \tag{3.2}$$

One obtains simpler, more complete, and more useful relations when the Hamiltonian commutes with some one-body operator, of which the ground state can then be taken as an eigenstate.[7] Suppose then that $[\sum_{i=1}^N Q(i),\ H]=0$, with ψ chosen that $\sum_{i=1}^N Q(i)\psi=q\psi$. Q will usually correspond to an infinitesimal geometric symmetry, e.g., L_z or S_z. It follows at once that $[Q(1)+Q(2),\ \Gamma^{(2)}(1,2)]=0$, and from $[Q(1)+Q(2),\ H^{(2)}(1,2)]=0$, the eigenfunctions u_α of $H^{(2)}$ in (1.9) can be selected so that $[Q(1)+Q(2)]u_\alpha=q_\alpha u_\alpha$. Using representation (1.9), then,

$$0=[Q(1)+Q(2),\ \Gamma^{(2)}]=\sum_{\alpha,\beta}(q_\alpha-q_\beta)C_{\alpha\beta}|u_\alpha\rangle\langle u_\beta|,$$

and we conclude that $C_{\alpha\beta}=0$, when $q_\alpha\neq q_\beta$. Thus the geminal expansion is diagonal with respect to $Q(1)+Q(2)$. Appending the obvious evaluation of $\langle\sum Q(i)\rangle$, we may summarize as follows.

Condition 1. If $[\sum_1^N Q(i),H]=0$, and $\sum Q(i)\psi=q\psi$, the orthonormal geminals u_α in

$$\Gamma^{(2)}=\sum C_{\alpha\beta}|u_\alpha\rangle\langle u_\beta| \tag{3.3}$$

can be chosen so that

$$[Q(1)+Q(2)]u_\alpha(1,2)=q_\alpha u_\alpha(1,2)\ .$$

We then have $C_{\alpha\beta}=0$ unless $q_\alpha=q_B$, and $\sum q_\alpha C_{\alpha\alpha}=(2/N)q$.

The operator Q in (3.3) will most often be a component of angular momentum. The geminal expansion is further simplified through knowledge of the total angular momentum of the system. With the example of C^{++} in mind, let us first suppose that $[\sum_{i=1}^N\vec{M}(i)]^2\psi=0$, where $\vec{M}$ is either $\vec{L}$ or $\vec{S}$. Then $\sum_1^N M_\pm(i)\psi=0$, where $M_\pm=M_x\pm iM_y$, so that

$$[M_\pm(1)+M_\pm(2),\ \Gamma^{(2)}(1,2)]=0\ .$$

Now the u_α can be taken as $M_z(1)+M_z(2)$, $[\vec{M}(1)+\vec{M}(2)]^2$ eigenstates, with eigenvalues m_α, M_α $(M_\alpha+1)$, respectively. If T denotes the raising of the eigenvalue m, and k is the corresponding multiplier

$$m_{T\alpha}=m_\alpha+1\ ,\quad M_{T\alpha}=M_\alpha\ ,\quad M_+u_\alpha=k_\alpha u_{T\alpha}\ , \tag{3.4}$$

where $k_\alpha\equiv[(M_\alpha-m_\alpha)(M_\alpha+m_\alpha+1)]^{1/2}$,

it follows that

$$\begin{aligned}0&=[M_+(1)+M_+(2),\ \sum_{\alpha\beta}C_{\alpha\beta}|u_\alpha\rangle\langle u_\beta|]\\&=\sum_{\alpha\beta}C_{\alpha\beta}k_\alpha|u_{T\alpha}\rangle\langle u_\beta|-\sum_{\alpha\beta}C_{\alpha\beta}k_{T^{-1}\beta}|u_\alpha\rangle\langle u_{T^{-1}\beta}|\\&=\sum(C_{\alpha\beta}k_\alpha-C_{T\alpha T\beta}k_\beta)|u_{T\alpha}\rangle\langle u_\beta|,\end{aligned}$$

or $C_{\alpha\beta}k_\alpha=C_{T\alpha T\beta}k_\beta$.

Similarly, the commutator

$$0=[M_-(1)+M_-(2),\ \sum C_{\alpha\beta}|u_\alpha\rangle\langle u_\beta|]$$

implies that

$$C_{\alpha\beta}k_\beta = C_{T\alpha T\beta}k_\alpha\ .$$

Thus if $C_{\alpha\beta}\neq 0$, we must have $k_\alpha = k_\beta$, and since $m_\alpha = m_\beta$ follows from (3.3), $M_\alpha = M_\beta$ as well. Furthermore, all elements of the chain have the same weight: $C_{T\alpha T\beta} = C_{\alpha\beta}$. In summary, then,

Condition 2. If $[\sum \vec{M}(i)]^2\psi = 0$, then $C_{\alpha\beta}=0$ unless

$$m_\alpha = m_\beta, \quad M_\alpha = M_\beta\ . \tag{3.5}$$

Furthermore, $C_{T\alpha T\beta} = C_{\alpha\beta}$.

The quantum number m is irrelevant not only for the geminal weights $C_{\alpha\beta}$, but also for most associated matrix elements. Thus if Q commutes with $\vec{M}$, then in computing $\mathrm{tr}Q\,\Gamma^{(2)}$, we require

$$\begin{aligned}\langle u_{T\alpha}|Q|u_{T\beta}\rangle &= \langle u_{T\alpha}|Q|M_+u_\beta\rangle/k_\beta\\ &= \langle M_-u_{T\alpha}|Q|u_\beta\rangle/k_\beta = \langle u_\alpha|Q|u_\beta\rangle,\end{aligned}$$

a common value for the whole chain. More explicitly, if we specify a geminal by quantum numbers L, S, and n for shell occupation of the electron pair, then m_L and m_S can be given any convenient values, and we have

$$\begin{aligned}&\Gamma^{(2)} = \sum (2L+1)(2S+1)C_{LS}(n,n')|nLS\rangle\langle n'Ls|,\\ &\mathrm{tr}\Gamma^{(2)}Q = \sum (2L+1)(2S+1)C_{LS}(n,n')\langle n'LS|Q|nLS\rangle\ .\end{aligned} \tag{3.6}$$

In particular, of course,

$$E = \tfrac{1}{2}N\sum (2L+1)(2S+1)C_{LS}(n,n)\langle nLS|H^{(2)}|nLS\rangle\ . \tag{3.7}$$

It is also apparent that any model restrictions[8] we care to impose with rotationally invariant model Hamiltonians will employ $\Gamma^{(2)}$ only in the form (3.6). In other cases, however, the implicit definition

$$\begin{aligned}|nLS\rangle\langle n'LS| \equiv (2L+1)^{-1}(2S+1)^{-1}\\ \times\sum_{m_Lm_S} |nLSm_Lm_S\rangle\langle n'LSm_Lm_S|\end{aligned} \tag{3.8}$$

is required.

IV. NUMERICAL RESULTS FOR TRIAL DENSITY MATRIX FOR C^{++}

As we have pointed out, a good bound to $E_0(C^{++})$ with $\Gamma^{(2)}$ expanded in helium geminals certainly requires some contribution from the autoionizing continuum. But is the Pauli restriction strong enough to raise the states employed by Grimley and Peat so appreciably? The model calculation on the noninteracting system in Ref. 4 indeed showed the strength of this restriction. For an indication of its potential for improvement of previous results, we now test the multiparameter trial density matrix of (2.2) for Pauliability.

If the trial density matrix (2.2) is required to satisfy (2.3), the off-diagonal elements drop out. The triplet and P weights then simplify by virtue of (3.8). The triplet weights are also related by (3.2), which now reads $\mathrm{tr}[\vec{S}(1)+\vec{S}(2)]^2\ \Gamma^{(2)}(1,2)=1$, and the singlet weights are then related by normalization. Finally, we use the fact that the maximum geminal occupation for $N=4$ is $1/(N-1)=\frac{1}{3}$ (without bothering to use the somewhat stronger condition of Ref. 5), resulting in the restricted form for the trial two-matrix

$$\begin{aligned}\Gamma^{(2)}_t(1'2'|12) = w|1^1S\rangle\langle 1^1S| + 3y|2^3S\rangle\langle 2^3S|\\ +(\tfrac{1}{2}-w)|2^1S\rangle\langle 2^1S| + (\tfrac{1}{2}-3y)|2^3P\rangle\langle 2^3P|\ ,\end{aligned} \tag{4.1}$$

where $\frac{1}{6}\leq w\leq\frac{1}{3}$, $\quad 0\leq y\leq\frac{1}{6}$.

In terms of the same parameters, we now have

$$\begin{aligned}E_t = 18(e^2/a_0)[&wE(1^1S)+3yE(2^3S)\\ &+(\tfrac{1}{2}-w)E(2^1S)+(\tfrac{1}{2}-3y)E(2^3P)]\ ,\end{aligned} \tag{4.2}$$

where $E(1^1S)=2.903\,72$, $\quad E(2^3S)=2.175\,22$,

$E(2^1S)=2.145\,97$, $\quad E(2^3P)=2.133\,16$.

To sufficient accuracy for our purposes, we chose the S states of helium in the form (spin dependence understood)

$$\begin{aligned}u(\vec{r}_1,\vec{r}_2) &= \sum_{k,l} A_{kl}[\psi_{kS}(r_1)\psi_{lS}(r_2)\pm\psi_{lS}(r_1)\psi_{kS}(r_2)],\\ \psi_{kS}(r) &= [N_k/\sqrt{(4\pi)}]L^2_{k+1}(2\eta r)e^{-\eta r},\end{aligned} \tag{4.3}$$

where L^2_{k+1} denote the Laguerre polynomials, $\eta = 1.044$, and the indices go from one to seven. Similarly the P states were taken as

$$\begin{aligned}u(\vec{r}_1,\vec{r}_2) &= \sum_{k,l} B_{kl}[\psi_{kS}(r_1)\psi_{lP}(\vec{r}_2)-\psi_{kS}(r_2)\psi_{lP}(\vec{r}_1)],\\ \psi_{lP}(\vec{r}) &= \sqrt{(4\pi)}\,\psi_{lS}(r)\,Y_{1,m}(\theta,\phi)\ ,\end{aligned} \tag{4.4}$$

with the indices k, l going from one to five. The one-matrix $\Gamma^{(1)}$ was then obtained in terms of $\psi_{kS}(r')\psi_{lS}(r_1)$, $\psi_{kP}(\vec{r}_1')\psi_{lP}(\vec{r}_1)$ and proper spin factors, the latter causing double degeneracy of the eigenvalues of $\Gamma^{(1)}$. The resulting maximum $\Gamma^{(1)}$ eigenvalues and corresponding energies E_t are given in Table I for various values of the parameters w and y.

The $\lambda^{(1)}_{\max}$ given are not intended to be accurate to six digits, but this is not necessary to drive home the point that the addition of the nine ^3P states has very little effect in reaching the permitted upper bound of $\frac{1}{4}$ due to the Pauli restriction.

V. SYMMETRY CONDITIONS ON $\Gamma^{(2)}$ FOR $\vec{M}\neq 0$

For completeness, we consider next the case of

TABLE I. Effect of relative ground state and P-state occupation on maximum orbital occupation $\lambda_{\max}^{(1)}$ and ground-state energy for C^{++} trial density matrix. The P-state weight is $\frac{1}{18} - \frac{1}{3}y$; $-E_{\text{expt}} = 994.17$ eV.

w	y	$\lambda_{\max}^{(1)}$	$-E_t$ (eV)
5/30	0	0.290 390	1119.80
5/30	1/30	0.290 407	1111.86
5/30	2/30	0.290 431	1113.92
5/30	3/30	0.290 465	1115.98
5/30	4/30	0.290 515	1118.04
5/30	5/30	0.290 592	1120.10
7/30	0	0.305 985	1134.54
7/30	1/30	0.305 982	1136.60
7/30	2/30	0.305 980	1138.66
7/30	3/30	0.305 980	1140.72
7/30	4/30	0.305 981	1142.78
7/30	5/30	0.305 983	1144.84
10/30	0	0.330 031	1171.65
10/30	1/30	0.330 056	1173.71
10/30	2/30	0.330 089	1175.77
10/30	3/30	0.330 132	1177.83
10/30	4/30	0.330 188	1179.89
10/30	5/30	0.330 263	1181.95

a state which is not a simultaneous eigenfunction with $\vec{M} = 0$, e.g., the previously[4] considered Be^+ ground state. Let $[\sum \vec{M}(i)]^2 \psi = J(J+1)\psi$. It follows that for any S between 0 and $2J+1$, either $[\sum M_+(i)]^{2J+1-S}\psi = 0$, or $[\sum M_-(i)]^S \psi = 0$, or both. Hence $[\sum M_+(i),]^{2J+1} |\psi\rangle\langle\psi| = 0$, and consequently

$$\text{if} \quad [\sum \vec{M}(i)]^2 \psi = J(J+1)\psi, \tag{5.1}$$

$$\text{then} \quad [M_+(1) + M_+(2),]^{2J+1} \Gamma^{(2)} = 0.$$

Expanding out, we have

$$0 = \sum_{\alpha\beta S} C_{\alpha\beta}(-1)^S \binom{2J+1}{S} \times |[M_+(1) + M_+(2)]^{2J+1-S} u_\alpha\rangle\langle[M_-(1) + M_-(2)]^S u_\beta|$$

$$= \sum_{\alpha\beta S} C_{T^S\alpha T^S\beta}(-1)^S \binom{2J+1}{S} \times k_\beta \cdots k_{T^S-1\beta} k_{T^S\alpha} \cdots k_{T^2J+1\alpha} |u_{T^2J+1\alpha}\rangle\langle u_\beta| ,$$

so that $\sum_S C_{T^S\alpha T^S\beta}(-1)^S \binom{2J+1}{S} \times k_\beta \cdots k_{T^S-1\beta} k_{T^S\alpha} \cdots k_{T^2S\alpha} = 0.$

Let m be the common M_z value of α and β; M the total quantum number of α, $\bar{M}$ of β; k_m the multiplier for α, $\bar{k}_m$ for β. We then have

$$\sum_S \binom{2J+1}{S} (-1)^S \bar{k}_{-\bar{M}} \bar{k}_{1-\bar{M}} \cdots \times k_{m_+ S} k_{m_+ S+1} \cdots k_{M-1} C_{m_+ S} = 0,$$

or $-(\Delta_m)^{2J+1}(\bar{k}_{-M} \cdots \bar{k}_{m-1} k_m \cdots k_{M-1} C_m) = 0,$

where $\Delta_m f(m) \equiv f(m+1) - f(m)$.

This has the immediate solution

$$\bar{k}_{-M} \cdots \bar{k}_{m-1} k_m \cdots k_{M-1} C_M = p_{2J}(m) , \tag{5.2}$$

where $q_{2J}(m)$ is some polynomial in m of degree $2J$. In the same fashion, $[\sum M(i),]^{2J+1} |\psi\rangle\langle\psi| = 0$ gives rise to

$$k_{-M} \cdots k_{m-1} \bar{k}_m \cdots \bar{k}_{\bar{M}-1} C_m = \bar{p}_{2J}(m) , \tag{5.3}$$

some other polynomial.

What then are the consequences of the two polynomial relations? Most importantly, suppose $M \geq \bar{M}$, so that $\bar{k}_{-M} \cdots \bar{k}_{m-1} k_m \cdots k_{M-1}$ vanishes for $\bar{M} < m \leq M$ (as does C_m), a set of $M - \bar{M}$ values of m; for $p_{2J}(m)$ not to vanish identically, we thus need $2J \geq M - \bar{M}$. For $\bar{M} \geq M$, we go through the same process and conclude that $\bar{p}_{2J} \equiv 0$ unless $\bar{M} - M \leq 2J$.

Condition 3. If $[\sum \vec{M}(i)]^2 \psi = J(J+1)\psi$, then in the geminal expansion of $\Gamma^{(2)}$, $C_{\alpha\beta} = 0$ unless

$$|M_\alpha - M_\beta| \leq 2J . \tag{5.4}$$

Furthermore, when these conditions hold, not all of the coefficients of p_{2J} are independent. Since $k_m = k_{-1-m}$, we can write (5.3) as

$$\bar{k}_{-\bar{M}} \cdots \bar{k}_{-m-1} k_{-m} \cdots k_{M-1} C_m = \bar{p}_{2J}(m) ,$$

or on dividing into (5.2),

$$\frac{p_{2J}(m)}{\bar{p}_{2J}(m)} = \frac{\bar{k}_{-m} \cdots \bar{k}_{m-1}}{k_{-m} \cdots k_{m-1}} = \frac{(\bar{M}+m)!/(M+m)!}{(\bar{M}-m)!/(M-m)!}, \tag{5.5}$$

valid for both $m \leq 0$, and $m > 0$. If $\bar{M} \geq M$, the numerator and denominator are polynomials in m with no common divisor. Thus, we must have

$$p_{2J}(m) = [(\bar{M}+m)!/(M+m)!] f_{2J-(\bar{M}-m)}(m)$$

$$= (\bar{M}+m)(\bar{M}+1+m) \cdots (M+1+m) f_{2J-(\bar{M}-M)}(m), \tag{5.6}$$

which is in fact any polynomial of degree $2J$ which vanishes for $-\bar{M} \leq m \leq M$, as required for $C_{\alpha\beta}$. Combining with (5.2), we have then for some polynomial P

Condition 4. Explicitly, if $M_\beta \geq M_\alpha$,

$$C_m = \left(\frac{M_\beta + m!}{M_\alpha + m!} \frac{M_\beta - m!}{M_\alpha - m!}\right)^{1/2} P_{2J-(M_\beta - M_\alpha)}(m) . \tag{5.7}$$

M_β and M_α interchange roles when the inequality switches.

VI. NONHELIUM EXPANSION OF $\Gamma^{(2)}$

As a first goal, we should hope to obtain results for the lower bound as good as the upper bound of Hartree-Fock theory. In analogy with the configuration expansion which develops from Hartree-Fock, we can expand the two-matrix as

$$\Gamma^{(2)}(1'2'|12) = \sum_{klmn} \Gamma^{(2)}_{klmn} u_{kl}(1'2') u^*_{mn}(12) ,$$

where

$$u_{kl}(12) = (1/\sqrt{2})\,[\phi_k(1)\phi_l(2) - \phi_k(2)\,\phi_l(1)]. \quad (6.1)$$

In practice, the number of coefficients is enormous and one will always be forced to deal with a finite expansion, i.e., use a finite number of orbitals ϕ_k. A considerable reduction in the number of independent coefficients will again result from the symmetry conditions (3.3), (3.4), (5.4), (5.7), and a few more from evaluation of constants as in the last equations of (3.1) and (3.3). The situation with respect to the very powerful (2.3) and its generalization in (3.1) is somewhat different. We have noted that (2.3) used uncritically annuls off-diagonal elements of any finite expansion, a very bad convergence property. It is easy to see however that if for a finite number of orbitals ϕ_k, $k = 1, \ldots, P$ we use the less general restrictions

$$\mathrm{tr}[H^{(2)}, \Gamma^{(2)}]\,|\,\phi_l(1)\rangle\langle\,\phi_k(1)\,| = 0$$

for $1 \leq k \leq P$, $1 \leq l \leq P$, the convergence difficulty does not occur. Equation (3.1) is of course to be used similarly.

The aforementioned restrictions in the form of equalities reduce the number of independent coefficients enormously. It now becomes reasonable to impose the known inequalities – Pauli restriction, G-matrix condition, and others.[9] The results of such an attempt will be described in a future paper.

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