

To get an exact idea of the probability of presence of the second electron, one must think of this graph as of the meridian section of a repartition around the Ou axis. Furthermore we have to compute ψ^2 and to multiply by the weight function $r_2^2 \sin \theta_{12}$. The lines of equal probabilities are represented in Fig. 3. Without correlation, they would be symmetric with respect to the axis $\theta_{12} = 90^\circ$. With correlation, the repelling action of the fixed electron is obvious. The conversion factor from relative to absolute values is a product

$$10^{-1}N^{-1}8\pi^2a^2 \exp(-2ea) = 0.67,$$

where 10^{-1} stands for the scale of the graph, N^{-1} for the normalization, $8\pi^2$ for the angular coordinates of the $r_1r_2r_{12}$ triangle in space, and $a^2 \exp(-2ea)$ for the density of probability of the first electron.

We thank G. Faivre for assistance in preparing Table I.

TABLE I. Mean values in atomic units without and with correlation in a 27-term approximation.

	without φ	with φ
norm	0.40312	0.53551
potential energy	-5.7511	-5.8074
$\langle r_1^{-1} \rangle$	1.7040	1.6883
$\langle r_{12}^{-1} \rangle$	1.0650	0.9458
kinetic energy	2.9037	2.9037
total energy	-2.8474	-2.9037
$\langle r_1 \rangle$	0.8803	0.9298

TABLE II. Maximum and minimum of the correlation factor for different positions of the first electron (a is in atomic units of length).

a	0	0.25	0.50	0.75
φ_0	1	1.053	1.111	1.175
φ_a	1	0.894	0.820	0.763

Discussion on The Hartree-Fock Approximation

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LÖWDIN: I would like to comment on some peculiarities with respect to the symmetry properties. In the original atomic Hartree calculations [D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928); Repts. Prog. Phys. **11**, 113 (1948); *Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957)] it was assumed that the resulting orbitals would be symmetry-adapted and, in the calculations, the corresponding self consistent field potentials would always be replaced by their spherically symmetric part. The scheme was essentially refined when Slater [J. C. Slater, Phys. Rev. **35**, 210 (1930)] and Fock [V. Fock, Z. Physik **61**, 126 (1930)] suggested that the total wave function Ψ should be approximated by a single determinant built up from spin-orbitals, and the application of the variation principle lead then to the famous Hartree-Fock equations [V. Fock, Z. Physik **61**, 126 (1930)]. It seems to have been generally assumed that, if the total Hamiltonian H for the many-electron system had a certain symmetry property then the Hartree-Fock functions will also automatically be symmetry-adapted.

Delbrück [M. Delbrück, Proc. Roy. Soc. (London) **A129**, 686 (1930)] proved that, if the total system is spherically symmetric and one requires the total determinant to have 1S character, then the associated orbitals are eigenfunctions of the orbital angular momentum and of the spin. In the case of more general types of symmetry occurring in molecular and solid-state systems, it has later been proven [C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960); P. O. Löwdin, J. Appl. Phys. Suppl. **33**, 251 (1962)] that the assumption that the Hartree-Fock functions are symmetry-adapted, i.e., form a basis for the irreducible transformation, is always *self-consistent* and corresponds to a specific minimum of the total energy. The question I would like to raise is whether this is really an *absolute minimum* or not?

The question whether the extreme values of $\langle H \rangle$ associated with the variation principle are maxima, minima, or terrace points has been studied in some detail [D. J. Thouless, Nuclear Phys. **21**, 225 (1960); W. H. Adams, Phys. Rev. **127**, 1650 (1962)]. Adams uses the term "absolute minimum" to denote a point where the second variation of the total energy is positive definite, whereas we have here used the term to denote the lowest one of all possible minima. So far, however, there has not been found any simple criterion which guarantees the occurrence of an absolute minimum lower than any other possible minima.

Confusion may arise from the fact that the exact eigenfunction Ψ and the approximate eigenfunction in the form of a Slater determinant may have rather different properties. For instance, if Λ is a normal constant of motion satisfying the relation $H\Lambda = \Lambda H$, then every eigenfunction Ψ to H is automatically an eigenfunction to Λ or (in the case of a degenerate energy level) may be chosen in that way, so that

$$H\Psi = E\Psi, \quad \Lambda\Psi = \lambda\Psi. \quad (1)$$

For the exact eigenfunction, the second equation is hence essentially a consequence of the first. For the approximate eigenfunction D , one replaces the first eigenvalue relation by the variation principle $\delta\langle D|H|D\rangle = 0$. So far, no one has proven that, out of this principle, there follows the second equation $\Lambda D = \lambda D$, and this relation should then be considered as a *constraint* which necessarily raises the energy above the absolute minimum.

In the *conventional* treatment of the Hartree–Fock scheme, one apparently starts out from two basic equations:

$$\delta\langle D|H|D\rangle = 0; \quad \Lambda D = \lambda D; \quad (2)$$

and the corresponding energy minimum could then be said to be Λ -adapted. It is easily shown that, if Λ is a fundamental symmetric function of the one-electron operators $\Lambda_1, \Lambda_2, \Lambda_3, \dots, \Lambda_N$, then the spin-orbitals $\Psi_k(x_i)$ corresponding to the energy minimum are eigenfunctions to Λ_1 or can be chosen in that way. This is a special case of the general theorem mentioned above. [C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960); P. O. Löwdin, *J. Appl. Phys. Suppl.* **33**, 251 (1962)].

On the other hand, if one drops the symmetry constraint and considers only the relation

$$\delta\langle D|H|D\rangle = 0, \quad (3)$$

one obtains a *nonrestricted* Hartree–Fock scheme, and the solution D corresponding to the *absolute minimum* has now usually lost its eigenvalue property with respect to Λ , i.e., the corresponding Hartree–Fock functions are no longer symmetry-adapted. For open-shell systems, this type of behavior has been observed by several authors [J. C. Slater, *Phys. Rev.* **81**, 385 (1951); **82**, 538 (1951); *Rev. Mod. Phys.* **25**, 199 (1953); R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); G. W. Pratt, Jr., *Phys. Rev.* **102**, 1303 (1956); J. H. Wood and G. W. Pratt, Jr., *Phys. Rev.* **107**, 995 (1957); R. K. Nesbet and R. E. Watson, *Ann. Phys.* **9**, 260 (1960); L. M. Sachs, *Phys. Rev.* **117**, 1504 (1960); R. E. Watson and A. J. Freeman, *Phys. Rev.* **120**, 1125 (1960); *Phys. Rev.* **120**, 1134 (1960)], and the purpose of my remark is simply to emphasize that the same may happen even in closed-shell systems.

Slater's [J. C. Slater, *Phys. Rev.* **35**, 509 (1930)] fundamental study of the quantum-mechanical treatment of the hydrogen molecule and the VB- and MO-method shows that, for sufficiently separated atoms a and b , the single determinant $(a\alpha, b\beta)$ has a lower energy than the corresponding symmetry-adapted Hartree–Fock solution of type $(\sigma_a)^2$ depending on the fact that the latter has a wrong asymptotic behavior for $R \rightarrow \infty$. The detailed behavior for the equilibrium distance R_0 has not yet been investigated.

The benzene molecule has the symmetry D_{6h} , but the calculations reported using the alternant molecular orbital approach [R. Pauncz, J. de Heer, and P. O. Löwdin, *J. Chem. Phys.* **36**, 2247, 2257 (1962)] indicate that there are single determinants associated with the symmetry D_{3h} which have a considerably lower energy than the corresponding determinants of symmetry D_{6h} ; the discussion refers here to the situation at the equilibrium distance.

The most striking examples are perhaps found in solid-state theory. In considering a system of free electrons in a uniform positive background in a box, one had always believed that the plane waves would correspond to the solution of the Hartree–Fock equations leading to the lowest energy. However, by studying a one-dimensional Fermi gas with δ -function repulsions, Overhauser [A. W. Overhauser, *Phys. Rev. Letters* **4**, 415, 462 (1960); W. Kohn and S. J. Nettel, *Phys. Rev. Letters* **5**, 8 (1960); K. Sawada and N. Fukuda, *Prog. Theoret. Phys. (Kyoto)* **25**, 653 (1961); E. M. Henley and Th. W. Ruijgrok, *Ann. Phys.* **12**, 409 (1961); E. M. Henley and L. Wilets, *Ann. Phys.* **14**, 120 (1961); T. Arai, Technical Report, 1961, Argonne National Laboratories (unpub-

lished]) could show that there existed self-consistent solutions in the form of “giant spin waves” having a lower energy than the plane-wave state. This result looks, of course, paradoxical if one believes that the second relation in (2) follows from the first but becomes much more natural when realizing that one actually knows very little about the symmetry properties of the self-consistent field functions for the absolute minimum of the total energy.

In my opinion, the Hartree–Fock scheme based on a single Slater determinant D is in a dilemma with respect to the symmetry properties and the normal constants of motion Λ . The assumption that D should be symmetry-adapted or an eigenfunction to Λ leads to an energy $\langle H \rangle$ high above the absolute minimum, and the energy difference amounts to at least 1eV per electron pair and more. In the sense of Eckart’s criterion [C. Eckart, *Phys. Rev.* **36**, 877 (1930); B. A. Lengyel, *J. Math. Analysis Appl.* **5**, 451 (1962)], the absolute minimum of $\langle D|H|D \rangle$ leads certainly to a better wave function D , but the symmetry properties are now lost and the determinant is a “mixture” of components of various symmetry types. An elementary theorem in linear algebra tells us that these components are uniquely defined by D , that the “component analysis” is conveniently carried out in practice by means of a set of projection operators O , and that at least one of the components OD has a lower energy expectation value than the mixture D itself [P. O. Löwdin, *Rev. Mod. Phys.* **34**, 520 (1962)].

The antisymmetry requirement associated with the Pauli principle was introduced into the self-consistent field scheme by considering the “antisymmetric component” of the Hartree-product $\psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N)$ uniquely selected by the projection operator

$$O_{AS} = (N!)^{-1} \sum_p (-1)^p P$$

which changed the wave function into a Slater determinant. One way to solve the general “symmetry dilemma” seems to be to continue this line of thinking and to consider the various symmetry components defined by D as the actual wave functions. These wave functions, $\Psi = OD$, are still uniquely related to a simple Hartree product in the “independent particle model” but have the correct symmetry properties or are eigenfunctions to Λ .

Since the energy was optimized with respect to D , one may now obtain a further lowering of the absolute minimum by considering a specific component $\Psi = OD$ and by carrying out an additional variation. This leads to the so-called “extended Hartree–Fock scheme” [P. O. Löwdin, *Phys. Rev.* **97**, 1509 (1955); *Ann. Acad. Reg. Sci. Upsalien.* **2**, 127 (1958); *Advances in Chemical Physics*, edited by I. Prigogine, [Interscience Publishers, Inc., New York (1959)], Vol. 2, p. 270; *J. Appl. Phys. Suppl.* **33**, 251 (1962)], and I hope to be able to comment further on this approach in connection with Professor de Heer’s talk.

Perhaps the picture I have given of the “symmetry dilemma” in the Hartree–Fock scheme is too dark, but I definitely feel that the properties of the functions associated with the absolute energy minimum deserve further studies.

NESBET: Several authors have indicated a belief that there might be an unrestricted Hartree–Fock (UHF) single Slater determinant of lower energy than the usual Hartree–Fock function in closed shell situations, such as the ground states of Be, Ne and N₂. In order to discuss this issue, we should know the theory of the symmetry properties of Hartree–Fock functions.

The UHF equations are necessary and sufficient condition for the energy of a single Slater determinant to be stationary.

Since the UHF equations in canonical form are just linear eigenvalue equations, the canonical UHF orbitals are symmetry-adapted with respect to the symmetry group of the Hartree–Fock operator \mathcal{H}_0 . This operator is a Hermitian quadratic form in the occupied orbitals. The essential theorem follows from these statements [R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); *Phys. Rev.* **109**, 1017 (1958); *Rev. Mod. Phys.* **33**, 28 (1961)]; occupied UHF orbitals must span a representation of the group of \mathcal{H}_0 , i.e., canonical UHF orbitals always fill closed shells with respect to this group. Thus, the *group* is determined by a self-consistency condition, and in general it will be only a subgroup of the group of the many-particle Hamiltonian. Any group which has only one-dimensional irreducible representations is always a possible group of \mathcal{H}_0 . In most cases for atoms with open shell configurations, the UHF functions will distort to spheroidal symmetry

(axial group with inversion). Thus, s_0 and d_0 mix to become σ_0 in the 2P ground state of atomic boron.

This is a very real physical effect (core polarization) and has an important influence on hyperfine structure.

When the usual configuration has no open shells, the self-consistent symmetry conditions are satisfied by a closed shell wave function. This does not rule out the possible existence of another stationary function of lower energy for which \mathfrak{H}_0 has lower symmetry. There is no evidence that such UHF functions exist for closed-shell atomic ground states or for covalently bonded molecules near equilibrium, although such functions occur at large internuclear distances [R. K. Nesbet, *Phys. Rev.* **122**, 1497 (1961)]. Certain "excited" configurations must have rather low energy for this to occur—even for the Be atom the relevant numbers make this appear to be very unlikely.

FROESE: A Fortran program has been written to compute atomic Hartree-Fock wave functions numerically. The techniques, including the energy adjustment, were applied to the hydrogen equation with the resulting mean radius of a $1s$ wave function accurate to 5 digits, a $6s$ to 4 digits. On an IBM 7090, the computing time for an atom such as sodium was about 2 minutes.

This program was used to compute wave functions for the configuration $(1s)^2(2s)^2(2p)^6(nl)$ with a series of nl values, of Fe^{+15} , Al^{+2} , Mg^{+} and Na . Transition integrals were computed from the results and compared with those based on the screened hydrogenic approximation. It was found that for transitions with $\Delta n = 0$ the screened approximation was remarkably accurate, but the accuracy decreased as Z decreased. For transitions with $\Delta n = 1$, only in some instances was the screened approximation fairly accurate. Another factor entered besides the value of Z , namely the amount of cancellation in the evaluation of the integral. Those transitions for which a decrease in the principal quantum number is accompanied by an increase in screening have less cancellation and were the more accurate. For $\Delta n = 2$, the screened approximation gave poor results.

SINANOĞLU: The Hartree-Fock approximation gives good electron densities because it deals mainly with the long range parts of the Coulomb repulsions. The remaining parts are the "fluctuation potentials" M_{ij} in $(H - H_0)$ which are responsible for electron correlation. In contrast with an electron gas, M_{ij} 's in most atoms and molecules are of short range in going from orbital to orbital. Thus, they do not affect the density much, but cause pairwise additive correlation errors in energy.

The detailed form of the exact Ψ of a many electron system

$$\Psi = \phi_0(\text{H.F.}) + \{f_i\} + \{u_{ij}\} + \dots$$

shows the different correlation effects explicitly. The one electron terms arise from correlation trying to modify the H. F. orbitals. They can be calculated in closed form. Some typical cases show them to be negligible [Oktay Sinanoğlu and Debbie Fu-tai Tuan, *J. Chem. Phys.* **38**, 1740 (1963)]. This is why H. F. provides a norm for orbital pictures with simple correlation effects tacked on for only some properties like energy.

LÖWDIN: In your scheme, the wave function has to be renormalized, and the Hartree-Fock function gets a coefficient. I wonder whether, in this connection, it would be better to use the definition of correlation energy given by Green?

SINANOĞLU: For nonclosed shell systems, there seem to be about nine variants of the Hartree-Fock method. The definition of "correlation energy" will depend on which H. F. method is used.

Both the calculation of the H. F. wave function itself and the theory of correlations to be added on will be simplified if: (a) the same orbitals are used for terms arising from the same configuration (e.g., for 3P , 1D , 1S of $1s^22s^22p^2$), which preserves the picture of degeneracy in a central field; (b) if V_i , the H. F. potential is the same acting on any orbital of the nonclosed shell system; and (c) no off-diagonal H. F. energy parameters λ_{ij} exist.

These requirements are satisfied if the *average energy of the configuration* [J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II] is varied and then in the resulting one-electron equations each V_i is modified to become the same [such a method is discussed by A. J. Freeman, *Rev. Mod. Phys.* **32**, 273 (1960)] ("symmetry and

equivalence restrictions" of Nesbet). The fractions of orbital potentials added to or subtracted from V_i 's later appear as small perturbations in the correlation part.

GILDA M. HARRIS: Some of the perturbation expansion and diagram classification techniques now being used in the many-body problem, perhaps can be applied to the isolated many-electron atom. While these methods constitute a potentially useful approach, at the present time, a formal description of a partially ionized, multicomponent many-body system does not lead to a clear description of the nature of the few-particle bound states of atoms and molecules in such a "plasma." Therefore, looking at the problem from the other direction, I would like to suggest that it might also be worthwhile to make use of the progress already made in studying single atoms and molecules in helping to describe the many-body plasma.

One way that this knowledge can be used is to start with a description of the plasma in terms of structured components, i.e., atoms, molecules and ions rather than the more fundamental one which considers only bare nuclei and plane-wave electrons as the initial constituents. With this model, the total free energy of the system can be written in terms of the free energy of the components plus their interactions.

One problem that arises is how to treat the bound states of the atomic and molecular components included in the total system. To zero order, the energy eigenvalues of the isolated system could be used in the partition functions for the internal degrees of freedom. Even in this approximation there is a question of how to cut off the sum of these states since, for example, the boundary conditions on the wave functions and the energy required to ionize are different for an atom in a plasma than for an isolated atom in infinite volume. For a more accurate treatment, the perturbation of the isolated atom bound states by the surroundings should be considered. This can be done on many levels of sophistication. For example a plausible perturbing potential can be postulated and used in a Schrödinger equation for the isolated system to obtain new energy levels more appropriate to the system in a plasma. These energy values can then be used in the partition function for that species in the total free-energy expression for the plasma. The author has done this, for example, for two approximate perturbations: considering the effect of the plasma to be one of confinement only and also considering the effect to be a shielding of the pure Coulomb interactions within the system. Other suggestions and specific calculations have been made, and future ones would be most welcome.

Another problem is how to treat free-free interactions among components, i.e., repulsions and those attractive interactions that do not lead to the formation of few-particle bound states. For neutral-neutral and neutral-charge interactions, weak and short range potentials of interaction can be postulated and used in a series of correction terms to the free energy of an ideal gas in the manner of the virial coefficients. For the interactions among various charged particles, attention must be paid particularly to that between electrons and positive ions and nuclei. We wish to exclude from considerations those interactions which lead to bound states since these are already included to some approximation in the partition functions for the bound states of the individual species. Therefore some distinction must be made between free and bound electrons, allowing only the former to interact with the free ions of the system as independent components. An energy criterion such as a distinction between positive and negative energy electrons on an energy scale consistent with the bound-state description can be made. This is also a currently incompletely resolved problem.

Using some reasonable basis of the definition of a free electron, the problem remains as to how to include charge-charge interactions in the total free energy. A first approximation to this is the classical Debye polarization term which has been put on very sound footing as a correction to an ideal plasma by formal perturbation expansion techniques. The completely classical Debye term can give continuous and ever increasing negative potential energies. Therefore it is important, when using it with a system that has bona-fide quantum mechanically allowed negative energy states (bound states), to use it in connection with a definition of free electrons that excludes the creation of spurious negative energy states. A more elegant way to accomplish this would be to use the quantum mechanical Debye term which results from the treatment of plasmas starting with bare nuclei and plane wave electrons. In this case, the dynamic shielding resulting from the

wave nature of the electrons prevents the classically continuous negative energy distribution. Beyond this collective Coulomb interaction, other terms corresponding to local nonbonding Coulomb interactions could be approximated by some of the results and methods of scattering problems.

Thus, it seems a fair conclusion to state that, within the broad problem of considering the total energy and other properties of a many-body plasma, there are many subproblems that fall within the realm of few-particle atomic physics.