THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 156, No. 1 5 APRIL 1967

Hartree-Fock Theory: Slater Determinants of Minimum Energy

T. A. KAPLAN AND W. H. KLEINER
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

(Received 1 August 1966)

A theorem is proved (on the basis of physically reasonable assumptions) to the effect that in Hartree-Fock (HF) theory an electron can always be added to an N-electron system without raising its energy. The theorem is applied to show that the conventional HF wave function is unstable for certain negative atomic ions (H^-, Li^- B^-, N^-, N^{--}, O^-, O^{--}, Na^-, P^-), and that the typical extent of the instability is chemically significant. A consequence of the instability is that the lowest level in HF theory does not have the symmetry of the exact ground level. This is the case, in particular, for the closed-shell ions H^-, Li^-, O^{--}, and Na^-—a result contrary to some earlier expectations. The two-electron one-center system with fixed nuclear charge Ze (Z not restricted to integer values) is investigated in detail on the basis of a simplified model defined by specifying restrictions which the allowable determinantal wave functions must satisfy. The orbitals of the determinantal wave functions of the model are of the form $\psi_i = v_i\chi_i$, $i=1, 2$, where χ_i is a spin function and v_i is essentially of $1s$ hydrogenic form. As Z decreases, the model shows explicitly the onset of the instability described above. It further shows that for $Z>1$, any true minimum-energy determinant D_0 is bound (although the interesting question of whether D_0 is bound for $Z\leqslant 1$, apparently raised here for the first time, remains unanswered). A precise analogy between the electron problem and certain spin problems is defined. This analogy sheds light on the HF approximation. It leads to examples which show strikingly that it is important not to always impose symmetry restrictions on an otherwise restricted wave function; the analogy also makes clear, in a simple way, certain points fundamental to an understanding of HF theory. Some possible implications of the results of this paper for solid-state calculations are discussed.

I. INTRODUCTION

THE basis of an important part of the theory of the electronic structure of atoms, molecules, and crystals is the Hartree-Fock (HF) theory, in which a many-electron energy eigenfunction is approximated by a single Slater determinant of one-electron orbitals.[1–14] In this paper we report an investigation of some fundamental aspects of HF theory relating to ground Slater determinants.[15]

An elementary, but apparently new, theorem is presented in Sec. II relating the energy of a ground Slater determinant for an $(N+1)$-electron system to certain properties of the corresponding N-electron system. This theorem is used in Sec. III to demonstrate quite simply that the conventional HF approximation to the ground state is unstable for many negative atomic ions, and to provide a lower bound for the amount of the instability.

The theorem of Sec. II can also be used to demonstrate for some systems that a ground Slater determinant does not have the symmetry of an exact wave function of lowest energy. (Other approaches have been used in the past for this purpose, but never for closed-shell one-center systems.) The theorem is used in this way in Sec. IV, together with published numerical

---

* Operated with support from the U. S. Air Force.

[1] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[2] P. O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959).

[3] J. C. Slater, *Quantum Theory of Atomic Structure II* (McGraw-Hill Book Company, Inc., New York, 1960).

[4] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

[5] R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).

[6] P. O. Löwdin, J. Appl. Phys. **33**, 251S (1962).

[7] P. W. Anderson, *Concepts in Solids* (W. A. Benjamin, Inc., New York, 1963).

[8] P. O. Löwdin, Rev. Mod. Phys. **35**, 496 (1963).

[8a] P. O. Löwdin, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. O. Löwdin (Academic Press Inc., New York, 1966), 601.

[9] R. G. Parr, *The Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963).

[10] J. C. Slater, *Quantum Theory of Molecules and Solids I* (McGraw-Hill Book Company, Inc., New York, 1963).

[11] O. Sinanoğlu and D. F. Tuan, Ann. Rev. Phys. Chem. **15**, 251 (1964).

[12] A. J. Freeman and R. E. Watson, *Magnetism IIA* edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), 167.

[13] G. G. Hall and A. T. Amos, *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic Press Inc., New York, 1965), Vol. 1, p. 1.

[14] R. K. Nesbet, Adv. Chem. Phys. **9**, 321 (1965).

[15] A brief report of some of this work has been presented in Bull. Am. Phys. Soc. **11**, 234 (1966).

values, to establish the fact that for many closed-shell one-center systems (H^- is an example) the ground Slater determinants do not have the ${}^1S$ symmetry of the exact wave function of lowest energy.

These results imply, for those systems showing the instability, that the *ground Slater determinants are not known—even in a crude qualitative sense.* One reason this situation can occur, despite the extensive and very precise calculations that have been made over the past few decades, is that these calculations have typically forced the determinants being considered to have the symmetry presumed to be characteristic of the exact ground level.

As a first step towards understanding the nature of the variation with nuclear charge of ground Slater determinants for one-center systems, the system of two electrons moving in the Coulomb field of a fixed-point charge Ze is examined in detail in Sec. V. It should perhaps be emphasized that our purpose is not to obtain a ground wave function more accurate than one of the Hylleraas type.[16–19] Rather, the two-electron one-center system is viewed as a relatively simple system useful as a testing ground for the HF approximation. The class of determinants considered in Sec. V, which is highly restricted and very simple, provides some physical insight into the theorem of Sec. II and the source of the instability. The instability is exhibited explicitly, exemplifying the results of Secs. III and IV, and one can see in detail, on the basis of a very simple analysis, how the instability depends on Z.

Finally, the results are summarized and reviewed in Sec. VI.

Unfortunately there is no standard usage of terms in the literature on the HF approximation. To avoid confusion we therefore begin by stating some definitions.

The energy of a wave function Ψ is

$$E(\Psi)\equiv(\Psi,H\Psi)/(\Psi,\Psi)\,, \tag{1.1}$$

where H is the Hamiltonian. Every wave function considered in HF theory is a Slater determinant D. It is well known that D is invariant under any linear transformation of its orbitals, to within a constant factor.[20]

A *HF wave function* D_{HF} is a D for which $E(D)$ is stationary. The orbitals of D_{HF} can always be chosen to satisfy the HF equations.[21–24,14]

A D is *locally stable* if any sufficiently small variation of the orbitals never decreases the energy.[25,26]

A *ground Slater determinant* D_g is one with the lowest energy: $E(D_g)\leqslant E(D)$ for all D. A D_g is a D_{HF} and is locally stable. But a locally stable HF wave function is not necessarily a D_g; if it is not, then it is said to be *metastable.*

The difference $E(D)-E(\Psi_g)$ between the energy of a D and the energy of an exact ground-state wave function Ψ_g is a measure of the accuracy of D as an approximation to Ψ_g. When $D=D_{\mathrm{HF}}$, this difference is often called "the correlation energy." For several reasons we prefer not to use this terminology in this connection. One reason is that, so far as we are aware, formal definitions of "the correlation energy" given in the literature overlook the fact that the definition is ambiguous until the particular D_{HF} to be used is specified.

The quantities defined here are very difficult to calculate in practice: for a small number N of electrons (as in atoms and small molecules) it has been possible to obtain a good approximation to a HF wave function, of which we cite two examples[27,28]; but as far as we are aware no such wave function has been shown to be locally stable, let alone a ground HF wave function, even for N as small as 2. Indeed, although it might be possible to check local stability, no practical procedure is known for determining for a many-electron system with interaction, which HF wave function has the lowest energy.[8,8a] For very large N it is extremely difficult to obtain any HF wave function,[29] let alone a D_g.[30] The difficulty is not surprising considering the fact that one must deal with a complicated functional of a huge number of functions, the energy as a functional of the orbitals. Thus, determining a ground HF wave function and *knowing* that it is indeed a minimum energy determinant is far beyond present-day capabilities. As one might expect under such circumstances, a Slater determinant is found from time to time with an energy lower than that of an earlier HF wave function, or approximation thereto, showing that the latter was not a

---

[16] E. A. Hylleraas, Z. Physik **63**, 291 (1930).

[17] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[18] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, p. 241.

[19] A. L. Stewart, Advan. Phys. **12**, 299 (1963).

[20] No restrictions are imposed on the orbitals. In particular, an orbital is not necessarily a product of a function of the space coordinates and a function of the spin coordinate.

[21] A. Messiah, *Quantum Mechanics II* (John Wiley & Sons Inc., New York, 1963). See also, for example, Ref. 2, Eq. (II.4b) and Ref. 12, Eq. (3.3).

[22] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[23] V. Fock, Z. Physik **61**, 126 (1930).

[24] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[25] A formal criterion for local stability of a HF wave function has been developed recently (Refs. 4 and 26).

[26] W. H. Adams, Phys. Rev. **127**, 1650 (1962).

[27] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[28] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).

[29] To our knowledge there are for large N no HF wave functions given in the literature. We refer here to "realistic" models, such as electrons interacting, via Coulomb forces, with each other and some set of fixed point charges. For idealized models, such as the electron gas, it is sometimes easy to obtain some HF wave functions.

[30] Even for the electron-gas problem D_g is not known [A. W. Overhauser, Phys. Rev. **128**, 1437 (1962)]. For a fermion gas with δ-function interaction replacing the Coulomb interaction, the condition for local stability of the HF wave function formed by the determinant of plane waves of lowest energy has been reduced to a simple inequality (Ref. 4, pp. 27–28). Nonetheless, this wave function when locally stable, has not been shown to be a D_g, even for this relatively simple problem.

ground HF wave function. In this paper we exhibit some examples of this type.

It is interesting to consider in connection with the foregoing discussion the somewhat simpler, but quite analogous situation occurring for Heisenberg models of a system of N interacting quantum-mechanical spins. The analog of a Slater determinant D is a product

$$P=\prod_{i=1}^{N}\phi_i,$$

where ϕ_i is a single-spin state. In the case of N very large, it is very difficult to determine the analog P_g of a D_g for most of these models, as might have been anticipated. Nevertheless, in contrast to the situation for the electron problem, approaches have been found which have been successful in determining a P_g for many choices of the parameters in the Heisenberg Hamiltonian. These ideas are further clarified in Appendix A where the analogy between N-fermion models and N-spin models is defined precisely and discussed in more detail.

II. UPPER BOUND ON THE GROUND HF ENERGY

In this section we prove for many-electron systems with the usual nonrelativistic Hamiltonian

$$H=\sum_i\left(\frac{p_i^2}{2m}-\sum_\nu\frac{Z_\nu e^2}{|\mathbf{r}_i-\mathbf{R}_\nu|}\right)+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}\qquad(2.1)$$

the following

Theorem: Consider an N-electron system with the nuclei fixed in position and lying within a bounded region: $|\mathbf{R}_\nu|\leqslant R_{\max}$. If a physically reasonable Slater determinant D for this system has the property

$$D=O(r_i{}^pe^{-\gamma r_i})\qquad(2.2)$$

for large r_i, where p is finite and γ is positive, then

$$E(\tilde{D}_g)\leqslant E(D),\qquad(2.3)$$

where $\tilde{D}_g$ is the ground HF wave function for the corresponding $(N+1)$-electron system.

The theorem states, in other words, that the energy of the N-electron determinant D is an upper bound on the ground HF energy for the $(N+1)$-electron system. More pictorially, an electron can be added to the system without raising its energy. We note that the property (2.2) holds for all r_i if it holds for one, because of the antisymmetry of D. Also, the Coulomb potential of the nuclei is the same for the N-electron and the $(N+1)$-electron systems. The meaning of "physically reasonable" in the statement of the theorem is clarified in Appendix B.

The *proof* is as follows. We define the $(N+1)$-electron determinant

$$\tilde{D}(\kappa)=\mathcal{A}[D(1,2,\cdots,N)\phi_\kappa(N+1)],\qquad(2.4)$$

where $\mathcal{A}$ is the antisymmetrizer and

$$\phi_\kappa=(\kappa^3/\pi)^{1/2}e^{-\kappa r}\alpha,\qquad(2.5)$$

with α a one-electron spin function and $\kappa>0$. It is shown in Appendix B that

$$\lim_{\kappa\to0}E[\tilde{D}(\kappa)]=E(D).\qquad(2.6)$$

The relation (2.3) follows immediately from this together with the relation

$$E(\tilde{D}_g)\leqslant E[\tilde{D}(\kappa)],\qquad(2.7)$$

which is a consequence of the definition of $\tilde{D}_g$, and holds for all $\kappa>0$.

The physical content of (2.6) is apparent after a moment's reflection. According to (2.2), the electrons of D are essentially localized within a sphere of radius $r_0\cong\gamma^{-1}$; $\tilde{D}$ is obtained from D by adding an electron in the orbital ϕ_κ, which for κ sufficiently small becomes very spread out compared to r_0 and $R_{\max}$. Hence this electron spends very little time near the nuclei and the other electrons, so that its Coulomb interaction with them becomes very small; also its kinetic energy becomes small, both approaching zero as $\kappa\to0$.

Reviewing the logical structure of the proof, we observe that it depends neither on the class of wave functions being D's nor on the particular form of the Hamiltonian (2.1). In our discussion the D's were actually used only in the proof of (2.6). However, the physical argument of the preceding paragraph suggests that (2.6) is true also for more general classes of wave functions. It thus appears that the theorem can be considerably generalized. If the theorem can be extended, in particular, to the class of all wave functions (as seems likely), it follows that for one-center systems electron affinities are always non-negative: $E(\tilde{\Psi}_g)\leqslant E(\Psi_g)$. This more general theorem would not apply to the electron affinities of molecules, where the ground states of systems differing by one electron do not in general have the same nuclear configuration, and also vibrational energies can enter the definition of electron affinities in an important way.

III. THE INSTABILITY OF CONVENTIONAL HF STATES

The difference $\Delta\equiv E(D)-E(\tilde{D})$ is tabulated in Table I for some one-center systems. D and $\tilde{D}$ are respectively N- and $(N+1)$-electron Slater determinants for the systems A and A^-. The values of $E(D)$ and $E(\tilde{D})$ are taken from published calculations[31–33] in which, it is readily seen, D and $\tilde{D}$ satisfy (2.2). The theorem of Sec. II then applies, and it follows from (2.3) that if Δ is negative, $E(\tilde{D})$ exceeds the ground HF energy of the $(N+1)$-electron system by at least $|\Delta|$. Thus, when Δ is negative, the $\tilde{D}$ used to calculate the published $E(\tilde{D})$ cannot be a ground HF wave function $\tilde{D}_g$ for the $(N+1)$-electron system,[34] and $|\Delta|$ provides a measure of the discrepancy between $\tilde{D}$ and $\tilde{D}_g$. We see in Table I that a majority of the Δ values are negative, and have magnitudes which are chemically significant.

We note in passing that in regard to exact ground states, as opposed to ground HF states, the more general proposed theorem discussed at the end of Sec. II would contradict calculated results on A and A^- with $A^-=N^-$, N^{--}, and O^{--}, given in column 5 of Table IV of Ref. 32. This suggests that these calculations of the ground-state energies are in error.

IV. SYMMETRY CONSIDERATIONS

An interesting implication of these results concerns symmetry. There has been considerable recent interest in and discussion [8,8a,35,36,12] of the symmetry properties of HF wave functions. It is now generally understood that although a HF wave function is usually assumed to transform in the manner of an exact energy eigenstate, it need not. Many examples have been pointed out of systems with ground HF states which do not transform in the manner of an exact energy eigenstate, and, in particular, in the manner of an exact ground state. Most of the evidence[8] comes from systems with degenerate ground levels, although some comes from systems with nondegenerate ground levels: covalently bonded molecules with large enough internuclear distances.

The possibility that an atomic system with a nondegenerate ground state (a closed-shell one-center system) have a ground HF level with symmetry different from that of the exact ground level has been pointed out and discussed recently by Nesbet[35] and by Heine.[36] In contrast, this possibility was ruled out in a more recent review of the HF approximation.[37] Nesbet, using a qualitative criterion based on the nearness in energy of certain "excited" configurations, concludes that the actual occurrence of this possibility is unlikely. Heine, on the other hand, claims to prove that the usual ^1S HF wave function D for a two-electron one-center system is stable. His argument, however, uses a restricted variation from D, and is therefore not a valid proof (although he does attempt to show that this restriction does not affect the result of the proof).

The theorem of Sec. II and its application in Sec. III lead to the conclusion that closed-shell atomic systems do indeed exist which have a ground HF level with symmetry different from that of the exact ground level, in contradiction to the earlier views. Consider the one-center systems in Table I which are expected to be closed-shell (^1S) according to the conventional configurational description of their ground states.[38] Unless we assume that the errors in the calculated energies on which Table I is based are unreasonably large, we are forced to conclude that H^-, Li^-, O^{--}, and Na^- do *not* have ground HF wave functions with ^1S symmetry.[39,40]

V. THE TWO-ELECTRON ONE-CENTER SYSTEM

In this section we treat in some detail the two-electron atomic system with fixed nuclear charge Ze. In this case the Hamiltonian (2.1) takes the form

$$\mathcal{H}=f(x_1)+f(x_2)+g(x_1,x_2)\,, \qquad (5.1)$$

with $f(x)=-\frac{1}{2}\nabla^2-Z/r$ and $g(x_1,x_2)=1/|\mathbf{r}_1-\mathbf{r}_2|$. Atomic units[41] are used in (5.1) and throughout the rest of this section. In the present context we do not impose the ordinary physical restriction which restricts Z to integer values. The exact solutions of the corre-

---

[31] L. C. Green, M. M. Mulder, M. N. Lewis, and J. W. Woll, Jr., Phys. Rev. **93**, 757 (1954).

[32] E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).

[33] E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

[34] Clementi and McLean state in Ref. 32 that the type of instability that we exhibit here probably would occur, and to avoid it they find it important to introduce certain constraints on the orbitals.

[35] R. K. Nesbet, Rev. Mod. Phys. **35**, 498 (1963).

[36] V. Heine, Czech. J. Phys. **B13**, 619 (1963).

[37] Reference 12, p. 235, comment about restriction (iv).

[38] The ground level of each of the two-electron one-center systems H^-, He, Li^+, Be^{++}, $\cdots$ is known from theoretical considerations to have ^1S symmetry.

[39] For H^- the best published calculation of the ground ^1S HF energy $E(D(^1S)_g)$ is that of Green *et al.* (Ref. 31) in which a three-parameter trial wave function gave the energy value $E_3=-0.487825$ a.u. These authors argue that the three-parameter function gives a good approximation to $D(^1S)_g$, but no quantitative estimate of the energy error $\epsilon\equiv E_3-E(D(^1S)_g)$ was given. Further evidence indicating that this 3-parameter function is quite accurate—perhaps surprisingly so—is provided by more recent calculations of Roothaan *et al.* (Ref. 27) using more flexible variational trial functions to approximate $D(^1S)_g$ for larger $Z(\geqslant 2)$: When orbitals containing up to 13 parameters were used, the energy was found to be lowered from the three-parameter values by at most only about 10^{-5} a.u. for $Z=2$, 3 and smaller amounts for $Z\geqslant 4$. This suggests that the error for H^- is no more than about 10^{-4} a.u., that is, $\epsilon\ll|\Delta|$, where Δ is given in Table I. It would, of course, be interesting to have calculations of the type in Ref. 27 extended to the case $Z=1$. The calculations on Li^-, O^{--}, and Na^- in Refs. 32 and 33 are quite similar to those of Ref. 27, so we expect errors of similar magnitudes.

[40] The conclusion of footnote 39, that $\epsilon\ll|\Delta|$ for H^-, has been further substantiated by very recent calculations of D. Ellis and P. Ros (unpublished): the lowest value of $E(D(^1S))$ they obtained was -0.487924 a.u., corresponding to a six-exponential space orbital of the form $\sum c_i \exp(-\alpha_i r)$ with $(c_i,\alpha_i)=(0.484552, 0.4)$, $(0.191794, 0.5948)$, $(0.316376, 1)$, $(0.067697, 1.4532)$, $(0.018547, 2.7709)$, $(-0.004246, 4.1)$; it is estimated that the energy can be lowered by at most 0.0001 a.u. by using a better choice of coefficients for the given exponentials. The value $E(D(^1S))=-0.48793$ a.u., very close to that of Ellis and Ros, is given in Table V of C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960), but no wave function is specified.

[41] H. Shull and G. G. Hall, Nature **184**, 1559 (1959).

Table I. Symmetry-restricted Hartree-Fock energies of some one-center systems A and the corresponding system with one more electron A^-. $\Delta = E(D) - E(\tilde{D})$ where D and $\tilde{D}$ are the symmetry-restricted determinants[a] for A and A^-, respectively.

A	A^-	Δ (a.u.)
$H(^2S)$	$H^-(^1S)$	-0.01217
$Li(^2S)$	$Li^-(^1S)$	-0.004496
$B(^2P)$	$B^-(^3P)$	-0.00986
$C(^3P)$	$C^-(^4S)$	$+0.02017$
$N(^4S)$	$N^-(^3P)$	-0.07902
$N^-(^3P)$	$N^{--}(^2P)$	-0.29287[b]
$O(^3P)$	$O^-(^2P)$	-0.01988
$O^-(^2P)$	$O^{--}(^1S)$	-0.30506[b]
$F(^2P)$	$F^-(^1S)$	$+0$ 05007
$Na(^2S)$	$Na^-(^1S)$	-0.0043
$Al(^2P)$	$Al^-(^3P)$	$+0.0011$
$Si(^3P)$	$Si^-(^4S)$	$+0.0351$
$P(^4S)$	$P^-(^3P)$	-0.0200
$S(^3P)$	$S^-(^2P)$	$+0.0334$
$Cl(^2P)$	$Cl^-(^1S)$	$+0.0947$

[a] $\tilde{D}$ for H^- are from Ref. 31; all other values are from Table IV of Ref. 32 and Table V of Ref. 33.
[b] These values are somewhat uncertain according to Ref. 32.

sponding Schrödinger equation

$$(\mathcal{H} - W)\Psi = 0 \tag{5.2}$$

are either singlets or triplets, and the ground state is known[38] to be a ^1S, so that this is a closed-shell system. Approximate solutions of (5.2) have been comprehensively reviewed recently.[18,19] Here we are concerned with the HF approximation to the minimum-W Ψ; as a first step towards understanding HF theory for this simple system we consider a model for the HF approximation based on Slater determinants D^{model} defined by three assumptions ([1]–[3]) to be discussed in turn. In D the orbitals ψ_i, $i=1$, 2, can be assumed to be orthogonal without loss of generality. We do not make this assumption, although we do assume them to be normalized: $\langle\psi_i|\psi_i\rangle = 1$.

(1) Each orbital ψ_i is a product

$$\psi_i(x) = u_i(\mathbf{r})\chi_i(s) \tag{5.3}$$

of a space orbital u_i and a spin function χ_i, both normalized: $\langle u_i|u_i\rangle = \langle\chi_i|\chi_i\rangle = 1$; χ_i is the eigenfunction, with eigenvalue $\frac{1}{2}$, of the component $\mathbf{s}\cdot\mathbf{n}_i$ of the spin-angular momentum $\mathbf{s}$ in the direction of some unit vector $\mathbf{n}_i$. Using (5.3) in D and substituting into (1.1) we find that the energy $E(D)$ reduces to

$$E = E(u_1,u_2,\mu) = \frac{A - B\mu}{1 - C\mu}, \tag{5.4}$$

where

$$\begin{aligned} A &= \langle u_1u_2|\mathcal{H}|u_1u_2\rangle, & B &= \langle u_1u_2|\mathcal{H}|u_2u_1\rangle, \\ C &= |\langle u_1|u_2\rangle|^2, & \mu &= |\langle\chi_1|\chi_2\rangle|^2, \end{aligned} \tag{5.5}$$

with the overlap matrices $\langle u_1|u_2\rangle$ and $\langle\chi_1|\chi_2\rangle$ satisfying $0 \leqslant C \leqslant 1$ and $0 \leqslant \mu \leqslant 1$. The energy (5.4) is a monotonic function of μ; it therefore suffices to treat only the parallel spin ($\mu = 1$) and antiparallel spin ($\mu = 0$) cases. For parallel spins, D is a triplet. For antiparallel spins, D is a singlet if $|\langle u_1|u_2\rangle| = 1$; otherwise it is a singlet-triplet mixture. If $\langle u_1|u_2\rangle = 0$, then $C = 0$ and $B > 0$, so that $E(\mu=1) - E(\mu=0) = -B < 0$, and, as expected, the lowest energy is attained by the triplet.

In passing we note that, starting with the energy expression (5.4), one can obtain a system of restricted Hartree-Fock (RHF) equations in the same way as the HF equations are obtained. It can be shown that a solution of these RHF equations provides also a solution of the HF equations (we have shown this only for the present special case). The converse, that a solution of the HF equations with orbitals having the space-spin product form is also a solution of the RHF equations, is a special case of the following self-evident general theorem: Any solution of the HF equations must be a solution of restricted HF equations obtained by considering a restricted class of determinants containing the given HF wave function.

(2) The space orbitals u_1 and u_2 are spherically symmetrical. D then represents an S state; the converse is also true.[42] ^1S HF wave functions incorporate assumptions [1] and [2] and also $u_1 = u_2$. Previous approximations to ^1S HF wave functions[27,31] for two-electron one-center systems have already been discussed[39,40] in this paper. In contrast to the earlier work we do not assume $u_1 = u_2$ with a fairly complicated form for the orbital, but rather we allow $u_1 \neq u_2$, assuming a very simple form for the two orbitals. Namely, we assume

(3) u_1 and u_2 are of $1s$ hydrogenic form v:

$$\begin{aligned} v_1(\mathbf{r}) &= (\alpha_1^3/\pi)^{3/2} e^{-(\alpha_1 + i\alpha_1')r}, \\ v_2(\mathbf{r}) &= (\alpha_2^3/\pi)^{3/2} e^{-(\alpha_2 + i\alpha_2')r}, \end{aligned} \tag{5.6}$$

where the four α's are real; also $\alpha_1 > 0$ and $\alpha_2 > 0$. The coefficients in the exponents are allowed to be complex for the sake of generality. This restricted problem is worthwhile for two reasons. It provides a model which is simple to analyze, and we expect that the results will show many of the features to be expected when less restricted orbitals u_i are used.

Results

For the model thus defined by assumptions (1)–(3) the coefficients A, B, and C in (5.4) and (5.5) become

$$\begin{aligned} A &= \kappa^2 - 2\left(Z - \frac{5}{16}\right)\kappa + \left(1 - \frac{3}{4\kappa}\right)\lambda^2 + \frac{1}{8\kappa^3}\lambda^4 + \rho^2 + \sigma^2, \\ B &= CF, \quad C = [(\kappa^2 - \lambda^2)/(\kappa^2 + \sigma^2)]^3, \\ F &= \kappa^2 - 2\left(Z - \frac{5}{16}\right)\kappa - \lambda^2 - \left(1 - \frac{3}{4\kappa}\right)\sigma^2 + \frac{1}{8\kappa^3}\sigma^4 + \rho^2, \end{aligned} \tag{5.7}$$

---

[42] M. Delbrück, Proc. Roy. Soc. (London) **A129**, 686 (1930).

where we have introduced new parameters κ, λ, ρ, and σ

$$\begin{aligned}\kappa&=\tfrac{1}{2}(\alpha_1+\alpha_2)\,, & \rho&=\tfrac{1}{2}(\alpha_1'+\alpha_2')\,,\\ \lambda&=\tfrac{1}{2}(\alpha_1-\alpha_2)\,, & \sigma&=\tfrac{1}{2}(\alpha_1'-\alpha_2')\,,\end{aligned}\tag{5.8}$$

which are real and satisfy the relations $\kappa>0$ and $0\leqslant\lambda^2/\kappa^2<1$. The antiparallel spin energy E_a is clearly minimum when $\rho=\sigma=0$. We have little doubt that the same is true for the parallel spin energy, the triplet energy, E_t (see Appendix D).

Antiparallel Spins

To determine the minimum energy for the antiparallel spin case we make use of the energy expression [A from (5.7) with $\rho=\sigma=0$]

$$E_a=E_a(\kappa,\lambda\,;Z)=\kappa^2+(\tfrac{5}{8}-2Z)\kappa+\left(1-\frac{3}{4\kappa}\right)\lambda^2+\frac{1}{8\kappa^3}\lambda^4 \tag{5.9}$$

together with its first and second derivatives

$$\frac{\partial E_a}{\partial\kappa}=2\kappa+\tfrac{5}{8}-2Z+\frac{3\lambda^2}{4\kappa^2}-\frac{3\lambda^4}{8\kappa^4}\,, \tag{5.10a}$$

$$\frac{\partial E_a}{\partial\lambda}=2\lambda\left(1-\frac{3}{4\kappa}+\frac{\lambda^2}{4\kappa^3}\right), \tag{5.10b}$$

$$\frac{\partial^2 E_a}{\partial\kappa^2}=2-\frac{3}{2\kappa}\frac{\lambda^2}{\kappa^2}+\frac{3}{2\kappa}\frac{\lambda^4}{\kappa^4}\,, \tag{5.11a}$$

$$\frac{\partial^2 E_a}{\partial\kappa\partial\lambda}=\frac{3\lambda}{2\kappa^2}\left(1-\frac{\lambda^2}{\kappa^2}\right), \tag{5.11b}$$

$$\frac{\partial^2 E_a}{\partial\lambda^2}=2-\frac{3}{2\kappa}+\frac{3}{2\kappa}\frac{\lambda^2}{\kappa^2}\,, \tag{5.11c}$$

and the determinant

$$\Delta=\frac{\partial^2 E_a}{\partial\kappa^2}\frac{\partial^2 E_a}{\partial\lambda^2}-\left(\frac{\partial^2 E_a}{\partial\kappa\partial\lambda}\right)^2. \tag{5.12}$$

The stationary points are determined by

$$\partial E_a/\partial\kappa=\partial E_a/\partial\lambda=0$$

together with $\kappa>0$ and $0\leqslant\lambda^2/\kappa^2<1$. From (5.10a) and (5.10b) it follows that there is one singlet stationary point (κ_s,λ_s) with $\lambda_s=0$, and four nonsinglet stationary points. Two of the nonsinglet stationary points, $(\kappa_{ns},\lambda_{ns})$ and $(\kappa_{ns},-\lambda_{ns})$ with $\lambda_{ns}\neq0$, are locally stable and are degenerate; the other two are unstable (and degenerate) and will henceforth be ignored in this section. [A stationary point is locally stable if (5.11a), (5.11c), and (5.12) are positive; it is unstable if any of these quantities is negative.] A detailed examination (see Appendix C) yields the results given in Table II concerning these points. The singlet and nonsinglet stationary energies in Table II are equal for $Z=Z_c^{\text{model}}=1.0773$. This value lies in the range $17/16<Z\leqslant13/12$ where both the singlet and nonsinglet stationary points are locally stable. The singlet stationary point is thus metastable for $17/16<Z<Z_c^{\text{model}}$ and the nonsinglet stationary point is metastable for $Z_c^{\text{model}}<Z\leqslant13/12$.

We note that the more spread out of the two nonsinglet orbitals has orbital exponent $\kappa-|\lambda|$ which decreases monotonically to zero as Z decreases from 13/12 to 1. In other words, this orbital becomes more spread out as Z decreases, becoming spacially unbound as $Z\rightarrow1$.

When the nonsinglet minimum energy occurs arbitrarily near the boundary $|\lambda|=\kappa$, it may be at a nonstationary point, in that $\partial E/\partial\lambda$ need not vanish. This is, in fact, the situation for $0<Z<1$, in which case $\kappa_{\text{ns}}=\frac{1}{2}Z$ and $E_{a,\min}(Z)=-\frac{1}{2}Z^2$.[43]

We conclude that for antiparallel spins the minimum energy as a function of Z is given by

$$\begin{aligned}E_{a,\min}(Z)&=E_a(\kappa_{\text{ns}},\lambda_{\text{ns}}\,;Z)\,, & 0<Z&\leqslant Z_c^{\text{model}}\\ &=E_a(\kappa_s,0\,;Z)\,, & Z_c^{\text{model}}&\leqslant Z\,.\end{aligned}\tag{5.13}$$

This is plotted in Fig. 1. Also plotted are the metastable values of the antiparallel spin energy.

Triplet

The triplet energy expression is more complicated than the antiparallel spin energy expression. For this reason and because the minimum triplet energy never lies below the minimum antiparallel spin energy E_a for $Z>0$, we only outline the calculation for the triplet (in Appendix D) and give results: the minimum triplet energy is plotted in Fig. 1 and tabulated in Appendix D.

Discussion

It is interesting to examine how these results are related to the theorem of Sec. II. Letting $\tilde{D}_g$ in (2.3) represent a ground HF wave function of the two-electron system and D a ground wave function of the corresponding one-electron system, we conclude from (2.3) that the ground HF energy of the two-electron one-center system never exceeds the $1s$ hydrogenic energy $E_{1e}=-\frac{1}{2}Z^2$. In particular, for $Z=1$ the negative value of $\Delta=E_{1e}-E(D(^1S))$ given in Table I showed that the ^1S HF wave function considered there is not a ground HF wave function: D_g lies below $D(^1S)$ by at least $|\Delta|$. The analog of the theorem of Sec. II, of the

---

[43] We note that for $0<Z<1$ a small variation about the minimum energy point in (α_1,α_2) space does not represent a small variation of D^{model}, in that

$$\lim_{\delta_1\to0}\lim_{\alpha_1\to0}\int|D(\alpha_1+\delta_1,\,\alpha_2)^{\text{model}}-D(\alpha_1,\alpha_2)^{\text{model}}|^2d\tau_1d\tau_2\neq0,$$

where the integral includes summation over spin coordinates. As a consequence, the occurrence of the minimum energy Slater determinant at a nonstationary point in (α_1,α_2)-space does not imply that it occurs at a nonstationary point in the set of determinants.

TABLE II. Results concerning stationary points of the antiparallel spin energy. (A pair of unstable nonsinglet stationary points discussed in Appendix C is not included in the table.)

	Singlet	Nonsinglet
Stationary points exist for	$\frac{5}{16} \leqslant Z$	$1 \leqslant Z \leqslant 13/12$
with	$\kappa_s = Z - \frac{5}{16}$	$\kappa_{ns} = \frac{2}{3} - \frac{1}{6}(13-12Z)^{1/2}$
	$\lambda_s = 0$	$\lambda_{ns} = \kappa_{ns}(3-4\kappa_{ns})^{1/2}$
Stationary energy	$-\left(Z - \frac{5}{16}\right)^2$	$\frac{1}{54}[46 - 72Z - (13-12Z)^{3/2}]$
Local stability	for $Z > \frac{17}{16}$, local minimum $\frac{5}{16} < Z < \frac{17}{16}$, saddle point min (max) with respect to $\kappa(\lambda)$	$1 \leqslant Z \leqslant 13/12$, local minima

type discussed at the end of that section and applicable to the present model, results from varying D only within the subset of D^{model}'s. This leads to an analog of (2.3) in the form $E(D_g^{\text{model}}) \leqslant E_{1e}$, which shows that the singlet energy E_s is not minimum for the model in the range $Z < 1.0669\cdots$, where $E_{1e} < E_s$.

It is noteworthy that for $Z \leqslant 1$ our results for the model give no information about the ground HF wave function not already known from the theorem of Sec. II. On the other hand, for $Z > 1$ the model calculation does give additional information by providing a D, namely D_g^{model}, for which $E(D) < E_{1e}$. This proves that D_g is bound for $Z > 1$.

This raises an interesting question which to our knowledge has not been answered (or even asked): Is D_g bound also for $Z = 1$?

Concerning the physical origin of the nonsinglet ground level: in the ground state of the two-electron one-center system there is, as usual, a competition between the tendency on the one hand to lower the interelectron Coulomb energy by spatially separating the distributions of the two electrons and on the other hand, to lower the nuclear Coulomb attraction energy by concentrating the electrons near the nucleus. As Z is lowered, at least one sharp transition occurs when the former tendency dominates. The ground HF and ground model wave functions exhibit a transition at $Z = Z_c > 1$ at which the ${}^1S$ symmetry is lost. There is no transition of this type for the exact ground level. The HF value Z_c^{HF} is unknown, although Ros and Ellis have obtained an approximate result $1.05 < Z_c^{\text{HF}} < 1.075$ using flexible variational space orbitals of the type mentioned in Ref. 40, indicating that Z_c^{HF} is close to the value $Z_c^{\text{model}} = 1.0773$ mentioned earlier in this section. The model transition at Z_c^{model} reflects in the model wave function a spatial correlation of the electrons of a radial (or in-out) type, which is the only type of spatial correlation allowed by the restriction to orbitals each of which is a product of a spherical spatial function and a spin function.

A second type of transition occurs at $Z = Z_c'$ where the ground-level wave function (or functions) becomes unbound: For the exact ground level, $0 \leqslant Z_c'^{\text{exact}} < 1$.[44] The question raised previously as to whether D_g is bound for $Z = 1$ is equivalent to asking whether $Z_c'^{\text{HF}} < 1$. For the simple model of this section, $Z_c'^{\text{model}} = 1$, determined by the intersection of the minimum nonsinglet and the one-electron energy curves.

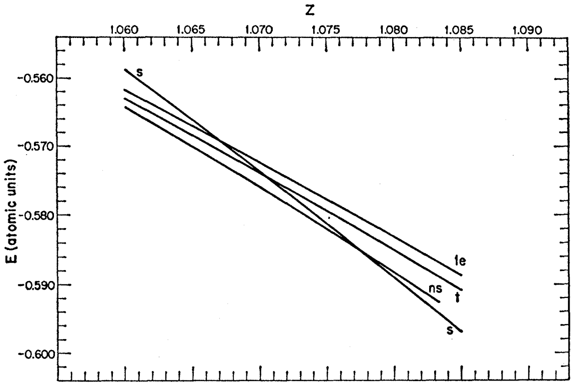

FIG. 1. Crossing points for energies as a function of Z occurring in the model of Sec. V. The one-electron energy E_{1e}, the triplet energy E_t, and the nonsinglet antiparallel spin energy E_{ns} are all equal to -0.5 at $Z = 1$. The singlet energy E_s moves down from the upper left, crossing successively the curves for E_{1e}, E_t, and E_{ns}. The coordinates (Z,E) of the crossing points are: s-$1e$ (1.06694, -0.56918), s-t (1.07036, -0.57436), s-ns (1.07727, -0.58487). The right-hand endpoint of E_{ns} occurs at (1.08333, -0.59259).

---

[44] We note that as Z decreases the exact minimum energy triplet first becomes unbound at $Z = 1$, since it is unbound for $Z = 1$ (see Ref. 18, p. 240) and it lies below the minimum energy triplet of the model for $Z > 1$, which is bound for $Z > 1$. Also, the minimum energy HF triplet, which lies between the minimum energy exact and model triplets, becomes unbound at $Z = 1$.

VI. SUMMARY AND CONCLUSION

To summarize: We have pointed out a useful simple theorem to the effect that an upper bound on the energy $E(D_g)$ of a minimum-energy Slater determinant D_g for an N-electron system is provided by the energy of an $(N-1)$-electron Slater determinant. We applied the theorem to show that for most of the negative atomic ions for which HF calculations have been presented in the literature, the HF wave functions calculated differ from the ground HF wave functions in symmetry and by chemically significant energies. The two-electron one-center system was discussed using a very simple model, providing a concrete and detailed illustration of previous results.

These results dramatize the fact that no practical criterion is known for determining whether a Slater determinant is one of lowest energy. They also show that errors due to neglect of "correlation effects," when judged by the size of the "correlation energy," can be significantly smaller than usual estimates indicate. That results for this type for closed-shell one-center systems should be noticed and pointed out only at this late date in the history of the development of HF theory seems to us remarkable, particularly in the case of the relatively simple two-electron one-center systems. These observations suggest to us that the Slater determinant has hitherto unappreciated and unexploited potentialities as a useful, visualizable, and relatively simple, approximate many-electron wave function, in particular with regard to relaxation of conventional restrictions on the orbitals. Criteria of goodness of approximation other than how well the approximate energy represents the exact energy—the one criterion used in this paper—are often appropriately used in practice. How well a D_g or a good approximation to a D_g satisfies such other criteria remains to be seen, of course, and is an important consideration. Our point is that the problem of determining a D_g is worth exploring in greater depth, particularly for solids with their great complexity where it is difficult enough to use the HF approach let alone more sophisticated approaches developed in recent years which can in principle give more accurate approximations.[45]

Note added in proof. Perkins[45a] has independently examined the model of Sec. V and finds that the singlet is not the only stationary Slater determinant. However, his claim that the singlet energy is a true minimum for $Z\geqslant 17/16=1.0625$ is in error: the singlet energy is a true minimum only for $Z\geqslant Z_c^{\text{model}}=1.0773$. The singlet is only *metastable* for Z in the range $17/16<Z<Z_c^{\text{model}}$; it is the nonsinglet which is stable in this range (see Fig. 1). Going outside this model by using more general radial orbitals, Perkins finds a tendency for one of the orbitals to become spread out as Z is lowered toward $Z=1$, a feature also of the model of Sec. V, as pointed out there.

ACKNOWLEDGMENT

We wish to thank V. J. Mason for obtaining the numerical results presented in Fig. 1 and Table III.

APPENDIX A: AN ANALOGY BETWEEN THE N-ELECTRON PROBLEM AND N-SPIN MODELS

As indicated in the Introduction there is a direct analogy between the HF approximation for N-fermion models and the product approximation for N-spin models, that is, between "single-particle" approximations for these two types of models. It is worthwhile to examine this analogy in more detail here because it can shed light on HF theory, particularly since there has been significant progress in solving problems within the product approximation for N-spin models.

Instead of N electrons each with operators $\mathbf{r}_i$, $\mathbf{p}_i$, $\mathbf{s}_i$ (position, momentum, and spin), and functions of these, one has N "spins" as the particles of the spin-model, each with its spin operator $\mathbf{S}_i$. Whereas for electrons the spin quantum numbers S_i are all $\frac{1}{2}$, for the spin-models each S_i can be any positive multiple of $\frac{1}{2}$. Instead of the electron Hamiltonian function H of $\mathbf{r}_i$, $\mathbf{p}_i$, $\mathbf{s}_i$, one has a spin-Hamiltonian function H_s of the $\mathbf{S}_i$. To be explicit, we consider for H_s the form

$$H_s=-\sum_{ij} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j-\sum_{ij} K_{ij}S_{iz}S_{jz}, \qquad \text{(A1)}$$

where i and j run from 1 to N; the subscripts i are usually associated with the atomic positions and the z components of $\mathbf{S}_i$ with some direction in some crystal structure, and the parameters J_{ij}, K_{ij} (and also the S_i) are then chosen to reflect the symmetry of that structure. The problem analogous to determining a ground wave function Ψ_g of H (Ψ_g is in the Hilbert space spanned by all Slater determinants D) is the determination of a ground spin-state $\Psi_g{}^s$ of H_s ($\Psi_g{}^s$ is in the Hilbert space spanned by all product states $P=\prod_{i=1}{}^N \phi_i$, where ϕ_i is a single-spin state). The analog of a single determinant D is a single product P.

---

[45] The instability of the free O^{--} ion discussed in Sec. III suggests that an oxide crystal would be a promising system for a HF approach with orbital restrictions relaxed. The HF approaches customarily used [see, for example, J. Yamashita and M. Kojima, J. Phys. Soc. Japan **7**, 261 (1952) and S. Nagai, *ibid.* **20**, 1366 (1965)] are based on an ionic model, the oxygen orbitals corresponding to a symmetry-restricted (^1S) determinant for O^{--}. The fact that the ground HF energy for free O^{--} is at least 8 eV below the energy of the conventional ^1S HF wave function, an energy difference of the order of magnitude of usual environmental energies— for example, crystal-field splittings and bandwidths— suggests that in a minimum energy Slater determinant for the crystal the orbitals related to the oxygen will not correspond to those in a determinant for O^{--} ions in a ^1S state.

[45a] J. F. Perkins, J. Chem. Phys. **43**, 4184 (1965). We are indebted to S. T. Epstein for pointing out this reference to us.

The analog of each of the four definitions given in the Introduction is easily provided for the spin problem by substituting P for D, H("Hartree") for HF, and single-spin state for orbital.

The spin problem referred to above, in which there has been progress, is the determination of a ground H state, P_g. This is, of course, the analog of the problem of finding a ground HF wave function D_g. We will not go into any detail here about the work on the spin problem, since it has been amply documented,[46–48] but will confine ourselves to a few remarks intended to illuminate and make use of the analogy. We restrict our attention to the large-N case.

It is easy to find many H states; this contrasts with the typical difficulty of finding HF wave functions. For example, any P in which all the orbitals ϕ_i are quantized along the z axis is a stationary point of $E(P)$, i.e., an H state; we will call these *collinear* P's. This is true for any values of the parameters J_{ij}, K_{ij}, and S_i.

However, the fact that one possesses these H states is of little help in solving the real problem of interest, namely the determination of a P_g. It could be considered to be of some help if one knew that one's list of P_{H}'s included *all* P_{H}'s, but one often does not know this. Even if one did have a complete list of the P_{H}'s, the enormous number of them plus the difficulty in ordering their energies as a function of a few parameters would render it practically impossible to straightforwardly determine the minimum.[49,50]

The statements of the previous paragraph are quite obvious, and their analogs for the electron problem are valid. Yet many who work on HF theory do not seem to be aware of these concepts, surprise being evoked when they are told, after expending large amounts of computer time to obtain an accurate D_{HF}, that their D_{HF} is only one of many D_{HF}'s, that their D_{HF} might not be a D_g, and that, in fact, it might not even be close to a D_g. One of the uses of the analogy is to make evident these concepts which are essential to an understanding of HF theory.

Despite the great difficulty of finding a P_g, it has been possible to do so for some spin models by means of special techniques.[46–48] This may be regarded as an encouraging sign, *vis-à-vis* the electron problem, at least perhaps for some highly idealized fermion problems.

Finally, the spin problem provides rather striking examples of the inadequacy of the standard type of symmetry restriction in which the wave function P is required to transform in the manner of an exact energy eigenstate. As one example, suppose in H_s that $K_{ij}=0$, i and j run over the positions $\mathbf{n}$ in a simple cubic lattice with $J_{\mathbf{nm}}=J(\mathbf{n}-\mathbf{m})$, $J_{\mathbf{nm}}=0$ unless $\mathbf{n}$ and $\mathbf{m}$ are nearest neighbors and $J_{\mathbf{nm}}=J<0$ for nearest neighbors—a situation obviously leading to antiferromagnetism. The Hamiltonian H_s commutes with $\mathbf{S}^2$, where $\mathbf{S}=\sum_{i=1}^{N}\mathbf{S}_i$. The exact energy eigenstates can, therefore, be chosen to be eigenstates of $\mathbf{S}^2$ also, and it is often helpful in practice to require this when dealing with exact energy eigenstates. This suggests that we impose the same requirement on the approximate wave function P. Let us therefore require that P be an eigenstate of $\mathbf{S}^2$. The problem then, in this restricted Hartree theory, is to determine a lowest energy P that is an eigenstate of $\mathbf{S}^2$. (This is completely analogous to a type of restriction conventionally used in symmetry-restricted HF theory.) We see from the following theorem that in this case the symmetry restriction alone largely determines P.

Theorem[51]*:* A product state P which is an eigenstate of $\mathbf{S}^2$ *must* be of the form $\prod_{i=1}^{N}\psi_s(i)$ where $\psi_s(i)$ is the eigenstate of S_{iz} with the maximum eigenvalue S; S_{iz} is the Cartesian component of $\mathbf{S}_i$ along an arbitrary direction z, this direction being the same for all spins i.

According to the theorem, the only P's which are eigenstates of $\mathbf{S}^2$ are *ferromagnetic* (with maximum value of $\mathbf{S}^2$). Thus, within the Hartree approximation, the restriction of requiring P to be an eigenstate of $\mathbf{S}^2$ leads, in the present example of a Heisenberg antiferromagnet, to the worst possible description.

APPENDIX B: PROOF OF EQUATION (2.6)

In this Appendix we prove the relation (2.6), namely, $\lim_{\kappa\to 0}\Delta_\kappa=0$, where

$$\Delta_\kappa\equiv E(\tilde{D}(\kappa))-E(D). \tag{B1}$$

We first obtain a convenient expression for Δ_κ using expressions for D and $\tilde{D}(\kappa)$ in which the orbitals are

---

[46] J. M. Luttinger, Phys. Rev. **81**, 1015 (1951).

[47] T. A. Kaplan, Bull. Acad. Sci. USSR, Phys. Ser. **28**, 328 (1964) (Columbia Technical Translations), and references contained therein.

[48] D. H. Lyons and T. A. Kaplan, J. Phys. Chem. Solids **25**, 645 (1964).

[49] In the case of the quantum-mechanical Ising spin-model ($J_{ij}=0$) one *does* know the complete list of P_{H}'s, namely the set of all collinear P's with the individual spins quantized along the z axis. Nevertheless, the difficulty of determining a P_g straightforwardly is enormous (see Refs. 46 and 47). It *is*, however, possible to find a P_g for some choices of the Ising model parameters by using the method of Luttinger and Tisza (Ref. 46) or the method of Ref. 48, but for other choices, these and other known methods fail (Ref. 48).

[50] It might be worthwhile bringing out the following point. As stated in Ref. 49, the entire set of P_{H}'s in the case $J_{ij}=0$ consists of the $(2S+1)^N$ collinear P's. This set of course is complete in the Hilbert space. Further, each one of these P's remains a P_{H} when the J_{ij} change from zero. But there are nonzero values of the J_{ij} for which *other* P's become P_{H}'s—showing that the *number* of P_{H}'s can be *greater* than the dimensionality of the space. Thus the set of all states satisfying $\delta[(P,HP)/(P,P)]=0$ (all P_{H}'s) is probably unsatisfactory as an approximation to the set of eigenstates of the Hamiltonian H_s. This situation provides a clear illustration of what Pekar [Zh. Eksperim. i Teor. Fiz. **18**, 525 (1948)] seemed to be trying to say in connection with the analogous HF problem. (His statement, made without proof, that there are *more* D_{HF}'s than there are exact energy eigenstates is clouded by the fact that in the HF problem one begins with a Hilbert space of infinite dimensionality.)

[51] For a proof of this theorem see T. A. Kaplan and W. H. Kleiner, MIT, Lincoln Laboratory, Technical Note No. 1967-15, (unpublished).

orthonormal. If

$$D=\mathcal{A}[\psi_1(1)\psi_2(2)\cdots\psi_N(N)] \tag{B2}$$

then, from (2.4), it follows that

$$\tilde{D}(\kappa)=c\mathcal{A}[\psi_1(1)\psi_2(2)\cdots\psi_N(N)\phi_\kappa(N+1)]. \tag{B3}$$

Without loss of generality we choose the ψ_i to be orthonormal and write $\tilde{D}(\kappa)$ in terms of orthonormal orbitals as

$$\tilde{D}(\kappa)=c'\mathcal{A}[\psi_1(1)\psi_2(2)\cdots\psi_N(N)\bar{\phi}_\kappa(N+1)], \tag{B4}$$

where

$$\bar{\phi}_\kappa\equiv a(\phi_\kappa-\sum_{i=1}^{N}\psi_i S_i), \tag{B5}$$

with

$$S_i=(\psi_i|\phi_\kappa) \tag{B6}$$

and

$$a=(1-\sum_{i=1}^{N}|S_i|^2)^{-1/2}. \tag{B7}$$

In (B3) and (B4), c and c' are normalization constants. Using the standard expression for the energy (1.1) of a determinant of orthonormal orbitals we then find

$$\Delta_\kappa=(\bar{\phi}_\kappa|f|\bar{\phi}_\kappa)+\sum_{i=1}^{N}[(\psi_i\bar{\phi}_\kappa|g|\psi_i\bar{\phi}_\kappa)-(\psi_i\bar{\phi}_\kappa|g|\bar{\phi}_\kappa\psi_i)], \tag{B8}$$

where

$$f=\frac{p^2}{2m}-\sum_\nu\frac{Z_\nu e^2}{|\mathbf{r}-\mathbf{R}_\nu|}, \tag{B9}$$

$$g(1,2)=\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}, \tag{B10}$$

and

$$(ab|g|cd)\equiv\int d\xi_1 d\xi_2 a(1)^*b(2)^*g(1,2)c(1)d(2), \tag{B11}$$

$\int d\xi$ standing for the usual integral over space and sum over spin coordinates.

To prove that $\lim_{\kappa\to0}\Delta_\kappa=0$, we prove that each term on the right-hand side of (B8) vanishes as $\kappa\to0$. Since[52]

$$|(\psi_i\bar{\phi}_\kappa|g|\bar{\phi}_\kappa\psi_i)|\leqslant(\psi_i\bar{\phi}_\kappa|g|\psi_i\bar{\phi}_\kappa), \tag{B12}$$

it suffices to show that in the limit each term of

$$(\bar{\phi}_\kappa|f|\bar{\phi}_\kappa)=a^2\{(\phi_\kappa|f|\phi_\kappa)-\sum_n[(\phi_\kappa|f|\psi_n)S_n+\text{c.c.}]+\sum_{jn}(\psi_j|f|\psi_n)S_j^*S_n\} \tag{B13}$$

and of

$$(\psi_i\bar{\phi}_\kappa|g|\psi_i\bar{\phi}_\kappa)=a^2\{(\psi_i\phi_\kappa|g|\psi_i\phi_\kappa)-\sum_n[(\psi_i\phi_\kappa|g|\psi_i\psi_n)S_n+\text{c.c.}]+\sum_{jn}(\psi_i\psi_j|g|\psi_i\psi_n)S_j^*S_n\} \tag{B14}$$

vanishes. For this purpose it is a sufficient condition that the following quantities exist:

$$(\psi_i|\psi_i),\quad\int d\mathbf{r}|\psi_{n+}(\mathbf{r})||\mathbf{r}-\mathbf{R}|^{-1},\quad(\psi_i|f|\psi_j),$$

$$\int d\mathbf{r}d\mathbf{r}'|\psi_{i\sigma}(\mathbf{r})|^2|\psi_{n+}(\mathbf{r}')||\mathbf{r}-\mathbf{r}'|^{-1},\quad(\psi_i\psi_j|g|\psi_i\psi_n),$$

where $\psi_{i\sigma}(\mathbf{r})$ is defined by $\psi_i=\psi_{i+}(\mathbf{r})\alpha+\psi_{i-}(\mathbf{r})\beta$, β being the usual spin function orthogonal to α. This condition is weak and will almost invariably be satisfied in practice. The term "physically reasonable" occurring in the statement of the theorem of Sec. II refers to D's which satisfy the above condition.

The rest of the proof involves a straightforward calculation. Here we simply illustrate the type of argument used by discussing the overlap integrals S_i:

$$|S_i|=|(\phi_\kappa,\psi_i)|\leqslant(\kappa^3/\pi)^{1/2}\int e^{-\kappa r}|\psi_{i+}(\mathbf{r})|d\mathbf{r}\leqslant(\kappa^3/\pi)^{1/2}\int|\psi_{i+}(\mathbf{r})|d\mathbf{r}=O(\kappa^{3/2}). \tag{B15}$$

The last step requires that $\int|\psi_{i+}(\mathbf{r})|d\mathbf{r}$ be bounded, which follows from (2.2) and normalizability of ψ_i. Consequently, $\lim_{\kappa\to0}a=1$. In a similar manner we find that the matrix elements in (B13) and (B14) involving ϕ_κ have the following behavior for small κ:

$$(\phi_\kappa|f|\phi_\kappa)=O(\kappa),\qquad(\phi_\kappa|f|\psi_n)=O(\kappa^{3/2}),$$
$$(\psi_i\phi_\kappa|g|\psi_i\phi_\kappa)=O(\kappa),\quad(\psi_i\phi_\kappa|g|\psi_i\psi_n)=O(\kappa^{3/2}).$$

It is then clear that (B13), (B14), and hence Δ_κ vanish in the limit $\kappa\to0$, proving (2.6).

APPENDIX C: STATIONARY POINTS OF THE ANTIPARALLEL SPIN ENERGY

The calculation for the singlet stationary point is very simple. The analysis for the nonsinglet stationary points is more intricate, so we record here some details of it for easy reference. In this case setting (5.10b) equal to zero gives for λ

$$\lambda^2=\kappa^2(3-4\kappa). \tag{C1}$$

Substituting (C1) into the remaining equations of

---

[52] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951). Although Roothaan's proof explicitly assumed the orbitals to be functions of space only, reinterpretation of the symbols in his formal proof leads directly to (B12).

(5.9)–(5.12) we find

$$E_a = -2\kappa^3 + 4\kappa^2 - (2Z + \tfrac{1}{2})\kappa\,, \tag{C2}$$

$$\partial E_a/\partial\kappa = -6\kappa^2 + 8\kappa - (2Z + \tfrac{1}{2})\,, \tag{C3}$$

$$\partial^2 E_a/\partial\kappa^2 = (24\kappa^2 - 28\kappa + 9)/\kappa > 0\,, \tag{C4a}$$

$$\partial^2 E_a/\partial\kappa\partial\lambda = 3\lambda(2\kappa - 1)/\kappa^2\,, \tag{C4b}$$

$$\partial^2 E_a/\partial\lambda^2 = (3 - 4\kappa)/\kappa\,, \tag{C4c}$$

$$\Delta = 4(3 - 4\kappa)(2 - 3\kappa)/\kappa\,. \tag{C5}$$

From $\partial E_a/\partial\kappa = 0$ and (C3) one finds that

$$\kappa = \tfrac{2}{3} \pm \tfrac{1}{6}(13 - 12Z)^{1/2}.$$

The corresponding energy is given by

$$\begin{aligned} E_a &= \tfrac{1}{9}\{(13 - 12Z)\kappa - (4Z + 1)\} \\ &= \{46 - 72Z + (13 - 12Z)^{3/2}\}/54. \end{aligned}$$

For κ to be real we must have $Z \leqslant 13/12$. From (C1) and the constraint $0 \leqslant \lambda^2/\kappa^2 < 1$, we see that a nonsinglet stationary point exists only for $\frac{1}{2} < \kappa \leqslant \frac{3}{4}$. Consequently, there is a pair of degenerate stationary points $(\kappa_{\mathrm{ns}}, \pm\lambda_{\mathrm{ns}})$ with $\kappa_{\mathrm{ns}} = \frac{2}{3} - \frac{1}{6}(13 - 12Z)^{1/2}$, $\lambda_{\mathrm{ns}} = \kappa_{\mathrm{ns}}(3 - 4\kappa_{\mathrm{ns}})^{1/2}$ in the range $1 < Z \leqslant 13/12$, and another pair $(\kappa_{\mathrm{ns}}', \pm\lambda_{\mathrm{ns}}')$ with $\kappa_{\mathrm{ns}}' = \frac{2}{3} + \frac{1}{6}(13 - 12Z)^{1/2}$, $\lambda_{\mathrm{ns}}' = \kappa_{\mathrm{ns}}'(3 - 4\kappa_{\mathrm{ns}}')^{1/2}$ in the range $17/16 \leqslant Z \leqslant 13/12$.

From (C4a), (C4c), and (C5) we see that a nonsinglet stationary point is locally stable if $\kappa < \frac{2}{3}$. It follows that the points $(\kappa_{\mathrm{ns}}, \pm\lambda_{\mathrm{ns}})$ are locally stable in the range $1 < Z < 13/12$, while $(\kappa_{\mathrm{ns}}', \pm\lambda_{\mathrm{ns}}')$ are unstable throughout the range in which they are defined.

Nonstationary Minimum Energy

The nonsinglet minimum energy for $0 < Z \leqslant 1$, which occurs near the boundary $|\lambda| = \kappa$, is obtained simply by substituting $\lambda^2 = \kappa^2$ into (5.9) and finding the minimum with respect to κ.

APPENDIX D: THE TRIPLET ENERGY E_t

To examine $E_t(\kappa,\lambda,\rho,\sigma; Z) = (A - B)/(1 - C)$ with A, B, C given by (5.7) we notice first that since $\partial E_t/\partial\rho = 2\rho$, stationary points of E_t occur only for $\rho = 0$. Replacing the remaining parameters κ, λ, σ by κ, $x = \lambda^2/\kappa^2$, $y = \sigma^2/\kappa^2$ $(0 \leqslant x < 1,\ y \geqslant 0)$ and minimizing with respect to κ, we find that E_t reduces to

$$E_t(x,y;Z) = -\frac{(A_1 - CF_1)^2}{4(A_2 - CF_2)(1 - C)} \tag{D1}$$

corresponding to

$$\kappa(x,y;Z) = -\frac{(A_1 - CF_1)}{2(A_2 - CF_2)}\,, \tag{D2}$$

where

$$\begin{aligned} &A_1 = \tfrac{1}{8}x^2 - \tfrac{3}{4}x - 2Z + \tfrac{5}{8}\,, \quad A_2 = 1 + x + y\,, \\ &F_1 = \tfrac{1}{8}y^2 + \tfrac{3}{4}y - 2Z + \tfrac{5}{8}\,, \quad F_2 = 1 - x - y\,, \\ &C = [(1 - x)/(1 + y)]^3. \end{aligned} \tag{D3}$$

The expression (D1) represents the energy only for those values of x, y, Z for which $\kappa(x,y;Z) > 0$. An examination of $E_t(x,y;Z)$ for $y \ll 1$ and $y \gg 1$ together with a sampling of values of $E_t(x,y;Z)$ leads us to conclude that its minimum with respect to y always occurs for $y = 0$. Results of minimizing $E_t(x,0;Z)$ with respect to x are given in Table III and are plotted in Fig. 1.

TABLE III. The minimum triplet energy $E_{t,\,\mathrm{min}}$ (in atomic units) as a function of Z, for the model of Sec. V. For $0 < Z < 1$, $E_{t,\,\mathrm{min}}$ coincides with the minimum antiparallel-spin energy and the one-electron energy: $E_{t,\,\mathrm{min}}(Z) = -\frac{1}{2}Z^2$ with $\kappa = \frac{1}{2}Z$, $|\lambda| = \kappa^-$.

Z	$E_{t,\,\mathrm{min}}$	κ_{min}	λ_{min}
1.000	−0.5000	0.5000	0.5000^-
1.005	−0.5050	0.5047	0.5003
1.010	−0.5101	0.5091	0.5009
1.020	−0.5204	0.5172	0.5027
1.030	−0.5308	0.5250	0.5049
1.040	−0.5414	0.5325	0.5074
1.060	−0.5629	0.5469	0.5127
1.065	−0.5684	0.5505	0.5141
1.070	−0.5740	0.5540	0.5155
1.075	−0.5795	0.5575	0.5170
1.080	−0.5851	0.5610	0.5184
1.085	−0.5907	0.5644	0.5199
1.100	−0.6078	0.5747	0.5243
1.500	−1.1718	0.8323	0.6548
2.000	−2.1606	1.1448	0.8238
3.000	−5.0717	1.7660	1.1636
4.000	−9.2240	2.3862	1.5035
5.000	−14.6163	3.0062	1.8432
10.000	−60.1762	6.1057	3.5405