REVIEWS OF MODERN PHYSICS VOLUME 39, NUMBER 1 JANUARY 1967

Approximate Wave Functions for Molecules and Crystals Using Perturbation Theory

JEREMY I. MUSHER*

Belfer Graduate School of Science, Yeshiva University, New York, New York

The use of Rayleigh–Schrödinger perturbation theory for obtaining accurate approximate wave functions for molecules and crystals and particularly for the hydrogen molecule is discussed in some detail for a variety of approximate Ψ_0's. Emphasis is laid on the nonunique choice of the zeroth-order wave functions, and the criterion of "goodness" is suggested to include the ability to obtain higher-order corrections rather than just the expectation value of the total Hamiltonian. The calculation of electric and magnetic properties is also described and comparisons are made for the few calculated values available. Problems of symmetry and spin in the treatment of weakly interacting atoms and ions as in "molecular" crystals are discussed at length and a few related topics are treated in Appendixes.

I. INTRODUCTION

This paper is concerned with approximate wave functions for molecules and crystals and with procedures for improving these wave functions systematically utilizing the Rayleigh–Schrödinger perturbation theory. There are often advantages to solving for corrections to an approximate solution rather than solving for the entire function itself and thus perturbation theoretic procedures are of interest even though it is well known that by using an expansion in a complete set of functions and solving the secular equations one can, in principle, obtain a wave function to any desired degree of accuracy.

We are particularly concerned with the various approximate wave functions for the hydrogen molecule and their perturbation theoretic corrections, as models for calculations on larger molecules and crystals. We also examine the approximate wave functions for crystals in the tight-binding picture and consider how they may be improved by perturbation theory, but we are not concerned with the various band descriptions and the recent collective-excitation descriptions, as they do not obviously gain much from analogies with molecules. The perturbation theoretic approach discussed here may have some utility in improving the band descriptions—as intimated in the studies using pseudopotentials—but that is a subject for further study. This paper was written on the assumptions that perturbation theory can be a useful tool in studying molecules and that the experience gained from studying molecules can be useful in the study of crystals.

In Sec. II we give a discussion of Rayleigh–Schrödinger perturbation theory from our own somewhat different point of view. In Sec. III we present the various relatively simple wave functions for the hydrogen molecule, construct Hamiltonians of which they are eigenfunctions, and describe their corrections using perturbation theory and the calculation of their electric and magnetic properties. The simple product and antisymmetrized product schemes for crystal wave functions are discussed in Sec. IV and the generally unsuspected difficulties for improving these wave functions are discussed.

II. PERTURBATION THEORY

A. The Inhomogeneous Partial Differential Equations

Since the present study is concerned with the ability to solve for molecular and crystal electronic wave functions using perturbation theory, it is pertinent to give some discussion of perturbation theory itself, particularly since we are interested in the explicit solutions to the partial differential equations (p.d.e.'s) themselves which may or may not involve infinite set expansions as described in textbooks. Interest in explicit solutions to perturbation theoretic problems was revived some years ago by the work of Dalgarno and colleagues, and Schwartz on a number of one- and two-electron problems, although their work was preceded by the work of others, notably Sternheimer, dating back to the 1920's. An exhaustive review of the subject was given recently by Hirschfelder, Brown, and Epstein[1] which gives further references. The present discussion is considerably narrower in scope—dealing only with the time-independent Rayleigh–Schrödinger approach—and has a rather different emphasis.

Consider the spin-free nonrelativistic time-independent Schrödinger equation

$$(H-E)\psi=0 \qquad (2.1)$$

for which H can be written as

$$H\equiv H_0+\lambda H_1, \qquad (2.2)$$

H_0 is called the unperturbed Hamiltonian and λH_1, the perturbation Hamiltonian where λ is an arbitrary (and sometimes, dummy) parameter.

---

* This work was partially supported by the National Science Foundation.

[1] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quantum Chem. 1, 255 (1964).

A particular eigenfunction, ψ, of Eq. (2.1) and its eigenvalue, E, can be formally expanded in powers of the parameter λ

$$\psi=\psi_0+\lambda\psi_1+\lambda^2\psi_2+\cdots$$
$$\equiv|0\rangle+\lambda|1\rangle+\lambda^2|2\rangle+\cdots \tag{2.3a}$$
$$E=E_0+\lambda E_1+\lambda^2E_2+\cdots, \tag{2.3b}$$

where it is assumed that ψ_0 is a particular normalized nondegenerate solution (not necessarily the ground state) of

$$(H_0-E_0)|0\rangle=0. \tag{2.4a}$$

ψ_0 does not have to be normalized but it does have to be nondegenerate for otherwise one has to apply degenerate perturbation theory. This restriction prevents ψ_0 from being complex, for since H is a Hermitian operator, if $\psi_0^*\neq$ const. $\times\ \psi_0$ then ψ_0 and ψ_0^* are linearly independent solutions of (2.4a) possessing the same energy eigenvalue. As an example, the two plane waves $\exp(ikx)$ and $\exp(-ikx)$ are both eigenfunctions of $p_x^2/2m$ of energy $\hbar^2k^2/2m$.

The expansions for ψ and E will, in general, converge for $|\lambda|\leq\rho$, where the radius of convergence ρ is a positive number or trivially zero. ρ can be crudely defined as the largest value of λ for which

$$\|\lambda H_1\| < \|H_0\| \tag{2.5}$$

where the norm is defined by

$$\|g\| = \sup_{f\varepsilon\mathcal{L}^2}(gf, gf)/(f,f).$$

Clearly since the usual perturbation, e.g., $-e\mathcal{E}z$, is unbounded in the usual space, e.g., $-\infty>z>\infty$, the relation (2.5) between norms cannot be satisfied for all $f\varepsilon\mathcal{L}^2$. In other words, although the subject has not been adequately investigated, it appears that for many usual quantum-mechanical problems, the radius of convergence is zero. Then the formal expansions for ψ and E must be considered as asymptotic expansions in the limit $\lambda\rightarrow0$, i.e.,

$$\psi=\lim_{\lambda\rightarrow0}(\psi_0+\lambda\psi_1+\cdots)\sim\psi_0+\lambda\psi_1+\cdots \tag{2.6}$$

and similarly for E. (The symbol $\sim$ signifies "asymptotically equal to".) In accord with the theory of asymptotic expansions, for a given finite λ and for a given range of the variable, e.g., $x\leq X(\lambda)$, a particular $n(X,\lambda)$th partial sum of the sequence $\{\psi_n\}$ will be a good approximation to ψ, i.e.,

$$\psi(x,\lambda)\,|_{x\leq X(\lambda)}\approx\psi^{(n)}\equiv\sum_{i=0}^{n(x,\lambda)}\lambda^i\psi_i(x) \tag{2.7a}$$

and similarly

$$E(\lambda)\approx E^{(n')}\equiv\sum_{i=0}^{n'(\lambda)}\lambda^iE_i, \tag{2.7b}$$

where the symbol $\approx$ signifies "approximately equal to" and the partial sums are said to "semi-converge." The lack of absolute convergence of the expansions for ψ and E only means that it is not possible to obtain solutions to any desired degree of accuracy. The accuracy obtainable in practice is generally very well within the region of experimental interest. For example the energy of the helium atom has been calculated[2] using perturbation theory to eight significant figures and with apparent convergence through 13th order in λ. This means that the relation (2.5) holds for that subset of $\mathcal{L}^2$ consisting of the first n elements of the sequence $\{\psi_n\}$ and closely related functions. The fact that ρ might well equal zero implies that eventually there may come an n_0 for which

$$(\psi_{n0},\lambda^2H_1^2\psi_{n0})\geq(\psi_m,H_0^2\psi_m)$$

for some $m\leq n_0$. At this point the partial sums of ψ and E $(n\geq n_0)$ will begin to diverge. In any case, questions of convergence are usually avoided—n_0 may be as large as 100—and it is generally assumed that the perturbation is sufficiently weak that the first few terms of the expansions of ψ and E adequately represent the corrections to ψ_0 and E_0. (We thus exclude the problems of many-body theory for which the energy is not an analytic function of λ.)[2a] These corrections would be linear, quadratic, cubic, etc. in a smallness parameter λ, which might be the strength $\mathcal{E}$ of an external electric field. It is more general however, to set the parameter λ equal to 1, and consider the smallness, and hence the semiconvergence incorporated into the functional form of H_1, as must be done in treating atoms and molecules. We thus accept the results of formal perturbation theory as explicitly valid and the expansions are assumed to converge absolutely to the highest order of interest.

When the expansions of (2.3) are substituted into (2.1) we obtain the sequence of equations which follow (2.4a),

$$(H_0-E_0)|1\rangle=(E_1-H_1)|0\rangle, \tag{2.4b}$$
$$(H_0-E_0)|2\rangle=(E_1-H_1)|1\rangle+E_2|0\rangle, \tag{2.4c}$$
$$(H_0-E_0)|3\rangle=(E_1-H_1)|2\rangle+E_2|1\rangle+E_3|0\rangle, \tag{2.4d}$$
$$(H_0-E_0)|4\rangle=(E_1-H_1)|3\rangle+E_2|2\rangle+E_3|1\rangle+E_4|0\rangle, \tag{2.4e}$$

etc.

Since H_0 is a partial differential operator, if these equations are solved in sequential order, each equation is merely an inhomogeneous partial differential equation for the appropriate correction to ψ_0. We have thus

---

[2] C. W. Scherr and R. E. Knight. Rev. Mod. Phys. **35**, 436 (1963).

[2a] See, however, the demonstration by L. B. Mendelsohn [Phys. Rev. **141**, 113 (1966)] which shows that ψ for the helium atom is not analytic in $z-1$ as generally believed. The importance of logarithmic terms has also been discussed by C. L. Pekeris [Phys. Rev. **146**, 46 (1966)].

replaced the Schrödinger equation—a single homogeneous eigenvalue equation—by a different single homogeneous eigenvalue equation plus a sequence of inhomogeneous p.d.e.'s. We would only follow such a procedure if, despite the greater profusion of equations, the actual computational labor was, in fact, diminished. As it happens, the Schrödinger equation itself can be solved analytically only for a few one-electron problems, so that we must have recourse to other methods, the most useful of which has been the Rayleigh–Schrödinger perturbation theory, Eqs. (2.4). In using these equations the H_0 is chosen so that Eq. (2.4a) possess an easily obtained solution. (Or, one does the reverse, and chooses the ψ_0 first as in the case of the hydrogen molecule wave functions, and then determines the H_0 of which it is an eigenfunction. Incidentally, it is not, in general, necessary to find H_0 explicitly for such calculations.) Thus once the ψ_0 is obtained, the problem reduces to finding the corrections, linear, quadratic, etc. in some parameter by approximate means rather than trying to find an approximate total solution in one fell swoop. It is therefore usually worthwhile to look for a "quick and dirty" ψ_0, if one exists, and to devote the greater efforts to obtain the correction ψ_1 instead of trying to find the best possible ψ_0 with such a great deal of labor that no time or interest is left to carry out the calculation for the first correction term, ψ_1.

The energy corrections are easily obtained from the sequence of equations (2.4) by multiplying the successive equations on the left by ψ_0^* and integrating, i.e., multiplying on the left by $\langle 0 |$. Since H_0 is assumed to be Hermitian, all the left-hand sides vanish, so that

$$E_1 = \langle 0 | H_1 | 0 \rangle, \tag{2.5a}$$

$$E_2 = \langle 0 | H_1 - E_1 | 1 \rangle, \tag{2.5b}$$

$$E_3 = \langle 0 | H_1 - E_1 | 2 \rangle - E_2 \langle 0 | 1 \rangle, \tag{2.5c}$$

$$E_4 = \langle 0 | H_1 - E_1 | 3 \rangle - E_2 \langle 0 | 2 \rangle - E_3 \langle 0 | 1 \rangle, \tag{2.5d}$$

etc.

E_1 is thus obtained from ψ_0 and H_1 alone without the solution of any of the inhomogeneous p.d.e.'s. (Note that $E_0 + E_1$ is merely the expectation value of the total Hamiltonian, H, for the approximate or "trial" function ψ_0.) E_2, however, requires the solution, ψ_1, of the first p.d.e., and E_3 apparently requires the solution ψ_2, etc. Actually, as shown by Hylleraas, knowledge of the wave function corrections to order n provide the energy corrections to order $2n+1$, and not to the apparent order $n+1$. For example, since

$$\langle 0 | (H_1 - E_1) = \langle 1 | (E_0 - H_0)$$

and

$$(E_0 - H_0) | 2 \rangle = (H_1 - E_1) | 1 \rangle - E_2 | 0 \rangle,$$

the integral

$$\langle 0 | H_1 - E_1 | 2 \rangle$$

in E_3 can be rewritten, eliminating ψ_2, as

$$\langle 1 | H_1 - E_1 | 1 \rangle - E_2 \langle 1 | 0 \rangle$$

to give

$$E_3 = \langle 1 | H_1 - E_1 | 1 \rangle - 2E_2 \langle 0 | 1 \rangle$$

in terms of only ψ_0 and ψ_1. The general theorem is demonstrated as follows. From Eqs. (5) E_n is given by

$$E_n = \langle 0 | H_1 - E_1 | n-1 \rangle - \cdots$$

where the string of terms on the right-hand side

$$-\sum_{i=2}^{n-1} E_i \langle 0 | n-i \rangle$$

is not written explicitly, as they obscure the argument, but which the reader can convince himself are adequately taken care of. This energy can be transformed through the sequence, identical with that for E_3 above,

$$\begin{aligned} E_n &= \langle 1 | E_0 - H_0 | n-1 \rangle - \cdots, \\ &= \langle 1 | H_1 - E_1 | n-2 \rangle - \cdots, \\ &= \langle 2 | E_0 - H_0 | n-2 \rangle - \cdots, \\ &= \langle 2 | H_1 - E_1 | n-3 \rangle - \cdots \end{aligned}$$

which ends at either

$$E_n = \langle (n-1)/2 | H_1 - E_1 | (n-1)/2 \rangle - \cdots$$

if $n-1$ is even, or at

$$\begin{aligned} E_n &= \langle (n/2-1) | H_1 - E_1 | (n/2) \rangle - \cdots \\ &\equiv \langle (n/2) | H_1 - E_1 | (n/2-1) \rangle - \cdots \end{aligned}$$

if $n-1$ is odd.

In general we are only interested in the lowest orders of perturbation theory, and often only the first nonvanishing contribution, despite the above demonstration which has only been included for completeness. An interesting procedure for obtaining higher orders of perturbation theory connections in something like a geometric progression is due to Hirschfelder. By a transformation he finds the correction after $\lambda\psi_1$ to be $\lambda^2\psi_2 + \lambda^3\psi_3$ and, in general, from the nth-order wave functions he calculates immediately the wave function correct through the $(2n+1)$th order.

B. Approximate Methods of Solution

The p.d.e.'s of perturbation theory can be solved by any of the usual methods for treating such equations. If an exact solution in closed form can be found by trial-and-error this is best of all. Otherwise various substitution, transform, and expansion methods can be applied in search of analytic and series solutions, and numerical and variational methods can be applied in search of very accurate approximate solutions. In some cases asymptotic series expansions can be found whose leading terms, as in the saddle-point method, are fair or good approximations to the exact solutions, although not a great deal has been done in this direction. The Ritz variational procedures—which is equivalent to expanding the solution in a limited set of functions is the most useful method of solution of the p.d.e.'s and hence we discuss it here at some length.

The solution of the p.d.e.'s of perturbation theory by a variational procedure is sometimes called Hylleraas–Bethe–Salpeter variational–perturbation theory[3] (which name is actually a misnomer since it is the usual equations of perturbation theory that are solved approximately by the variational technique). As is well known, a variational principle can be derived from many equations—the Euler equations—of mathematical physics, just as equations of physics can be derived from so-called physical variational principles (Principle of Action, Principle of Least-Time, etc.). Thus if we have a partial differential equation—which is homogeneous or inhomogeneous—

$$D[u]=0 \tag{2.8}$$

the boundary conditions of which can be expressed as

$$\int uD[u]=0$$

and

$$\int u^2<\infty$$

and a functional $L[\phi]$ of a general function ϕ such that for any arbitrary variation of ϕ

$$\delta L[\phi]=\int \delta\phi D[\phi]$$

then if ϕ satisfies the condition

$$\delta L[\phi]=0 \tag{2.9}$$

it also satisfies the differential equation (2.8), so that

$$u=\phi.$$

[If, as is usually the case, the solution to (2.8) is unique then

$$\delta L[\phi]=0$$

implies that L is an extremum. The mathematical descriptions of the variational calculus are to a great extent concerned with the problem of finding whether L is an extremal (an absolute maximum or minimum) or an external (an inflection point). This then involves detailed discussion of the corresponding differential equations—the Euler equations. For functions which do not vanish at the boundaries, e.g., possessing ingoing or outgoing wave boundary conditions, the variational principle must be somewhat modified.]

The functional $L[\phi]$ is often easily found. For the solution to the Schrödinger equation—not using perturbation theory— the usual "Schrödinger variational principle" writes

$$L[\phi]=\langle\phi\mid H\mid\phi\rangle/\langle\phi\mid\phi\rangle \tag{2.10}$$

for which satisfying Eq. (2.9) implies that $\phi=\psi$, the solution to the Schrödinger equation (2.1) and

$$E=\langle\psi\mid H\mid\psi\rangle/\langle\psi\mid\psi\rangle=L[\psi].$$

To illustrate the (albeit trivial) nonuniqueness of the variational principle for a given problem, we choose a different functional $L'[\phi]$ by

$$L'[\phi]=\langle\phi\mid H-E\mid\phi\rangle$$

where, by the boundary conditions

$$E=\langle\phi\mid H\mid\phi\rangle/\langle\phi\mid\phi\rangle.$$

Thus, using the definition $L[\phi]$ above

$$\delta L'[\phi]=2\langle\delta\phi\mid H-E\mid\phi\rangle-\langle\phi\mid\phi\rangle\delta L[\phi]$$

from which we see directly that

$$\delta L'[\phi]=0$$

implies that

$$\phi=\psi$$

satisfying the Schrödinger equation since we know that

$$\delta L[\psi]=0.$$

The extremum value of $L'[\phi]$ vanishes, i.e.,

$$L'[\psi]=0$$

and does not equal the energy value E, as contrasted with the extremum of $L[\phi]$ which equals E. This variational principle would presumably not be used since it is, formally at least, more complicated. The fact, however, that the extremum of the functional must not necessarily equal the desired energy eigenvalue, is of some practical importance.[4]

For the solution to the first-order perturbation theory equation Eq. (2.4b) the "Hylleraas–Bethe–Salpeter variational principle" writes

$$L[\phi]=\langle\phi\mid H_0-E_0\mid\phi\rangle+2\langle\phi\mid H_1-E_1\mid\psi_0\rangle \tag{2.11}$$

for which

$$\delta L[\phi]=0$$

implies that

$$\phi=\psi_1$$

which satisfies

$$(H_0-E_0)\mid 1\rangle=(E_1-H_1)\mid 0\rangle$$

where again, and to no great advantage, the extremum value of $L[\phi]$ gives the desired energy:

$$L[\psi_1]=E_2.$$

---

[3] E. Hylleraas, Z. Physik **65**, 209 (1930); and H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1957), Vol. 35, p. 208. See also Ref. 41 below.

[4] J. I. Musher, Ann. Phys. (N.Y.) **32**, 416 (1965).

Similar variational principles can be written for any successive order of perturbation theory, where it must be remembered that the energy corrections to order n should be solved for [Eqs. (4)] before using the variational procedure for ψ_n.

The usual method for obtaining the variational solution to the perturbation theory equation is by the application of the Ritz procedure.[5a] ϕ is expanded in a subset of a complete set of functions with arbitrary coefficients

$$\phi=\sum_{n=1}^{N}c_n\phi_n,$$

where the ϕ_n are polynomials, transcendental functions, or the products of such functions with an exponential such as ψ_0, etc. Substitution of ϕ into the variational principle for ψ_1, Eq. (11), gives

$$\delta\sum_{n,m}\left[c_n{}^*c_m\langle n\mid H_0-E_0\mid m\rangle+2c_n{}^*\langle n\mid H_1-E_1\mid 0\rangle\right]=0$$

which, when the coefficients of the independent variations $\delta c_n{}^*$ are set equal to zero, gives the system of linear equations for the c_m

$$\sum_m c_m\langle n\mid H_0-E_0\mid m\rangle+\langle n\mid H_1-E_1\mid 0\rangle=0 \qquad n=0,1,\cdots,N. \quad (2.12)$$

This procedure is no different from letting

$$\psi_1=\sum_{m=1}^{N}c_m\phi_m$$

and substituting directly into the first-order perturbation theory equation itself, to give

$$\sum_{m=1}^{N}(H_0-E_0)c_m\phi_m=(E_1-H_1)\psi_0$$

which when multiplied on the left by $\phi_n{}^*$ and integrated gives Eq. (12). Thus when the Ritz procedure is applied, the term variational solution is somewhat of a misnomer, since the same result is obtained by expanding the solution directly in a limited set of functions. Furthermore, when the ϕ_n are eigenfunctions of H_0 of eigenvalue E_n, then the coefficients of Eq. (2.12) are obtained immediately as

$$c_n=\langle n\mid H_1-E_1\mid 0\rangle/(E_0-E_n)$$

just as in textbook first-order perturbation theory. This shows that utilization of only a one- or two-term "trial function" in a "variational" calculation is essentially no different from utilization of one or two "excited states" in a usual perturbation theory calculation. Since the inclusion of only a few excited states in a perturbation theory calculation is known to give highly inaccurate results, by implication the inclusion of only a few terms in a variational trial function—even though one might choose the important arbitrary functions ϕ_n more judiciously than one can choose the important excited states— should be treated with the greatest caution. Obviously the accuracy obtainable using a simple trial function depends on the degree to which the exact function can be approximated by the terms of the trial function with the best choice of linear parameters, and this in turn depends on the exact nature of ψ_0, H_0, and H_1. A trivially poor set of functions to describe the perturbation of a ls -hydrogen atom by an external field, with $H_1=-e\mathcal{E}z$, would be

$$\psi_1=(az^2+bz^3+\cdots)\psi_0$$

since ψ_1, must have the same symmetry as $z\psi_0$ and hence must be of the form (assumed regular in r at the origin)

$$\psi_1=[(a/r)+b+cr+\cdots]z\psi_0.$$

In fact the exact solution in this case is [5b]

$$\psi_1\propto(1+\tfrac{1}{2}r)z\psi_0$$

so that a single-term variational trial function

$$\psi_1=az\psi_0=bH_1\psi_0$$

can represent the exact function relatively well. This accounts for the success of simple trial functions—and the Unsöld approximation, which is in a sense equivalent—in some perturbation theory calculations. An example where this type of trial function would be highly inadequate is the ls-hydrogen atom with $H_1\propto\delta(r)/r^2$, the nuclear hyperfine interaction. The exact solution is

$$\psi_1\propto[(a/r)+br+c\log r]\psi_0$$

any single term of which is not likely to exhibit the proper behavior, and certainly a function of the form

$$\psi_1\propto a[\delta(r)/r^2]\psi_0=bH_1\psi_0$$

would give a decidedly poor approximation. It is clear that the correct solution must be of the form

$$\psi_1\propto(a/r)\psi_0+(b/r)\psi_1{}',$$

where $\psi_1{}'$ is everywhere nonsingular. No linear combination of nonsingular functions can adequately represent ψ_1 in all regions of space.

When we refer to variational solutions to the equations of perturbation theory we generally assume that calculations are performed until a defined degree of convergence is obtained. This is generally done by increasing the size of the set of functions until convergence is obtained. It is easier in practice to follow the convergence of the energy rather than that of the wave function, especially when the expansion is in nonorthogonal functions. To date calculations of this

---

[5] (a) W. Ritz, J. F. Reine Angew. Math. **135,** 1 (1909). For a discussion of the important problem of the rate of convergence of such variational expansions see C. Schwartz, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), p. 241. (b) L. Pauling, Proc. Roy. Soc. (London) **A114,** 181 (1927).

kind have only been performed for the helium atom, the hydrogen molecule as discussed below, and the London–van der Waals interaction of two hydrogen atoms.

Those with experience in solving for the total ψ by the Schrödinger–Ritz variational procedure should note the important simplification in using the Hylleraas–Bethe–Salpeter variational principle for the perturbation theory corrections. The former involves an unknown eigenvalue as well as the unknown wave functions, and hence the first step is the solution of a determinantal equation for the allowed values of E. The latter involves no unknown other than the wave function which is obtained by the solution of a simple system of N linear equations. The labor involved in obtaining perturbation theory corrections is thus much less than in obtaining accurate total wave functions directly.

III. HYDROGEN MOLECULE

A. Zeroth-Order Wave Functions[6]

The Hamiltonian for the hydrogen molecule in the Born–Oppenheimer approximation, for which the two nuclei are fixed at A and B, separated by a distance R is,

$$\begin{aligned} H(R) &\equiv -\tfrac{1}{2}(\nabla_1^2+\nabla_2^2) - r_{1A}^{-1} - r_{1B}^{-1} - r_{2A}^{-1} - r_{2B}^{-1} \\ &\qquad + r_{12}^{-1} + R^{-1} \\ &\equiv T+V, \end{aligned} \tag{3.1}$$

where the constants $\hbar$, m, and e have been set equal to one. Since the Hamiltonian is spin-independent the solution to the two-electron Schrödinger equation

$$H\Psi(\mathbf{x}, \boldsymbol{\sigma}) = E\Psi(\mathbf{x}, \boldsymbol{\sigma}) \tag{3.2a}$$

is separable in the coordinates of space and spin, so that $\Psi(\mathbf{x}, \boldsymbol{\sigma})$ can be written as the product of a spin-independent function $\psi(\mathbf{x})$ which is an eigenfunction of

$$H\psi(\mathbf{x}) = E\psi(\mathbf{x}) \tag{3.2b}$$

and a spin function $\Sigma(\boldsymbol{\sigma})$, which is an eigenfunction of $\mathbf{S}^2$, such that the total wave function $\Psi(\mathbf{x}, \boldsymbol{\sigma})$ is antisymmetric under exchange of the particle space and spin coordinates. When $\Sigma(\boldsymbol{\sigma})$ has eigenvalue $S=0$, then it is antisymmetric, and

$$\Sigma = 2^{-\frac{1}{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{3.3}$$

so that only the symmetric spatial solutions of Eq. (3.2b) can multiply $\Sigma(\boldsymbol{\sigma})$ to give an allowed $\Psi(\mathbf{x}, \boldsymbol{\sigma})$. On the other hand, if $\Sigma(\boldsymbol{\sigma})$ is one of the three eigenfunctions of $\mathbf{S}^2$ having eigenvalue $S=1$, then it is symmetric, and only the antisymmetric spatial solutions of Eq. (3.2b) can multiply $\Sigma(\boldsymbol{\sigma})$ to give an allowed $\Psi(\mathbf{x}, \boldsymbol{\sigma})$. Thus the eigenfunctions of H lie in two disjoint sets, one of which multiplies the $S=0$ eigenfunctions, Eq. (3.3) to give the singlet manifold of functions $\Psi(\mathbf{x}, \boldsymbol{\sigma})$, and the other multiplies the set of $S=1$ eigenfunctions to give the triplet manifold. We are interested in the singlet $\Psi(\mathbf{x}, \boldsymbol{\sigma})$ of lowest energy which describes the hydrogen molecule in its ground electron state, and are concerned with various approximations to the spatial part of this function and with ways of improving these approximations using perturbation theory. For purposes of illustration we also briefly discuss approximations to the lowest state in the triplet manifold.

The first wave function to be used for the hydrogen molecule was that of Heitler and London,[7] the so-called Valence Bond function (unnormalized)

$$\psi_0(\mathrm{VB}) = \phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2), \tag{3.4}$$

where $\phi_A(i)$ and $\phi_B(i)$ are the $1s$-hydrogen-like wave functions for effective charge Z

$$\phi_N(i) = (Z^3/\pi)^{\frac{1}{2}} \exp(-Zr_{iN}). \tag{3.5}$$

The subscript zero on the $\psi_0(\mathrm{VB})$ refers to the fact that this is an approximate wave function, there being no subscript to indicate that we are treating the ground state. Also neither the Z dependence nor the R dependence is indicated explicitly except when a particular choice of these parameters has been made.

Inspection shows that $\psi_0(\mathrm{VB})$ is an eigenfunction of the zeroth-order Hamiltonian

$$\begin{aligned} H_0(\mathrm{VB}) &= T - [1+P_{12}] \\ &\quad \times \{[(Z/r_{1A}) + (Z/r_{2B})]\phi_A(1)\phi_B(2)\}\psi_0^{-1} \end{aligned} \tag{3.6}$$

of eigenvalue $2E_H(Z)$, twice the energy of the hydrogen-like orbitals, where P_{12} permutes the indices 1 and 2. Note that H_0 cannot be written as the sum of single-particle operators because of its explicit dependence upon ψ_0. Since this H_0 is the unique local Hamiltonian (up to a constant) of the form $H_0 = T + V_0$, the potential term could have been found by Sternheimer's procedure[8] and thus H_0 could have been written equivalently as

$$H_0(\mathrm{VB}) = T - (T\psi_0)/\psi_0 + \text{constant} \tag{3.7}$$

where the constant is most conveniently taken as the eigenvalue, $2E_H$, of the Hamiltonian of (3.6).

The other popular wave function for the hydrogen molecule is that based on the molecular orbital picture of Hund and Mulliken, although the first explicit calculations using this were first published in the

---

[6] For a general discussion of the hydrogen molecule, see M. Kotani, K. Ohno, and K. Kayama, *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1961), Vol. 35, Part 2, p. 1. See A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. **32**, 211 (1960) for a bibliography of hydrogen molecule calculations.

[7] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

[8] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); **96**, 951 (1954); **115**, 1198 (1959); and **127**, 812 (1962). See also R. Makinson and J. Turner, Proc. Phys. Soc. (London) **66**, 857 (1953).

late thirties by Hellmann[9a] and Coulson.[9b] This so-called Molecular Orbital wave function, is (unnormalized)

$$\psi_0(\mathrm{MO}) = (\phi_A+\phi_B)(1)(\phi_A+\phi_B)(2) \tag{3.8}$$

using the same notation as above. It is an eigenfunction of the separable Hamiltonian

$$H_0(\mathrm{MO}) \equiv h_0(1)+h_0(2)$$
$$= T-\sum_{i=1}^{2}\left[\frac{Z}{r_{iA}}\frac{\phi_A(i)}{(\phi_A+\phi_B)(i)}+\frac{Z}{r_{iB}}\frac{\phi_B(i)}{(\phi_A+\phi_B)(i)}\right] \tag{3.9}$$

also of eigenvalue $2E_H(Z)$ and which could also have been obtained by Sternheimer's procedure.

An even simpler wave function for the hydrogen molecule was recently proposed by the author.[10] This Non-Symmetrical wave function, which was rejected by Heitler and London on the grounds of its poor binding and its lack of electron symmetry, is

$$\psi_0(\mathrm{NS}) = \phi_A(1)\phi_B(2) \tag{3.10}$$

and it is an eigenfunction of the separable but nonsymmetrical Hamiltonian

$$H_0(\mathrm{NS}) \equiv h_0(1)+h_0(2) = T-(Z/r_{1A})-(Z/r_{2B}) \tag{3.11}$$

with eigenvalue $2E_H(Z)$. Contrary to some expectations the nonsymmetrical nature of $\psi_0(\mathrm{NS})$ does not introduce any special problems into calculations using perturbation theory as long as the total Hamiltonian is spin-independent.

An interesting and neglected wave function for the hydrogen molecule, proposed by Wick[11] which can be called a Geometrical-product Molecular Orbital wave function, uses products of atomic wave functions on each atom, and is (unnormalized)

$$\psi_0(\mathrm{GMO}) = \phi_A(1)\phi_B(1)\phi_A(2)\phi_B(2)$$
$$= \exp[-Z'(\xi_1+\xi_2)] \tag{3.12}$$

giving its explicit form in terms of a single confocal elliptical coordinate for each electron, $\xi_i = (r_{iA}+r_{iB})/R$, where $Z'=RZ$. $\psi_0(\mathrm{GMO})$ is an eigenfunction of the separable (non–hermitian) Hamiltonian in spheroidal coordinates

$$H_0(\mathrm{GMO}) = -(1/R^2)[(\partial^2/\partial\xi_1^2)+(\partial^2/\partial\xi_2^2)] \tag{3.13}$$

but also, and more interesting, an eigenfunction of the (Hermitian) separable Hamiltonian in Cartesian coordinates

$$H_0(\mathrm{GMO}) = T+\sum_i\{-(Z/r_{iA})-(Z/r_{iB})$$
$$+[\phi_A(i)\phi_B(i)]^{-1}\nabla\phi_A(i)\cdot\nabla\phi_B(i)\} \tag{3.14}$$

of eigenvalue $E_0=4E_H(Z)$ so that for this to be a good approximate function $Z^2\sim\frac{1}{2}$. This emphasizes the fact that $\phi_A(1)\phi_B(1)$ is a fair approximation to the H_2^+ molecular-ion, and that clearly the electrons should not feel the effect of the entire nuclear attraction since they should serve to screen each other from the nuclei. This wave function could, therefore, also have been called an Approximate Ion wave function.

In 1931 Hylleraas[12] proposed a nonsymmetrical wave function using exact H_2^+ molecular-ion wave functions which was never actually used in computations. Hylleraas suggested that the second electron of the hydrogen molecule should be superimposed on the solution for the H_2^+ ion ($Z=1$) and therefore experience an effective Z for each nucleus of $\frac{1}{2}$. The Non-Symmetrical Ion wave function is (unnormalized)

$$\psi_0(\mathrm{INS}) = \phi_I(1,Z_1)\phi_I(2,Z_2), \tag{3.15}$$

where $\phi_I(i,Z_i)$ is the exact solution to a (pseudo-) hydrogen molecular-ion of nuclear charge Z_i for the ith electron, and $\psi_0(\mathrm{INS})$ is an eigenfunction of the nonsymmetrical Hamiltonian

$$H_0(\mathrm{INS}) = T-\frac{Z_1}{r_{1A}}-\frac{Z_1}{r_{1B}}-\frac{Z_2}{r_{2A}}-\frac{Z_2}{r_{2B}} \tag{3.16}$$

Wallis and Hulburt[13] have studied in detail the use of Ion functions suggested by Hylleraas and they retained the electron symmetry by not using two different values of Z in (15) but rather determined the optimum single value of Z in

$$\psi_0(\mathrm{I}) = \phi_I(1,Z)\phi_I(2,Z) \tag{3.17}$$

which is an eigenfunction of the separable Hamiltonian, which contains the electrons equivalently,

$$H_0(\mathrm{I}) = T-\sum_{i=1}^{2}\left(\frac{Z}{r_{iA}}+\frac{Z}{r_{iB}}\right). \tag{3.18}$$

They also studied the symmetrical wave function made by symmetrizing $\psi_0(\mathrm{INS})$ for two screening constants Z and Z'

$$\psi_0(\mathrm{IS}) = \phi_I(1,Z)\phi_I(2,Z')+\phi_I(1,Z')\phi_I(2,Z) \tag{3.19}$$

which is the exact analog of the Valence Bond wave function only using Ion functions of different Z's instead of atomic functions of different nuclei. This type of wave function has also been referred to as an Open Shell function (which has been symmetrized) by analogy with calculations on the helium atom. The H_0 for $\psi_0(\mathrm{IS})$ is analogous to the $H_0(\mathrm{VB})$ of (3.6) so we do not write it explicitly.

The Hartree and Hartree–Fock wave functions for the hydrogen molecule are one and the same. By definition they are the approximate solution to the

---

[9] (a) H. Hellmann, *Einfuehrung in die Quantenchemie* (Deuticke, Vienna, 1937). (b) C. A. Coulson, Proc. Cambridge Phil. Soc. **34,** 204 (1938).

[10] J. I. Musher, J. Chem. Phys. **42,** 2633 (1965).

[11] G. C. Wick, Nuovo Cimento **10,** 118 (1933).

[12] E. Hylleraas, Z. Physik **71,** 739 (1931).

[13] R. F. Wallis and H. M. Hurlbut, J. Chem. Phys. **22,** 774 (1954).

Schrödinger equation of lowest energy of the form

$$\psi_0(\mathrm{H})=\psi_0(\mathrm{HF})=\phi_0(1)\phi_0(2). \tag{3.20}$$

The Hartree and Hartree–Fock Hamiltonians are different, however, as was recently emphasized by Dickson and Sokoloff.[14] If the Coulomb and exchange operators are defined by

$$J_\phi(i)\theta(i)=\theta(i)\int d\tau_j \frac{|\phi(j)|^2}{r_{ij}}$$

$$K_\phi(i)\theta(i)=\phi(i)\int d\tau_j \frac{\phi^*(j)\theta(j)}{r_{ij}}, \tag{3.21}$$

respectively, then

$$H_0(\mathrm{H})\equiv h_0^{\mathrm{H}}(1)+h_0^{\mathrm{H}}(2)\equiv T-\sum_i\left[r_{iA}^{-1}+r_{iB}^{-1}-J_\phi(i)\right] \tag{3.22}$$

and

$$H_0(\mathrm{HF})\equiv h_0^{\mathrm{HF}}(1)+h_0^{\mathrm{HF}}(2)$$
$$\equiv T-\sum_i\left[r_{iA}^{-1}+r_{iB}^{-1}-2J_\phi(i)+K_\phi(i)\right]. \tag{3.23}$$

The eigenvalues $E_0(\mathrm{HF})=E_0(\mathrm{H})$ of these Hamiltonians are not the Hartree or Hartree–Fock energies, $E_{\mathrm{H}}=E_{\mathrm{HF}}$ since the latter are given by the expectation value of the total Hamiltonian $\langle 0|H|0\rangle$ and not just that of $H_0(\mathrm{HF})$ or $H_0(\mathrm{H})$.

The energies for the various ψ_0's, defined by the expectation value of H, $\langle 0|H|0\rangle$, and equivalent to E_0+E_1 in a perturbation theory scheme, are given in Table I. The values are given both for the optimum value of Z as determined variationally, as well as for $Z=1$, except for the NS wave function for which optimizing Z had negligible effect on the energy and for which three value of Z are given for purpose of illustration. It can be seen that all the energies save that for the NS $(Z=0.8)$ and GMO $(Z=1)$ wave functions are within 20% of the experimental value indicating that they should be reasonably good starting functions for perturbation theory calculations.

B. Perturbation Theory Corrections

Since each of the ψ_0's can be considered the leading term in an expansion for the exact ψ of the form

$$\psi=\psi_0+\lambda\psi_1+\cdots, \tag{3.24}$$

where λ is a dummy index, the first-order corrections, ψ_1, can be found as solutions to the inhomogeneous partial differential equations [Eq. (2.4a)]

$$(H_0-E_0)\psi_1=(E_1-H_1)\psi_0 \tag{3.25}$$

where λH_1 is defined by

$$\lambda H_1\equiv H-H_0. \tag{3.26}$$

The expansion in λ is also parametrically dependent on both R and Z, but whereas the partial sums [defined by Eqs. (2.7)] $\psi^{(n)}$ and $E^{(n)}$ for n large are essentially independent of Z (assuming that they converge) they remain, of course, dependent on R].

Thus the first-order correction to the Valence Bond wave function is the solution to the two-electron equation[15]

$$[H_0(\mathrm{VB})-E_0(\mathrm{VB})]\psi_1(\mathrm{VB})=(E_1-r_{12}^{-1}-R^{-1})\psi_0(\mathrm{VB})$$
$$+(1+P_{12})\left\{\left[r_{2A}^{-1}+r_{1B}^{-1}-\frac{Z-1}{r_{1A}}-\frac{Z-1}{r_{2B}}\right]\phi_A(1)\phi_B(2)\right\}. \tag{3.27}$$

Since H_0 is not separable in the coordinates of the two electrons, this equation cannot be simplified into one-electron or single-particle excitation terms and two-electron or two-particle excitation terms. Equation (3.27) does not possess an exact solution and presumably it can only be solved variationally. Defining a function

$$f(12)\equiv\psi_1/\psi_0 \tag{3.28}$$

which does not, in general, belong to $\mathfrak{L}^2$, and an operator

$$G(12)\equiv-(2)^{-1}\sum_{i=1}^{2}(\psi_0\nabla_i^2+2\nabla_i\psi_0\cdot\nabla_i) \tag{3.29}$$

the left-hand side can be rewritten as

$$G(12)f(12) \tag{3.30}$$

and the variational equivalent of (3.27) becomes

$$\delta[\langle 0|fGf|0\rangle+2\langle 0|f(H_1-E_1)|0\rangle]=0. \tag{3.31}$$

Furthermore, because of the properties of inhomogeneous partial differential equations, $f(12)$ can be written as[16]

$$f(12)=\sum f_k(12), \tag{3.32}$$

where the f_k are the solutions to

$$G(12)f_k=A_k \tag{3.33}$$

---

[14] R. J. Dickson and J. Sokoloff, Phys. Rev. **141**, 32 (1966). A recent calculation of F. W. Byron and C. J. Joachim [Phys. Rev. **146**, 1 (1966)] has shown the different types of convergence of the two expansions, one being monotonic and the other being oscillatory.

[15] The equation for the total correction to ψ_0 (VB), i.e., χ, where $\psi=\psi_0+\chi$, was given by Heitler and London.[7]

[16] An inhomogeneous partial differential equation $L[u]=\phi$ of specified boundary conditions possesses a unique solution if $(u_0,\phi)=0$, where u_0 is the solution to the homogeneous equation $L[u]=0$. Therefore if the solution to the inhomogeneous equation $L[u]=\phi_1+\phi_2$ exists, it can be obtained as $u=u_1+u_2$ in terms of the solutions to the two equations $L[u_1]=\phi_1+kf$ and $[u_2]=\phi_2-kf$, where f is *any* function satisfying the same boundary conditions as u and the ϕ_i with k the appropriately determined constant. One has only to be careful about singularities which occur in ϕ_1 and ϕ_2 separately but which cancel out in $\phi_1+\phi_2$, e.g., as when $\phi_1=(e^2/r_{12})\alpha(r_1)\beta(r_2)$ and $\phi_2=-(e^2/r_{12})\alpha(r_2)\beta(r_1)$ on the surface $r_1=r_2$. One way to handle this would be to use the same set of expansion functions for both u_1 and u_2, which unfortunately would remove the utility of the separation in the first place.

and the sum of the A_k are the right-hand side of (3.27), i.e.

$$\sum_k A_k = (E_1 - H_1)\psi_0. \tag{3.34}$$

The (nonunique) division into the A_k, for example, as

$$A_1 = (E_1' - r_{12}^{-1} - R^{-1}) \tag{3.35a}$$

$$A_2 = P_{12}A_3$$
$$= \left[E_1'' + r_{2A}^{-1} + r_{1B}^{-1} - \frac{Z-1}{r_{1A}} - \frac{Z-1}{r_{2B}} \right] \phi_A(1)\phi_B(2), \tag{3.35b}$$

where E_1' and E_1'' are derived from the boundary conditions, may prove useful due to the more rapid convergence of the variational equivalents of the equations for the f_k than that of the equation for f itself.

The first-order perturbation theory equation for the remaining simple wave functions can be separated into one- and two-particle excitation terms because the corresponding H_0's are separable, i.e., they can be written as the sum of two one-particle operators, $h_0(i)$. For example, the first-order correction to $\psi_0(\mathrm{MO})$, which is the solution to

$$(H_0 - E_0)\psi_1(\mathrm{MO}) = (E_1 - r_{12}^{-1} - R^{-1})\psi_0(\mathrm{MO})$$
$$+[1+P_{12}]\left\{\left[\left(r_{1A}^{-1} - \frac{Z-1}{r_{1B}}\right)\phi_B(1) + \left(r_{1B}^{-1} - \frac{Z-1}{r_{1A}}\right)\phi_A(1)\right](\phi_A+\phi_B)(2)\right\} \tag{3.36}$$

can be written as

$$\psi_1 = [f(1) + f(2) + f'(12)]\psi_0, \tag{3.37}$$

where the $f(i)$ are solutions to the one-electron equations

$$G(i)f(i) \equiv -\tfrac{1}{2}[(\phi_A+\phi_B)(i)\nabla_i^2 + 2\nabla_i(\phi_A+\phi_B)(i)\cdot\nabla_i]f(i)$$
$$= [1+P_{AB}]\{[E_1' + r_{iA}^{-1} - \{(Z-1)/r_{iB}\} - g(i)]\phi_B(i)\} \tag{3.38}$$

and $f'(12)$ is the solution to

$$[(\phi_A+\phi_B)(2)G(1) + (\phi_A+\phi_B)(1)G(2)]f'(12) = [E_1'' - r_{12}^{-1} - R^{-1} + g(1) + g(2)]\psi_0 \tag{3.39}$$

with the $g(i)$ defined by

$$g(i) \equiv \int (\phi_A+\phi_B)^2(j) r_{ij}^{-1} d\tau_j. \tag{3.40}$$

Thus the Molecular Orbital wave function can be written as

$$\{[1+\lambda f + \mathcal{O}(\lambda^2)](\phi_A+\phi_B)\}(1)\{[1+\lambda f + \mathcal{O}(\lambda^2)](\phi_A+\phi_B)\}(2) + \lambda f'(12)\psi_0 + \mathcal{O}(\lambda^2) \tag{3.41}$$

and the Non-Symmetrical, Geometrical Molecular Orbital, and Ion ψ_0's can be written in the same form as well. The Hartree and Hartree–Fock functions, however, by virtue of their definition which excludes single-particle excitations to first-order, can be written as

$$[\phi_0 + \mathcal{O}(\lambda^2)](1)[\phi_0 + \mathcal{O}(\lambda^2)](2) + \lambda f'\phi_0(1)\phi_0(2) + \mathcal{O}(\lambda^2), \tag{3.42}$$

where the f' is either $f'(\mathrm{H})$ or $f'(\mathrm{HF})$. The Natural Orbital description of a molecular wave function due to Löwdin and colleagues,[17] which is of some popularity, writes the exact (spatial) wave functions as

$$\psi = \chi_0(1)\chi_0(2) + \sum_{i=1}^{\infty} \chi_i(1)\chi_i(2) \tag{3.43}$$

in which the term $\chi_0(1)\chi_0(2)$, the first "Natural Orbital," presumably provides the dominant contribution to ψ. It is trivial to observe that since λ is a relatively small (dummy) quantity for the MO, HF, and H expansions (as well as for the GMO, NS, and I expansions),

$$(1+\lambda f)(\phi_A+\phi_B) \approx \phi_0 \approx \chi_0 \tag{3.44}$$

so that the single-particle orbital plus the first-order single-particle corrections in the various approximate schemes all give good approximations to the first Natural Orbital and thus also to the Hartree–Fock orbital.[18] This provides a noniterative procedure for finding approximate solutions to the Hartree–Fock equation for the two-electron system of the hydrogen

---

[17] P.-O. Löwdin, Svenska Kem. Tidskrift **67**, 369 (1955); P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); H. Shull, J. Chem. Phys. **30**, 1405 (1959).

[18] See also G. V. Nazaroff and J. O. Hirschfelder, J. Chem. Phys. **39**, 715, 3155 (1963).

TABLE I. Hydrogen molecule energies ($R=1.4a_0$).

ψ_0	Z	$E^{(1)}$	$E^{(n)}$ [a]
VB[b]	1	−30.4	⋯
VB[c]	1.166	−31.0	⋯
MO[d]	1	−29.9	⋯
MO[e]	1.197	−30.7	⋯
NS[f]	1	−27.3	⋯
NS[f]	1.2	−26.7	⋯
NS[f]	0.8	−16.3	⋯
GMO[g]	1	−18.3	−31.254 (2)
GMO[g]	0.597	−30.1	−32.198 (2)
INS[h]	1,0.5	($E_0\sim-26.4$)	⋯
I[i]	1	−29.2	−31.957 (5)
I[j]	0.7825	~-30.70	
HF[k]	⋯	−30.84	
"Exptl" [l]			−31.957

[a] The number in parenthesis gives the order in perturbation theory, and the energies are in eV.

[b] W. Heitler and F. London, Z. Physik **44**, 455 (1927), Y. Sugiura, Z. Physik **45**, 484 (1927).

[c] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[d] H. Hellmann, *Einführung in die Quantenchemie* (1937), p. 133, reevaluated by the author at $R=1.4a_0$.

[e] C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937).

[f] J. I. Musher, J. Chem. Phys. **42**, 2633 (1965).

[g] B. Liu, W. D. Lyon, and W. Byers Brown, J. Chem. Phys. **44**, 562 (1966).

[h] E. Hylleraas, Z. Physik **71**, 739 (1931). Hylleraas discusses only the nonsymmetrical wave function but does not calculate the energy. The E_0 given here is estimated by the author. R. F. Wallis and H. M. Hurlbut symmetrize this wave function to get the ψ_0 (IS) with energy of ~-30.89, in J. Chem. Phys. **22**, 774 (1954).

[i] R. L. Matcha, thesis, University of Wisconsin (to be published). Matcha has recalculated the H_2^+ wave functions to give the necessary accuracy. He also obtains $E^{(3)}$ of −31.931 which is probably slightly more accurate than the value of −31.940 determined by B. Kirtman and D. R. Decious, J. Chem. Phys. **44**, 830 (1966).

[j] R. F. Wallis and H. M. Hurlbut, reference given in i above. The approximate sign $\sim$ is due to the fact that they take only the first two terms in one of the expansions for the H_2^+ functions.

[k] W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 205 (1960). This is a correction of 0.01 eV over the value of C. A. Coulson, Proc. Cambridge Phil. Soc. **34**, 204 (1938).

[l] The best calculated nonrelativistic value in the zeroth-order Born–Oppenheimer approximation is from W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960). This is the number with which comparison should be made.

molecule. Schwartz and others[19] have shown explicitly that the bare nucleus wave functions for simple atoms corrected to include the first-order single excitations[20] gives good agreement for both energies and physical properties with the (zeroth-order) Hartree–Fock solution.

The fact that the first-order perturbation theory corrections to the Hartree–Fock solution of an electron gas could be written in terms of two-particle interactions was known in the 1930's when it was shown that this second-order perturbation theory energy diverges. In the 1950's this divergence was removed, following the work of Brueckner, by summing selected parts of the higher-order perturbation theory terms, thus indicating that the energy of the electron gas was not analytic in the perturbation parameter, λ(or e^2). The fact that perturbation theory corrections to the solution of a separable zeroth-order Hamiltonian could be written in terms of solutions to two-particle equations was apparently not appreciated by atomic and molecular physicists, who regularly use the separable Hartree–Fock Hamiltonian, until Sinanoğlu[21] pointed this out in 1961. Until that time perturbation theory corrections had only been applied to the two-electron systems of the helium atom and helium-like ions. Since then, Kelly, has performed very accurate calculations of E_2 and some higher-order terms for beryllium[22] and for the open shell atom, oxygen,[23] and Sinanoğlu and co-workers have obtained approximate solutions to the pair-correlation energies of Be[24] which compare relatively well with those of Kelly. Within the past year perturbation theory has, at last, been applied to molecules and the H_2^+ molecular ion—forcing the rewriting of an earlier version of this article completed in the summer of 1965—by Hirschfelder, Byers, Brown, Kirtman, and their colleagues.[25–28]

Liu, Lyons, and Brown[26] have calculated the first-order corrections to ψ_0(GMO) for two values of Z: $Z=1$ and that which minimizes E_0+E_1, $Z=0.598$. These are also given in Table I. They use double perturbation theory, separating λH_1(GMO) into the electron repulsion part

$$W=1/r_{12} \tag{3.45}$$

and the one-electron part

$$V=H-H_0-(1/r_{12}), \tag{3.46}$$

where their H_0 differs from our (3.14) by the constant $4E_H(Z)$. They thus did not separate ψ_1 into single and double excitations before performing the double perturbation theory—which might have converged even faster—but rather took advantage of the closed-form solution to the equation first-order in V and only had to determine the solution to the first-order equation in W variationally. In the same way, one could find the first-order corrections to the ψ_0(MO) using the first-order H_2^+ calculations of Sanders *et al.*[29] for the

---

[19] (a) C. Schwartz, Ann. Phys. (N.Y.) **6**, 156 (1959). (b) A. Matulis, U. Safronova, and V. Tolmachev, Lietuvos Fiz. Rinkinys **4**, 331 (1964) and works cited therein. (c) D. Layzer. Z. Horák, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N.Y.) **29**, 101 (1964). (d) Z. Horák, *Modern Quantum Chemistry* (Academic Press Inc., New York, 1965), Vol. II, p. 7. (e) G. G. Hall, L. L. Jones, and D. Rees, Proc. Roy. Soc. (London) **A283**, 194 (1965).

[20] The description of Hall *et al.* is in density matrix language but does not differ from the usual wave function description in any nontrivial way.

[21] O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961).

[22] H. P. Kelly, Phys. Rev. **131**, 684 (1963).

[23] H. P. Kelly, Phys. Rev. **144**, 39 (1966).

[24] D. F-T. Tuan and O. Sinanoğlu, J. Chem. Phys. **41**, 2677 (1964).

[25] W. D. Lyon, R. L. Matcha, W. A. Sanders, W. J. Meath, and J. O. Hirschfelder, J. Chem. Phys. **43**, 1095 (1965).

[26] B. Liu, W. D. Lyon, and W. Byers Brown, J. Chem. Phys. **44**, 562 (1966).

[27] B. Kirtman and D. R. Decious, J. Chem. Phys. **44**, 830 (1966).

[28] R. L. Matcha, thesis, University of Wisconsin (1965).

[29] W. A. Sanders, W. J. Meath, and J. O. Hirschfelder, University of Wisconsin Theoretical Chemistry Institute Report No. 44 (1964).

Finkelstein–Horowitz wave function—which is the same as the one-electron orbitals of $\psi_0(\mathrm{MO})$, justifying the statement that the MO wave function is also an Approximate Ion type of function—and only having to solve for the $1/r_{12}$ perturbed correction variationally.

Both second-order energies are in good-to-excellent agreement with the best calculated Born–Oppenheimer value of Kołos and Roothaan and therefore give every indication that perturbation theory ought to converge. Moreover, (a) the partial sums $E^{(2)}$ are essentially independent of Z for these two rather diverse values of Z; (b) the "natural" value of Z for this wave function is $2^{-\frac{1}{2}}$ and not 1, as the latter gives $E_0=4E_H$ instead of $2E_H$ which is in the vicinity of the exact total E; and (c) there is considerable advantage in choosing Z judiciously—some 14 kcal/mole better agreement for $E^{(2)}$—but the fact that the wave function with $Z=1$ gives a decidedly poor $E^{(1)}$ by no means precludes its ability to give accurate values for the higher partial sums.

Matcha[28] has used the exact H_2^+ ground-state wave functions in a variational calculation for the wave function through second-order and the energy through fifth order which is given in Table I. Decious and Kirtman[27] have used an accurate approximation to the exact H_2^+ wave function to calculate the first-order wave function variationally and the energy, through third-order which is also given in Table I where Matcha's somewhat more precise third-order result is given for comparison. The agreement of Matcha's fifth-order result with that of Kołos and Roothaan[30] is nothing short of spectacular while the agreement of the third-order results is at worst excellent. This demonstrates explicitly the convergence of a perturbation series expansion for a molecule, which is the first time such a convergence has been demonstrated. The fact that such rapid convergence was obtained using $Z=1$ instead of the optimal $Z=0.7825$, for which $E^{(1)}$ is 1.5 eV lower, illustrates the lack of sensitivity to the particular choice of Z, as long as it is a reasonable such choice. In practice, one should choose where effort is better expended: in optimizing Z or in performing higher-order perturbation theory calculations. One sees immediately that for the hydrogen molecule it is usually better to choose Z arbitrarily and calculate ψ_1 rather than to optimize Z and not obtain ψ_1 at all.

C. Generalization to Larger Molecules

It is unfortunately true that of all the wave functions for the hydrogen molecule discussed here, only two, $\Psi_0(\mathrm{HF})$ and $\Psi_0(\mathrm{I})$, bear easy generalization to large molecules for use in perturbation theoretic procedures. For systems of more than two electrons $\Psi_0(\mathrm{VB})$ becomes particularly unpleasant—which has led to its neglect over the past thirty years—but more important, the solution for the first-order perturbation theory equations is not expressible in terms of pair-corrections. The $\Psi_0(\mathrm{NS})$ and the $\Psi_0(\mathrm{H})$ are only legitimate starting points for perturbation theory calculations for two-electron systems for which the space and spin variables are separable since a valid Ψ_0 must be an eigenfunction of S^2 and S_z if the Ψ obtained via perturbation theory is to be. The $\Psi_0(\mathrm{GMO})$ might be generalized to larger molecules if one could find a way to generate excited states, but the behavior for large internuclear distances, at least at first glance, makes such a description seem rather unreasonable. A fully antisymmetrized intuitive $\Psi_0(\mathrm{MO})$ for a large molecule can be written down as a single determinant, and using a procedure outlined by Epstein a separable but nonlocal $H_0(\mathrm{MO})$ of which $\Psi_0(\mathrm{MO})$ is an eigenfunction, could be constructed. Perturbation theory could then be applied, but the labor might be prohibitive. The use of $\Psi_0(\mathrm{HF})$ in perturbation theory calculations is now well appreciated since the work of Sinanoğlu,[21] even though no such calculations for molecules have yet been reported. This is unfortunate in view of the fact that the first-order correction to $\Psi_0(\mathrm{HF})$ is probably easier to obtain that $\Psi_0(\mathrm{HF})$ itself.

We are particularly hopeful for the utility of the generalization of $\Psi_0(\mathrm{I})$ to large molecules, a prospect which has been neglected until very recently—despite a Sinanoğlu paper of some years ago[31]—when several research groups[32] have initiated studies on atoms and on the hydrogen molecule. The beauty of the generalized $\Psi_0(\mathrm{I})$ is that the lowest $(N/2)$ one-electron solutions to the bare ion problem for given nuclear charges $\{Z_i\}$ can be easily obtained numerically without any two-electron integrals or iteration procedures. Then the major effort can be devoted to finding the first-order corrections, which itself should not be too difficult. We consider it to be of primary importance that the $\{Z_i\}$ are chosen judiciously, since the charges on a given nucleus must affect *all* the electrons alike. Such a choice might be the weighted average of the Slater shielding parameters for the electrons on the atom in question in the limit of large internuclear separation.

The significance of an arbitrary separable H_0 for atomic and molecular calculations has apparently not been appreciated previously, and a discussion of this is given in Appendix E. We feel, in fact, that the emphasis on finding self-consistent Ψ's has obscured the utility of solutions obtained from other separable H_0's—of which $\Psi_0(\mathrm{I})$ is an example—and we have the highest hopes for calculations using an H_0 similar to the Hartree–Fock Hamiltonian but not containing any nonlocal operators at all.

Hall and Rees[33] have outlined a nonsymmetrical

---

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

[31] O. Sinanoğlu, Phys. Rev. **122**, 493 (1961).

[32] The research groups of A. Dalgarno and E. B. Wilson, Jr., besides those of Refs. 19 and 25–28.

[33] G. G. Hall and D. Rees, Theoret. Chim. Acta **1**, 448 (1963).

perturbation theory procedure for diatomic hydrides which bears mentioning here. Their procedure writes the zeroth-order wave function for the molecule X–H as an N-electron atom with no interelectronic repulsions centered on X of variable charge, with the remaining Coulombic terms as the perturbation. This procedure corresponds to treating the hydrogen molecule as a helium atom of variable charge and a proton in zeroth-order. In view of the success of second-order perturbation theory for the H_2^+ molecular-ion with the zeroth-order wave function that of an H-atom plus a proton, this procedure might well be useful. As yet, however, the first-order wave function corrections and second-order energies have not been obtained for any of the diatomic molecules.

D. Convergence

Although the calculation using $\Psi_0(\mathrm{I})$ has demonstrated the convergence of a perturbation theory expansion in a particular case, some general comments are in order.

The question of convergence is a difficult one for all atomic and molecular problems involving perturbation theory since one rarely has to deal with bounded operators. The strongest statements that one can make in general—and these are based more on intuition rather than on proof—are: (1) the infinite expansions for the energy and the wave functions converge only in the limit that the perturbation parameter λ approaches zero; (2a) the partial sums of the leading few terms of the expansions for the ψ's are very good approximations to the exact ψ's for large regions of function space and the perturbation expansion *might* be asymptotic to the exact solution in the limit of certain variables approaching limit points; and (2b) the partial sums of the leading few terms of the energy expansion (as well as for the expectation value of any other operator) are approximately equal to the exact result. Notice, however, that if the argument of Ref. 2a applies to molecules as well, then convergence of a given series does not guarantee that the series sum is a good approximation to the exact solution.

The nonsymmetric perturbation theory procedure[10] provides a very simple demonstration of the questionable convergence of the perturbation theory expansion. The term $-1/r_{1A}$ is included in H_0 while the term $-1/r_{1B}$ is included in λH_1. Both of these terms take on the same values, although in different regions of r_1 space, and it is therefore not obvious why one can be considered small relative to the other. However, in the perturbation theory procedure λH_1 never appears by itself but always multiplies

$$\psi_0 = \exp[-(r_{1A}+r_{2B})]$$

and so what should be compared is the ratio r_{1A}/r_{1B} in the region in which ψ_0 is large, i.e., around center A. In this region the ratio is quite small, approaching zero at A itself. Thus an expansion up to ψ_i which is large in a region where $r_{1A}/r_{1B}\approx 1$ will provide a good approximation to the exact ψ and the corresponding expectation value of the energy and other operators will provide good approximations to the exact values.

The Non-Symmetrical wave function raises a different question of convergence: can a nonsymmetrical wave function converge to a wave function which is either spatially symmetric or antisymmetric by applying perturbation theory? The answer clearly must be yes, since in the absence of accidental degeneracy the convergence of the nonsymmetrical perturbation series to a solution of the Schrödinger equation requires that it converge to a solution of one symmetry or the other.[34] At large values of R, the lowest singlet state is nearly degenerate with the lowest triplet, so that convergence is not likely to be attained—such is the only possibility for the perturbation theoretic procedure to lead to a state of mixed symmetry. The validity of this type of argument rests on the separability of spatial and spin coordinates which only happens for two-electron systems or for N-electron systems of $S_z=\pm N/2$. In these cases alone, total symmetry (or anti-symmetry) is required of the spin-independent solution to the Schrödinger equation.

Therefore one should not be concerned that ψ_0 does not satisfy the Pauli principle. Since ψ_0 is only an approximate wave function, the Pauli principle, which is a *property* of the wave function, just as is the expectation value of r^2 or $1/r$, should also only be satisfied approximately. For the singlet wave function, this says that for the nth partially summed spatial wave function,

$$|\,(n)\,\rangle \equiv \psi^{(n)} \equiv \sum_{i=0}^{n} \lambda^i \psi_i \tag{3.47}$$

$$\langle (n)\,|\,(1-P_{12})\,|\,(n)\,\rangle = \mathcal{O}(\lambda^n) \tag{3.48}$$

instead of identically vanishing for all n as it does for the various symmetrical wave functions. In performing perturbation theory calculations on $\psi_0(\mathrm{NS})$, however, one must be careful to obtain a solution of the desired symmetry. Just as in any perturbation theory calculation one is not guaranteed to approach the ground state starting with a given ψ_0, here starting with a given nonsymmetric ψ_0, one is not guaranteed to approach a spatially symmetric state which, if it were the lowest such state, would be true ground state, of the system.

E. Excited State ψ_0's

Because of the historical role played by the Valence Bond and Molecular Orbital wave functions, it is often assumed that a particular choice of a ground

---

[34] The convergence of a nonsymmetrical perturbation theory procedure and a bare proton has been recently demonstrated by P. B. Bailey [Proc. Phys. Soc. (London) **85**, 1127 (1965)] over a large range of R.

state ψ_0 affords information about the first excited state. However, this particular argument is unique to the VB and MO schemes, as for both of these there is an obvious spatially antisymmetric function which is thus orthogonal to the approximate ground state function and which can be associated with the first excited triplet state. Furthermore, even in these cases, one has no evidence that the suggested function is a good approximation to the exact function.

The spatial part of the triplet VB function is (unnormalized)

$$^3\psi_0(\mathrm{VB})=\phi_A(1)\phi_B(2)-\phi_B(1)\phi_A(2) \qquad (3.49)$$

which is also identically equal to the spatial part of the MO function (unnormalized)

$$^3\psi_0(\mathrm{MO})=(\phi_A+\phi_B)(1)(\phi_A-\phi_B)(2) - (\phi_A-\phi_B)(1)(\phi_A+\phi_B)(2). \qquad (3.50)$$

These wave functions are eigenfunctions of the nonseparable Hamiltonian

$$^3H_0(\mathrm{VB})={}^3H_0(\mathrm{MO}) = T-[1-P_{12}][(r_{1A}^{-1}+r_{2B}^{-1})\phi_A(1)\phi_B(2)](^3\psi_0)^{-1} \qquad (3.51)$$

so the corrections cannot be separated into single and double excitations as was possible for the singlet $\psi_0(\mathrm{MO})$.

The spatial part of the triplet NS wave function, cannot be simply obtained from the functions included in the singlet wave functions. It might have been thought that the NS spatial zeroth-order triplet should equal the spatial zeroth-order singlet, the one being corrected to give a symmetric function and the other an antisymmetric function. However this is not reasonable since the two exact wave functions must be spatially orthogonal, so that

$$([\psi_0(\mathrm{NS})+\lambda\psi_1(\mathrm{NS})+\cdots], [^3\psi_0(\mathrm{NS})+\mu^3\psi_1(\mathrm{NS})+\cdots])=\mathcal{O}(\lambda,\mu)$$

thus requiring

$$(\psi_0(\mathrm{NS}),{}^3\psi_0(\mathrm{NS}))=0$$

and thus giving the only obvious choice of $^3\psi_0(\mathrm{NS})$ to be

$$^3\psi_0(\mathrm{NS})=\phi_A(1)\phi_B'(2)-\phi_A'(1)\phi_B(2),$$

where ϕ_A' and ϕ_B' are the $2s$-atomic wave functions. But this, too, gives trouble, and the answer to the problem is not obvious.

The GMO singlet wave function does not suggest a possible triplet, or at best, suggests the $^3\psi_0(\mathrm{VB})$ by use of the second spheroidal coordinate. Some triplet states for the Ion, Hartree, and Hartree–Fock wave functions can be obtained using the single-particle wave function of the ground singlet, but only by including an additional orbital generated from the zeroth-order Hamiltonian.

Since it is not possible in general to relate the lowest triplet wave function to the functions used in the lowest singlet wave function, we feel the MO hypothesis which uses N atomic functions to generate N Molecular Orbitals to be arbitrary and probably unjustifiable. Also we consider with suspicion the assumption that a single function[35,36] $\Phi(1,2)$ can be used to generate both a singlet and a triplet ψ_0 in a nontrivial manner and attempts in this direction are discussed in Appendix A.

F. Electric and Magnetic Properties

It is often of interest to know the electric and magnetic properties of a molecule or a crystal as well as its energy and wave function. We discuss briefly the way of obtaining some of the simple properties, electric polarizability, magnetic susceptibility, etc. for approximate wave functions of the hydrogen molecule, and give a few examples of explicit calculations.

Consider an isolated molecule whose wave function and energy eigenvalue are expanded in powers of a parameter λ. If this molecule is subjected to a weak external field, e.g., a magnetic field $\mathbf{H}$, then the wave function and the energy of the interacting molecule are expandable in a double power series in λ and $\mathbf{H}$. A typical property of the molecule such as its scalar diamagnetic susceptibility

$$\chi=-\mathbf{H}^{-1}(\partial E/\partial\mathbf{H})\,|_{\mathbf{H}=0}$$

can be obtained from the terms in E bilinear in $\mathbf{H}$ and to all powers of λ. Thus the total susceptibility is

$$\chi=\chi_0+\lambda\chi_1+\lambda^2\chi_2+\cdots.$$

It is easily seen that χ_0 is the susceptibility calculated for a molecule of wave function ψ_0; χ_1 is the susceptibility calculated for the wave function $\psi_0+\lambda\psi_1$ but subtracting off χ_0 as well as the term quadratic in λ, etc. Similarly the ground-state expectation value of an operator, e.g., $\mathbf{r}$, which is related to the electronic dipole moment can be expanded in a series in λ

$$\langle\mathbf{r}\rangle=\langle\mathbf{r}\rangle_0+\lambda\langle\mathbf{r}\rangle_1+\cdots.$$

While the calculation of the zeroth-order term in the expectation value expansion only requires the zeroth-order ψ_0, the calculation of the zeroth-order term in the susceptibility requires the solution to the inhomogeneous partial differential equation linear in $\mathbf{H}$ or the equivalent infinite sum. Thus the zeroth-order scalar diamagnetic susceptibility χ_0 is given by

$$\chi_0=\tfrac{1}{3}\langle 0\,|\sum_i(r_i-R_i)^2\,|\,0\rangle + i\langle 0\,|\sum_i(r_i-R_i)\times\boldsymbol{\nabla}_i\cdot\,|\,01\rangle, \qquad (3.52)$$

---

[35] P.-O. Löwdin, (a) Rev. Mod. Phys. **34,** 80 (1962), (b) J. Appl. Phys. Suppl. **33,** 251 (1962).

[36] C. Herring, Rev. Mod. Phys. **34,** 631 (1962); C. Herring and M. Flicker, Phys. Rev. **134,** A362 (1964).

TABLE II. Zeroth-order electric and magnetic properties of the hydrogen molecule.[a]

ψ_0	Z	χ_0	α_0	σ_0	$\sigma_{0,H}{}^{\mathrm{HF}}$	$\chi_{0,0}{}^{\mathrm{HF}}$
NS	1.2	-0.69	4.3	24.4	-8.2	0.17
NS	1.0	-1.0	9.0	21.7	-6.7	0.17
NS	0.8	-1.56	22.0	19.0	-4.9	0.17
GMO[b]	0.594	-0.84	6.070 ± 0.005	···	···	0.003 ± 0.001[c]
VB	1.166	-0.87[d]	4.9[e]	24.6[e]	-5.0[f]	0.024[d]
VB	1.0	-1.09[e]	10.2[e]	24.4[e]	-4.0[e]	0.065[e]
MO	1.197	-0.82[d]	6.0[e]	25.5[e]	5.5[f]	0.020[d]
MO	1.0	-1.12[e]	12.0[e]	22.7[e]	-3.9[e]	0.029[e]
W[g]	···	···	5.3	···	···	···
HF	···	-0.85[h]	6.5[i]	26.5[j]	-5.7[j]	0.014[h]
Exptl.	···	-0.83[k], -0.86[l]	5.3[l](5.0)[o]	26.5[m]	-5.6[m]	0.014[n]

[a] The units are: $\chi_0(e^2a_0{}^2/mc^2)$, $\alpha_0(a_0{}^3)$, $\sigma_0(10^{-6})$, where the subscript H refers to a proton which served as the origin in the calculation, $\chi_{0,0}{}^{\mathrm{HF}}(e^2a_0{}^2/mc^2)$ where the second subscript, 0, refers to the bond midpoint which served as the origin.

[b] M. N. Adamov, T. K. Rebane, and R. A. Evaryestov, Teor. i Eksperim. Khim. **1**, 588 (1965). The limits given correspond to the upper and lower bounds for these properties. The parallel and perpendicular components of α_0 were determined separately, and we give only the average here. χ_0 is obtained by combining the calculation of G. C. Wick, Nuovo Cimento **10**, 118 (1933) with $\chi_{0,0}{}^{\mathrm{HF}}$ of these authors. The Z differs slightly from that reported in Table I since these authors use $R=1.417\ a_0$ instead of $1.4\ a_0$.

[c] G. C. Wick (see footnote b) obtained 0.019 using the "average energy approximation" with $\Delta E=16.6$ eV. The correct result shows that the true $\Delta E\times 80$ eV. W. Weltner, Jr. [J. Chem. Phys. **28**, 477 (1958)] gives other examples using this "approximation."

[d] J. Tillieu and J. Guy, Compt. Rend. **240**, 402 (1955). A two-term variational function was used and the second term made no change in the results to the accuracy reported. Parallel and perpendicular components were obtained.

[e] T. P. Das and R. Bersohn, Phys. Rev. **115**, 897 (1959). A single-term variational function was used. Parallel and perpendicular components were obtained.

[f] T. P. Das and R. Bersohn, Phys. Rev. **104**, 849 (1956) very slightly modified in Ref. e. A single term variational function was used.

[g] W refers to the wave function of S. Weinbaum [J. Chem. Phys. **1**, 593 (1933)] which is not discussed in the text. This calculation by M. G. Veselov and M. N. Adamov [Dokl. Akad. Nauk (SSSR) **57**, 235 (1947)] utilizes a two-term variational function and parallel and perpendicular components were also obtained. Das and Bersohn (Ref. e) obtained 4.97 using a single-term variational function.

[h] M. Karplus and H. J. Kolker, J. Chem. Phys. **38**, 1263 (1963). A four-term variational function was used, although the fact that the gauge of the vector potential was chosen at a proton, rather than at the bond midpoint, makes this not much better than a two-term variational function and the degree of convergence was fair. The parallel and perpendicular components were also obtained. The value of $\chi_{0,0}{}^{\mathrm{HF}}$ was deduced roughly from these data by the author. This calculation neglected the nonlocal potentials in the Hartree–Fock operator so that the value reported is actually the Hartree χ_0 and only the first term in an expansion for χ_0(HF) as discussed in the text.

[i] H. J. Kolker and M. Karplus, J. Chem. Phys. **39**, 2011 (1963) using the same procedure as in Ref. h.

[j] H. J. Kolker and M. Karplus, J. Chem. Phys. **41**, 1259 (1964) using the same procedure as in Ref. i.

[k] A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924).

[l] H. H. Landolt and R. Boernstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1951).

[m] J. I. Musher, Advan. Magnetic Resonance (to be published in 1967) based on A. Saika and H. Narumi, Can. J. Phys. **42**, 1241 (1964).

[n] Deduced by I. Espe [Phys. Rev. **103**, 1254 (1956)] from the experiments of N. F. Ramsey and co-workers. Espe has obtained accurate values for the independent-electron contribution to $\chi_{0,0}{}^{\mathrm{HF}}$ for two ψ_0's using four-term variational functions which show relatively good convergence. The Nordsieck ψ_0 gave 0.015 and the Newell ψ_0, 0.016.

[o] This is the theoretical value of E. Ishiguro *et. al.*, Proc. Phys. Soc. (London) **65**, 180 (1952) for $R=1.4$ with which the simple calculation should be compared. For comparison with the experimental value, one should average over the vibrations, and when this is done these authors obtain $\alpha_0=5.3280$. No such accurate calculation is available for the other molecular properties, so that comparison can only be made with the deceptive experimental values.

where $|\,01\rangle\equiv\psi_{01}$ is the solution to

$$(H_0-E_0)\,|\,01\rangle=-i\sum(r_i-R_i)\times\nabla_i\psi_0. \tag{3.53}$$

When H_0 can be expressed as a sum of one-electron operators—as in the MO, NS, GMO, I, H, and HF procedures—then ψ_{01} only involves single excitations and only one-particle partial differential equations need be solved. In order to find χ_0 for the singlet MO wave function, the one-electron equation

$$\begin{aligned}[h_0(i)-\tfrac{1}{2}E_0]\psi_{01}(i)&\equiv G(i)\mathbf{f}(i)\\ &=i(r_i-R_i)\times\nabla_i(\phi_A+\phi_B)(i)\end{aligned} \tag{3.54}$$

using the notation of subsection B above, with

$$\psi_{01}(i)\equiv\mathbf{f}(i)\,(\phi_A+\phi_B)\,(i) \tag{3.55a}$$

must be solved so that

$$\psi_{01}=[\mathbf{f}(1)+\mathbf{f}(2)]\psi_0(\mathrm{MO}). \tag{3.55b}$$

On the other hand, in order to find χ_0 for the singlet VB wave function the two-electron equation

$$G(12)\mathbf{f}(12)=i\sum(r_i-R_i)\times\nabla_i\psi_0(\mathrm{VB}) \tag{3.56}$$

with

$$\psi_{01}=\mathbf{f}(12)\psi_0(\mathrm{VB}) \tag{3.57}$$

must be solved.

Accurate calculations for zeroth-order electric and magnetic properties have been performed only for ψ_0(GMO) for which Adamov, Rebane, and Evaryestov[37] have bounded α_0 and χ_0 from both above and below, and for ψ_0(NS) for which α_0, χ_0 and some other properties can be obtained analytically (Appendix B). These values are listed in Table II, where three different screening parameters are used for ψ_0(NS) in order to illustrate the Z dependence of the zeroth-order properties. The severe Z dependence observed suggests that calculations of electric and magnetic properties must be carried through at least first-order in λ before they be given any credibility. Also given in

---

[37] M. N. Adamov, T. K. Rebane, and R. A. Evaryestov, Teor. i Eksperim. Khim. **1**, 588 (1965).

Table II are the approximate value of electric and magnetic properties for $\psi_0(\text{VB})$ and $\psi_0(\text{MO})$ with two different screening parameters obtained by Tillieu and Guy[38] and Das and Bersohn[39] using one- and two-term trial functions in variational calculations for the f's of (3.55) and (3.57), etc. These results are also strongly Z-dependent, and closely parallel the Z dependence of the properties based on $\psi_0(\text{NS})$. More recently Karplus and Kolker[40] have calculated approximate values for these properties for $\psi_0(\text{HF})$ using four-term variational calculations and these are also given in Table II. Unfortunately no real convergence of the variational expansion was obtained, so that we do not know the accuracy of these zeroth-order results despite the good agreement with experiment. Also, these calculations neglected the nonlocal potentials in the Hartree–Fock operator[4] so that the properties given are actually the Hartree properties and only the first term in an expansion for the Hartree–Fock properties (see also Refs. 58 and 68 below). Notice also that agreement with experiment is not expected to be better than $\sim 10\%$ since for $\psi_0(\text{HF})$ the dummy parameter λ is of that order, while the Hartree–Fock energy is accurate to $\lambda^2 \sim 1\%$. A previous statement (Refs. 58 and 68) to the effect that agreement should be accurate to λ^2 was due to a trivial error and is incorrect.

A brief historical postlog is in order. The first discussion and calculation of electric and magnetic molecular properties in terms of an accurate solution to a variational problem with $\psi_1 = f\psi_0$, was in a paper by Veselov and Adamov[41] in 1947. These authors wrote down what we have, perhaps unfairly, called the Hylleraas–Bethe–Salpeter variational principle, took ψ_0 to be the Weinbaum function for the hydrogen molecule, and calculated the electric polarizability using a two-term variational function. In 1952 Guy and Harrand[42] wrote out the same variational procedure for the many-electron atom polarizability and in 1956 Tillieu and Guy[38] used this procedure to calculate the magnetic susceptibility of hydrogen for both $\psi_0(\text{VB})$ and $\psi_0(\text{MO})$ with a two-term variational function, demonstrating that adding the second term did not change the calculated result. Since the studies of these two groups—in which time the methods used by them became widely known through the work of Dalgarno and Schwartz, and the previous related work of Sternheimer[43]—no more accurate calculations on the hydrogen molecule appeared until last year when the Adamov and colleagues[37] calculated bounds to α_0 and χ_0 as discussed above, using the method of Rebane.[44] The calculation of secular properties, such as the frequency-dependent polarizability, requiring time-dependent perturbation theory, was also pioneered by Adamov,[45] who in 1956 used the differential equations for these properties subsequently rediscovered by Dalgarno and Schwartz and their followers.[46] Probably the most detailed and accurate variational calculation for a molecular property was that of Ishiguro *et al.*,[45b] who in 1952 calculated α_0 for the James and Coolidge wave function, expanding ψ_1 in terms of the same type of functions. The convergence obtained with a nine-term function for $\alpha_\perp$ is excellent, while that for a ten-term function for $\alpha_{||}$ is good.

IV. CRYSTALS

A. Introduction

It is of interest to describe atomic (and molecular) crystals in terms of their weakly interacting substituent parts, the atoms themselves.[47] This type of description is called the tight-binding or Heitler–London picture, and there are two accepted ways of constructing the crystal wave function. The first takes Ψ_0 as the simple product of the atomic wave functions while the second antisymmetrizes this product wave function. Both of these choices are arbitrary guesses at approximations to the exact wave function and their validity must be examined in detail just as we have done for the hydrogen molecule. Furthermore they only provide zeroth-order functions, and so methods to improve them, if possible by perturbation theory, are of importance. (But it should be remembered that for large systems the total overlap of Ψ_0 with the exact Ψ approaches zero). In this section we show how the simple product function can be improved by perturbation theory—even though it does not contain the spin correctly, and thus perturbation theory can never lead to an eigenfunction of S^2—and we show the

---

[38] J. Tillieu and J. Guy, Compt. Rend. **240,** 402 (1955).

[39] T. P. Das and R. Bersohn, Phys. Rev. **104,** 849 (1956).

[40] M. Karplus and H. J. Kolker, J. Chem. Phys. **38,** 1263 (1963); **39,** 2011 (1963); and **41,** 1259 (1964).

[41] M. G. Veselov and M. N. Adamov, Dokl. Akad. Nauk (SSSR) **57,** 235 (1947).

[42] J. Guy and M. Harrand, Compt. Rend. **234,** 616, 716 (1952). Although the many-electron treatment presented here is not exactly correct. See Ref. 4 above.

[43] See J. I. Musher, Ann. Phys. (N.Y.) **24,** 133 (1963) for references.

[44] T. K. Rebane, Vestn. Leningr. Gos. Univ., p. 20 (1965).

[45] (a) M. N. Adamov and I. S. Milevskaya, Opt. i Spektroskopiya **2,** 399 (1957). The $\alpha(w)$ for a ground-state hydrogen atom was reported in[46] M. N. Adamov, Dokl. Akad. Nauk SSSR **133,** 315 (1960). (b) E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. (London) **65,** 180 (1952).

[46] See J. I. Musher, Ann. Phys. (N.Y.) **27,** 167 (1964) for references. The above discussion shows that the "Dalgarno-Schwartz sum-rule technique" was indeed unknown to Adamov as was suggested in the Addendum to this article.

[47] For general discussions of crystal wave functions see, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Co., Inc., New York, 1940); R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963); and P. W. Anderson, *Concepts in Solids* (W. A. Benjamin, Inc., New York, 1963), along with various review articles in the Seitz and Turnbull *Solid State Physics* series. Recent works of interest are, for example, A. Gold, J. Phys. Chem. Solids **18,** 218 (1961), Phys. Rev. **124,** 1740 (1961); T. H. Keil and A. Gold, Phys. Rev. **136,** A252 (1964); and S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. **41,** 2911 (1964). The recent very promising calculations of J-L. Calais, using the AMO method [Arkiv Fys. **28,** 479, 511; **29,** 255 (1965)] should also be noted.

greater difficulties involved in improving the antisymmetrized function.

B. Simple Product Ψ_0[48]

Consider a crystal containing identical atoms at fixed points in a lattice. The total Hamiltonian for this system is

$$H=\sum T_i-\sum_{i,N} r_{iN}^{-1}+\sum_{i<j} r_{ij}^{-1}+\sum_{N<N'} r_{NN}{}'^{-1}, \quad (4.1)$$

where the sums are over electrons and nuclei. Assume now that each atom N (when isolated) possesses a Hartree–Fock (or other) single-determinant (nondegenerate) approximate wave function

$$\psi_0{}^N=\mathcal{A}[\nu_1(n_1)\nu_2(n_2)\cdots] \quad (4.2)$$

which is an eigenfunction of the atomic Hartree–Fock Hamiltonian

$$H_0{}^N=\sum_i h_N(i) \quad (4.3)$$

and where the single-particle orbitals $\nu_j(i)$ are eigenfunctions of $h_N(i)$ of eigenvalue $\epsilon_j{}^N$, i.e.,

$$[h_N(i)-\epsilon_j{}^N]\nu_j(i)=0. \quad (4.4)$$

Although it is not necessary, the functions ν_j are usually made to be orthogonal. The total atomic Hamiltonian H^N can be written as

$$H^N\equiv H_0{}^N+H_1{}^N=\sum_i h_N(i)+\sum_{i<j} g_{ij}{}^N \quad (4.5)$$

and corrections to $\psi_0{}^N$, which will not be considered here, could be found by the usual perturbation theory procedure. The zeroth-order and first-order energies of atom N are given by

$$E_0{}^N=\sum \epsilon_j{}^N \quad (4.6)$$

and

$$E_1{}^N=\langle 0_N \mid \sum g_{ij}{}^N \mid 0_N\rangle \quad (4.7)$$

where the Hartree–Fock energy is

$$E_{\mathrm{HF}}{}^N=E_0{}^N+E_1{}^N. \quad (4.8)$$

As a zeroth-order crystal wave function we take the simple product of approximate wave functions of the isolated atoms:

$$\mid 0\rangle\equiv\Psi_0\equiv\Phi_0=\prod_N \psi_0{}^N. \quad (4.9)$$

Since Ψ_0 does not contain all the electrons equivalently, the H_0, of which Ψ_0 is an eigenfunction such that

$$(H_0-E_0)\Psi_0=0 \quad (4.10)$$

also does not contain the electrons equivalently, and is therefore not symmetric under interchange of electrons between different atoms N. This H_0 is simply given by the sum of atomic Hamiltonians,

$$H_0\equiv H_\Phi=H_0{}^A(a_i)+\cdots+H_0{}^N(n_i)+\cdots \quad (4.11)$$

and

$$E_0=\sum_N E_N. \quad (4.12)$$

The total interaction Hamiltonian, λH_1, is given by

$$\lambda H_1\equiv H-H_0=\sum_N H_1{}^N+V, \quad (4.13)$$

where $\sum H_1{}^N$ contains the intra-atomic potential corrections due to the use of an approximate, single-determinant, solution for isolated atoms, and V contains the interatomic interaction potentials E_1 is then given by

$$E_1=\sum E_1{}^N+\langle 0 \mid V \mid 0\rangle. \quad (4.14)$$

For example, consider a lattice of hydrogen atoms (with parallel spins, although this restriction is not necessary) with

$$\Psi_0=\alpha(1)\beta(2)\gamma(3)\cdots \quad (4.15)$$

in which α, β, γ, $\cdots$ are 1s orbitals of parallel spin centered on the various atoms of the lattice, A, B, C, $\cdots$. The interaction Hamiltonian is

$$\lambda H_1=V=-\sum_{i\neq 1} r_{iA}^{-1}-\sum_{i\neq 2} r_{iB}^{-1}-\cdots$$
$$+\sum_{i<j} r_{ij}^{-1}+\sum_{N<N'} r_{NN}{}'^{-1}, \quad (4.16)$$

which provides the attraction of electron 1 to all centers other than A, etc. plus the interelectronic and internuclear repulsions. In general V can be written as a sum of interactions between pairs of atoms,

$$V=\sum_{N<N'} V_{NN}{}', \quad (4.17)$$

where each term $V_{NN}{}'$, is analogous to that for the H-atom lattice, i.e.,

$$V_{AB}=-r_{1B}^{-1}-r_{2A}^{-1}+r_{12}^{-1}+r_{AB}^{-1}, \quad (4.18)$$

the λH_1 of the hydrogen molecule in the Non-Symmetrical ψ_0. $V_{NN}{}'$ can thus be interpreted as the nonexpanded London–van der Waal's interaction potential between atoms N and N'.

Let Ψ_1 be the first-order perturbed wave function due to the interatomic interaction, V. By (4.17) Ψ_1 can be written as

$$\Psi_1=\sum_{N<N'} \Psi_1{}^{NN'}, \quad (4.19)$$

where

$$\Psi_1{}^{NN'}=\psi_1{}^{NN'}(\psi_0{}^N\psi_0{}^{N'})^{-1}\Psi_0 \quad (4.20)$$

with $\psi_1{}^{NN'}$ the solution to the equation

$$[\sum_i h_N(i)+\sum_j h_N(j)-E_0{}^N-E_0{}^{N'}]\psi_1{}^{NN'}$$
$$=[E_1{}^{NN'}-V_{NN}{}']\psi_0{}^N\psi_0{}^{N'}, \quad (4.21)$$

---

[48] This subsection is based on the author's treatment of intermolecular "forces" in Opt. i Spektroskopiya **20**, 793 (1966).

where

$$\langle 0 \mid V \mid 0 \rangle = \sum_{N<N'} E_1^{NN'}. \tag{4.22}$$

For the case of the H-atom lattice this is simply the London–van der Waals' (unexpanded) interaction between two H-atoms, and is a two-electron equation possessing both single- and double-excitations. For the general molecular case $\psi_1^{NN'}$ can be written as a sum of corrections due to the pairwise interactions of electrons one in each molecule. As shown in more detail elsewhere[48] $\psi_1^{NN'}$ can be written as

$$\psi_1^{NN'} = \sum_{\nu\nu'} F^{\nu\nu'}, \tag{4.23}$$

where ν and ν' are orbitals in molecules N and N', respectively, and

$$F^{\nu\nu'} = \mathcal{A}[\alpha(1)\cdots f^{\nu\nu'}(n)\nu(n)\cdots] \tag{4.24}$$

with

$$f^{\nu\nu'}(n) = \mathcal{A}[\alpha'(1')\cdots f^{\nu\nu'}(n,n')\nu'(n')\cdots]. \tag{4.25}$$

The two-electron function $f^{\nu\nu'}(n,n')$ is the solution to the two-electron partial differential equation

$$\begin{aligned}[h_0(n)+h_0(n')-\epsilon_\nu-\epsilon_{\nu'}]f^{\nu\nu'}(n,n')\nu(n)\nu'(n')\\ =[E_1^{\nu\nu'}-V(nn')]\nu(n)\nu'(n'),\end{aligned} \tag{4.26}$$

where $V(nn')$ is the two-electron interaction potential which for atoms of nuclei N and N' is uniquely written as

$$V(nn') = -r_{nN'}^{-1} - r_{n'N}^{-1} + r_{nn'}^{-1} + r_{NN'}^{-1}. \tag{4.27}$$

For molecules $V(nn')$ can be written in a unique, slightly more complicated way, but in practice it will be most useful to divide V_{int} into nonunique terms $V(nn')$ according to the localization of the orbitals ν and ν'. The sum of the $V(nn')$ must equal V.

The functions $f^{\nu\nu'}(nn')$ can be divided into terms corresponding to single excitations and double excitations as described above for the hydrogen molecule. It can be seen, therefore, that with the solution of a series of London–van der Waals' equations—it must be emphasized, in their unexpanded form—which involve only one and two electrons at a time, Ψ_1, and therefore the interaction energy to second-order in V alone and to first-order in the coupled inter- and intra-atomic interactions,

$$\langle \Psi_1 \mid V - \langle 0 \mid V \mid 0 \rangle + 2\sum_N (H_1^N - E_1^N) \mid 0 \rangle \tag{4.28}$$

can be readily obtained for the simple product Ψ_0. This fact makes the simple product Ψ_0 a desirable starting point for accurate calculations were convergence of the procedure assured.

Thus we return to the question as to whether a perturbation theory expansion converges or semiconverges. It is unfortunately true that when simple product, i.e., nonsymmetrical, wave functions are used for systems which contain more than two electrons the situation is fundamentally different from that discussed in Sec. IIID above and perturbation theory can never converge to a true solution unless all the electron spins are parallel, so that the wave function is separable in the coordinates of space and spin. The reason for this is easily seen. Since λH_1 contains no spin coordinates it cannot mix in states whose spin (symmetry) differs from that of Ψ_0, even though it is nonsymmetric in spatial coordinates and can mix in states of different spatial symmetry. Thus the application of perturbation theory to a nonsymmetric many-particle Ψ_0 will never enable the reaching of the state of correct many-particle symmetry. Said in other words, since λH_1 does not involve spin itself and can therefore not perturb the spin coordinates, Ψ_0 must contain spin, and therefore, particle symmetry exactly, i.e., the spin coordinates of all electrons must appear in Ψ_0 equivalently.

This argument can best be appreciated by the supposedly simple problem of two weakly interacting helium atoms. Let the nonsymmetrical Ψ_0 be

$$\Psi_0(1234) = \psi_0^A(12)\Sigma_0(12)\psi_0^B(34)\Sigma_0(34) \tag{4.29}$$

with $\psi_0^A(12)$ and $\psi_0^B(34)$ the exact spatial wave functions for the "isolated" helium atoms on centers A and B, respectively, separated by a distance R, and the Σ_0's the singlet spin wave functions. The Ψ_0 is a nondegenerate eigenfunction of the Hamiltonian

$$H_0 = h_A(12) + h_B(34) \tag{4.30}$$

the sum of separate helium atom Hamiltonians and the perturbation λH_1 is the obvious interaction among the respective nuclei and electrons. Now it is true that the exact four-electron Ψ can be written as a sum of products of total wave functions for the two helium atoms

$$\Psi(1234) = \sum_{ijkl} c_{ijkl}\psi_i^A(12)\Sigma_k(12)\psi_j^B(34)\Sigma_l(34) \tag{4.31}$$

of which $\Psi_0(1234)$ is one term of the complete set of functions in 1234-spatial and spin space on the right-hand side. However since λH_1 is independent of the spin coordinates, if perturbation theory were applied to $\Psi_0(1234)$ one could only obtain a $\Psi'(1234)$ of the form

$$\Psi'(1234) = \Sigma_0(12)\Sigma_0(34)\sum_{ij} c_{ij}\psi_i^A(12)\psi_j^B(34) \tag{4.32}$$

which is clearly not the complete set expansion of Eq. (4.31). Thus there is no possibility of using the simple product wave function for a convergent perturbation theory expansion even for the simple example of two weakly interacting helium atoms. In fact, to our knowledge, the first rigorous (antisymmetric) description of interacting atoms in terms of their isolated-atom wave functions has only recently been presented.

We have made one further remark on the use of nonsymmetrical wave functions elsewhere.[48] If it means anything to say that the two atoms are weakly interacting then the spins of the two systems can be considered as weakly coupled. Thus the operator of total spin, S^2, for the combined system is approximately equal to the sums of the spin operators of the separate atoms, i.e.,

$$S^2 \approx s_1^2 + s_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 + s_3^2 + s_4^2 + 2\mathbf{s}_3 \cdot \mathbf{s}_4 \qquad (4.33)$$

or equivalently that the operators

$$\mathbf{s}_1 \cdot \mathbf{s}_3,\ \mathbf{s}_1 \cdot \mathbf{s}_4,\ \mathbf{s}_2 \cdot \mathbf{s}_3 \text{ and } \mathbf{s}_2 \cdot \mathbf{s}_4 \approx 0. \qquad (4.34)$$

This implies that $\Psi_0(1234)$ is *almost* an eigenfunction of total spin S^2. In the limit of $R=\infty$ or before the application of λH_1, it does not make sense to treat the spin-coupling operators as nonvanishing—which is another way, at least in part, of applying the Pauli principle. It is perhaps not unreasonable to suppose that a perturbation theory wave function through first- or second-order based on the nonsymmetrical zeroth-order $\Psi_0(1234)$ will actually give a relatively good estimate of physical properties of the weakly interacting system, despite the lack of any possible semiconvergence to the true antisymmetrical solution.

It has often been pointed out that noninteracting systems, e.g., two helium atoms at infinity, can be described by a nonsymmetrical wave function.[49] If, however, the wave function is to be an eigenfunction of S^2, this is only true if the Hamiltonian is taken to be nonsymmetrical utilizing the fact that electrons can be distinguished when they are infinitely far apart, e.g., electrons 1 and 2 are infinitely far from electrons 3 and 4. This then implies that the Eqs. (4.33) and (4.34) are exact equalities since the coupling terms in S^2 must be dropped in order to be consistent with the nonsymmetrical choice of the Hamiltonian. When, however, the Hamiltonian is taken to be symmetrical, not utilizing the distinguishability of the electrons then although a nonsymmetrical wave function is an exact eigenfunction of H, it is not an eigenfunction of S^2, which must, in this case, contain all the cross products $\mathbf{S}_i \cdot \mathbf{S}_j$. It is the condition, that the wave function must be an eigenfunction of S^2 which specifies which linear combination of the degenerate nonsymmetrical eigenfunctions of H is appropriate. Such a statement, however, is only true for noninteracting systems since it is only for these that the nonsymmetrical functions are all exact eigenfunctions of the total H, so that the degeneracy in energy can never be split by diagonalizing in spin space.

C. Antisymmetrized Product Ψ_0

The problem of obtaining a good antisymmetrical wave function for a crystal is decidedly nontrivial and although numerous approximate wave functions have been discussed there has been no serious attempt to improve such a function systematically. The possibility of performing a very large "configuration interaction" calculation on a crystal seems doubtful, so that it is of interest to see how the antisymmetrized tight-binding wave function,

$$\Psi_0 \equiv \mathcal{A}\Phi_0 = \mathcal{A}\prod_N \psi_0^N \qquad (4.35)$$

using the notation of the previous section, can be improved by perturbation theory.

In the search for an H_0 for which Ψ_0 is an eigenfunction, we first looked for a differential operator, i.e., one containing no nonlocal potentials, since this would be unique up to a constant, and have the nice properties discussed above in the case of the hydrogen molecule. Such a Hamiltonian was not found, and analogy with the hydrogen molecule example led only to the operator

$$H_0 = \mathcal{A}[H_\Phi \Phi_0]/\mathcal{A}\Phi_0, \qquad (4.36)$$

where the H_Φ is defined in (4.11). This Hamiltonian, however, contains spin functions in the denominator, unless $S=\pm S_z=N/2$ so that Ψ_0 is separable in space and spin, and since the inverse of a spin function is not defined, such an H_0 can have only a formal interpretation. Only if perturbation theory corrections, e.g., Ψ_1' were to contain Ψ_0 explicitly, which they cannot do, could this H_0 be used in practice.

Recourse must therefore be had to H_0's containing integral operators—which can be considered to include spin projection operators—and we discuss briefly some of the various possibilities, each of which will have different convergence properties.

Epstein[50] has given a construction for a separable H_0 for Ψ_0 a single determinant which is the case here as long as the ψ_0^N are single-determinant approximate atomic wave functions. This H_0 is thus of the form

$$H_0 = \sum h_0(i), \qquad (4.37)$$

where the $h_0(i)$ contain nonlocal potentials constructed from the various atomic functions of Φ_0. As the procedure for obtaining the $h_0(i)$ is difficult to perform, the utility of this method has not yet been demonstrated. If the procedure is actually tractable then the separability of H_0 will enable Ψ_1 to be expressed as a sum of two-particle corrections exactly as in the Hartree–Fock case and thus this would be a most valuable method.

Epstein and Karl[51] have taken the Hamiltonian of (4.36) which they have written as

$$H_0 = T - (T\Psi_0)\Psi^{-1} + E. \qquad (4.38)$$

following Sternheimer,[8] and have removed the spins in the denominator by adding spin-projection operators to the $T\Psi_0$ in parenthesis. A slight modification of their procedure would expand Φ_0 in terms of space

---

[49] For example in D. M. Mattis, *The Theory of Magnetism* (Harper and Row, New York, 1965).

[50] S. T. Epstein, J. Chem. Phys. **41**, 1045 (1964); see also G. C. Ghirardi and A. Rimini, J. Math. Phys. **5**, 722 (1964).

[51] S. T. Epstein and J. H. Karl, Theoretical Chemistry Institute of the University of Wisconsin, Report No. 90 (1965).

and spin-separable functions (in a nonunique manner) as

$$\Phi_0=\sum_i \varphi_i(x)\chi_i(\sigma) \tag{4.39}$$

and define projection operators P_i such that

$$P_i\chi_j=\delta_{ij}\chi_i. \tag{4.40}$$

Since the φ_i are independent of spin, a set of unique local N-electron H_i can now be found such that

$$(H_i-E_0)\varphi_i=0 \tag{4.41}$$

by analogy with the Valence Bond Hamiltonian, or using Sternheimer's procedure, so that

$$[\sum_i H_iP_i-E_0]\Psi_0=0. \tag{4.42}$$

The first-order perturbation theory correction can be obtained from the solution to

$$[\sum_i H_iP_i-E_0]\Psi_1=[E_1-H+\sum_i H_iP_i]\Psi_0 \tag{4.43}$$

which separates into equations for the spatial functions, $\varphi_i^{(1)}$,

$$(H_i-E_0)\varphi_i^{(1)}=(E_1-H+H_i)\varphi_i, \tag{4.44}$$

where

$$\Psi_1=\sum_i \varphi_i^{(1)}(x)\chi_i(\sigma). \tag{4.45}$$

There is some question as to how to ensure that Ψ_1 is an eigenfunction of S^2 and S_z as is Ψ_0—see the discussion by Epstein and Karl—but although we have not succeeded in proving it, we feel that this should take care of itself since we have not lost any generality in defining Ψ_1 by (4.45).

There are other possible nonlocal H_0 such as

$$H_0=T-T\mid 0\rangle\langle 0\mid+E_0 \tag{4.46}$$

which looks like the Sternheimer-type H_0 of (4.38), and

$$H_0=E_0\mid 0\rangle\langle 0\mid \tag{4.47}$$

where for both

$$E_0=\langle 0\mid H\mid 0\rangle \tag{4.48}$$

and Ψ_0 is assumed normalized, but the utility of these is sometimes questionable. For example, using the H_0 of (4.47), Ψ_1 orthogonal to Ψ_0 is found exactly as

$$\Psi_1=E_0^{-1}(H-E_0)\mid 0\rangle \tag{4.49}$$

giving

$$E_2=E_0^{-1}\langle 0\mid H^2\mid 0\rangle-E_0 \tag{4.50}$$

so that the second-order partial sum is

$$E^{(2)}=E_0^{-1}\langle 0\mid H^2\mid 0\rangle \tag{4.51}$$

and the E_0's cancel out. The higher-order wave functions and energies can also be found exactly with

$$E^{(3)}=E_0^{-2}\langle 0\mid H^3\mid 0\rangle-E_0^{-1}\langle 0\mid H^2\mid 0\rangle+E_0, \quad \text{etc.} \tag{4.52}$$

but this expansion which looks simple appears to be nonconvergent, although an attempt should be made to sum it formally. If Ψ_0 were an eigenfunction of a differential operator contained in H, then this procedure gives

$$\Psi_1=E_0^{-1}H_1\Psi_0 \tag{4.53}$$

which has an artificial similarity to the Unsöld approximation and one-term variational expansions. An example is shown in Appendix D for which $E^{(2)}$ is an improvement on E_0 but for which $E^{(3)}$ diverges. (The general lack of convergence of these series is expected since $H_0\mid n\rangle=0$ for $n\neq 0$ so that $H_1\mid n-1\rangle$ cannot be considered to be small.)

An important implication of the above discussion is that when Ψ_0 is taken as an antisymmetrized product function of the form (4.35) then it is not possible to describe rigorously the interaction between atoms in terms of the London–van der Waals' interaction, since the total Hamiltonian is not separable into an isolated atom H_0 and a interatomic interaction potential, H_1.[52] It is important, therefore, to appreciate the fact that almost without exception tight-binding calculations in solids are concerned only with evaluating the expectation value of H over the Ψ_0 of (4.35)—giving E_0+E_1—the accuracy of which is unknown, as this Ψ_0 is an arbitrarily determined zeroth-order function; thus one should not be disturbed (or impressed) by the poor (or good) agreement with experiments obtained in such calculations. Also, it can be understood that the contributions to the lattice sums of E_1 from beyond a certain radius are significantly smaller than the error from not calculating the important terms of E_2 in any approximate scheme.

The question as to whether the improvements on the energy of the antisymmetrical Ψ_0 can be described, at least in part, in terms of a London–van der Waal's interaction, inspired the investigation of this problem by a non-Rayleigh–Schrödinger scheme. The author, in collaboration with Salem,[53] recently discussed the interaction energy of two molecules using a technique based on Feenberg perturbation theory which shows that, indeed, there is a term in the energy, which corresponds to a London–van der Waals interaction.

We demonstrate this as follows. Consider any complete set of antisymmetric functions of appropriate quantum numbers, Ψ_n, where Ψ_0 is defined by (1). Such a set could, for example, be constructed from the set of functions Φ_n defined as in (4.9) in the direct-product space of the complete sets of atomic wave

---

[52] There is some confusion in the literature on this point and many authors refer to the Van der Waals interaction as introducing corrections to such a Ψ_0. Furthermore some calculations assume orbitals on one atom to be orthogonal to orbitals on the other atoms in the presence of this interaction giving rise to terms only involving the r_{ij}^{-1} perturbation. When this is done by Schmidt-orthogonalization, the picture is even more confused because then the zeroth-order Hamiltonian, even for the simple product Ψ_0, can no longer be expressed as the obvious sum of atomic Hamiltonians.

[53] J. I. Musher and L. Salem, J. Chem. Phys. **44**, 2943 (1966).

functions *for each atom*, by

$$|\,n\,\rangle \equiv \Psi_n = \mathcal{A}\Phi_n \equiv \mathcal{A}\,|\,n'\,\rangle, \tag{4.54}$$

where the single index n denotes the ordered multiple $(i, j, \cdots)$ specifying atom 1 to be in the ith state, atom 2 in the jth state, etc. The energy in the vicinity of E_0 is obtained by approximately solving the secular equations

$$\sum_n \langle m\,|\,H-E\,|\,n\,\rangle C_n = 0 \qquad m=0, 1, \cdots \tag{4.55}$$

to give an energy of accuracy equivalent to second-order in perturbation theory of

$$E \approx E_0 + E_1 - \sum_{n\neq 0} \frac{|\,\langle 0'\,|\,\sum H_1^N + V - E_1\,|\,n\,\rangle\,|^2}{E_n - E_0}, \tag{4.56}$$

where E_n is the eigenvalue of

$$(H_\Phi - E_n)\Phi_n = 0 \tag{4.57}$$

analogous to (10) and using the definitions Eqs. (11) and (13), but where E_1 is defined differently as

$$E_1 = \langle 0'\,|\,\sum H_1^N + V\,|\,0\,\rangle \tag{4.58}$$

so that $E_0 + E_1$ is the same as for the Ψ_0 of (4.35). [Note the assumption that the Φ_n of (4.57)—including Φ_0—are all eigenfunctions of the same sum of atomic Hamiltonians.]

Since the sum in (4.56) contains matrix elements of $\sum H_1^N + V - E_1$ squared there will be terms in E quadratic in the inter-atomic potential, V, which is the London–van der Waals interaction, terms, effectively an inter-atomic interaction, which are bilinear in V and $\sum H_1^N$, the intra-atomic potential, as well as intra-atomic terms. Since Ψ_n can be written as

$$|\,n\,\rangle = \alpha\,|\,n'\,\rangle + (\mathcal{A} - \alpha)\,|\,n'\,\rangle \tag{4.59}$$

part of the sum in (4.56) can be written as

$$\sum_{n\neq 0} \frac{|\,\langle 0'\,|\,\sum H_1^N + V - E_1\,|\,n'\,\rangle\,|^2}{E_n - E_0} \tag{4.60}$$

which is identical with the second-order energy calculated for the simple product crystal wave function and obtainable from sums of pair interactions equivalent to the infinite sum. It might well be, as is often argued, that the "exchange-like" terms coming from the integrals over $(\mathcal{A} - \alpha)\,|\,n'\,\rangle$ are significantly smaller than the "non-exchange-like" terms included in (4.60). Thus a correction (and perhaps the dominant correction) to the energy of the antisymmetrized Ψ_0 is due to an effective London–van der Waals interaction. We feel, however, that such questions must be examined carefully, and, in particular, that the generally accepted descriptions in terms of "Coulomb" and "exchange" contributions cannot be used when accurate descriptions are called for, since they are based on an oversimplified picture of both the isolated systems and their interactions.

When it is not possible to divide H into H_Φ as done here, the procedure of Musher and Salem[53] can also be used to give the energy as

$$E \approx H_{00} - \sum{}' \frac{|\,H_{0n} - H_{00}S_{0n}\,|^2}{H_{nn} - H_{00}} \tag{4.61}$$

in an obvious notation, where (4.61) corresponds to their $E^{(0,1)}$, which is a slightly more accurate energy then that used in (4.56) above. However the direct use of an infinite sum procedure might only be possible for some simple problems, such as those of the cohesive energies of a hydrogen lattice or a helium lattice.[54]

Incidentally for the evaluation of the rather small cohesive energies, one must be careful that the perturbation procedure is carried to a suitably high degree of accuracy. Thus, just as it is unrealistic to expect the energy of Ψ_0 to give the cohesive energy, it must be investigated whether a second-order or third-order energy will suffice for a given problem. (One of the ways to improve the convergence is to use an orthogonalized set of functions Ψ_n since this has the effect of including some of the higher-order terms.)

Some of the ideas in the above discussion can be applied to descriptions of excited states in atomic and molecular crystals. We would only like to make the observation that the approximate wave function describing a localized excitation on one site is not necessarily an eigenfunction of the H_0 describing a localized excitation on another, and hence the two Ψ_0's are not necessarily degenerate in the sense of perturbation theory. Application of these ideas, however, are either straightforward or nontrivial if useful at all and it would be uninteresting to discuss the former, and premature to discuss the latter at this time.

V. CONCLUSIONS

We have reviewed the various simple wave functions for the hydrogen molecule and for molecular crystals and have considered in detail the means of improving them by a perturbation procedure and the possible convergence thereof. It is hoped that this discussion of well-accepted and certainly well-known material will aid in the appreciation of some of the more fine, and therefore, more interesting points involved. In the five Appendixes we make a number of remarks which we consider pertinent to the present discussion.

---

[54] Yaris has recently and independently treated the general problem of improving a wave function Ψ_0 by expanding in eigenfunctions of an arbitrary Hamiltonian, H_Φ, using the wave-operator procedure of scattering theory. His energy is given by

$$E = \langle 0\,|\,H_\Phi + V + HP(\Psi_0)(\epsilon - H_\Phi)^{-1}P(\Psi_0)H + \cdots\,|\,0\rangle,$$

where H is the total Hamiltonian, ϵ a constant which in general must not be an eigenvalue of H_Φ and $P(\Psi_0)$ is a projection operator which projects out Ψ_0. Equation (4.56) is obtained by letting $\epsilon = E_0$ which is possible when the term with zero in the denominator also has a zero numerator. [R. Yaris, J. Chem. Phys. **44**, 3894 (1966)].

ACKNOWLEDGMENTS

This paper was started when I was a guest of the Soviet Academy of Sciences in Leningrad during the winter of 1964-5 (in the Exchange Program jointly sponsored with the U.S. National Academy of Sciences) and the first draft was completed when I was a guest of the Hebrew University in Jerusalem in the summer of 1965. I am grateful for the kind hospitality I received during these travels, and for the invaluable opportunities for discussions, particularly with the members of the Department of Theoretical Physics at the University of Leningrad. I wish to thank especially S. T. Epstein, for a long correspondence on the subject matter of Sec. IV, and L. Salem, R. Yaris and many other colleagues for valuable discussions and criticism.

APPENDIX A. HYDROGEN MOLECULE USING PROJECTION OPERATORS

In discussions of the exchange integral, J, of the hydrogen molecule, defined as the energy of the lowest singlet minus the energy of the lowest triplet, Löwdin[35] and Herring[36] among others have considered a single spatial trial function $\Phi(12)$ possessing no particle symmetry and have defined molecular wave functions by means of projection operators operating on Φ. Thus, for a given $\Phi(12)$ they define two wave functions, a singlet, ${}^1\phi$ and a triplet ${}^3\phi$ by means of

$$ {}^1\phi(12)=\tfrac{1}{2}(1+P_{12})\Phi(12) \qquad \text{(A. 1a)} $$

and

$$ {}^3\phi(12)=\tfrac{1}{2}(1-P_{12})\Phi(12) \qquad \text{(A. 1b)} $$

using the identity

$$ \Phi(12)=\tfrac{1}{2}[\Phi(12)+\Phi(21)]+\tfrac{1}{2}[\Phi(12)-\Phi(21)] \qquad \text{(A. 2a)} $$

and therefore

$$ \Phi(12)={}^1\phi(12)+{}^3\phi(12). \qquad \text{(A. 2b)} $$

Such an argument, and the corresponding definition of J, are based on the *unscreened* valence bond procedure discussed above for which, if

$$ \Phi(12)=\phi_A(1)\phi_B(2) \qquad \text{(A. 3a)} $$

then

$$ {}^1\phi(12)={}^1\psi_0(\mathrm{VB}) \qquad \text{(A. 3b)} $$

and

$$ {}^3\phi(12)={}^3\psi_0(\mathrm{VB}). \qquad \text{(A. 3c)} $$

In other words a single $\Phi(12)$, using the projection operators of Eq. (A. 1), gives two relatively good wave functions, the lowest singlet and triplet valence bond functions.

Consider now a brief counter example which shows that if we try to improve both wave functions ${}^1\phi$ and ${}^3\phi$ then $\Phi(12)$ no longer possesses a nontrivial definition, or equivalently, if we try to improve one of the wave functions, say ${}^1\phi$, alone, retaining the simple form of $\Phi(12)$, then we do not in general improve ${}^3\phi$.

One simple way to improve the VB wave functions is to introduce screening constants Z_1 and Z_3 which minimize the energy for ${}^1\psi_0$ and ${}^3\psi_0$ respectively, equivalent to making the two functions satisfy the virial theorem.[55] It is clear that $Z_1\neq Z_3$ (except at $R\rightarrow\infty$) so that the only definition of $\Phi(12)$, for which the ϕ's of Eq. (A. 2) equal the improved ψ_0's, is the trivial one

$$ \Phi(12)={}^1\psi_0(Z_1)+{}^3\psi_0(Z_3) \qquad \text{(A. 4a)} $$

which written out explicitly is

$$ \Phi(12)=\tfrac{1}{2}(1+P_{12})\phi_{A,Z_1}(1)\phi_{B,Z_1}(2) + \tfrac{1}{2}(1-P_{12})\phi_{A,Z_3}(1)\phi_{B,Z_3}(2) \qquad \text{(A. 4b)} $$

and thus contains four terms instead of the one of Eq. (A. 3a). We could have, of course, defined $\Phi(12)$, such that ${}^1\phi$ equals the screened ${}^1\psi_0$, and retain the simple form of Eq. (A. 3a), i.e.,

$$ \Phi(12)=\phi_{A,Z_1}(1)\phi_{B,Z_1}(2) \qquad \text{(A. 5)} $$

except that now ${}^3\phi\neq{}^3\psi_0(Z_3)$ and is not necessarily an improvement on the unscreened ${}^3\psi_0$. Thus either $\Phi(12)$ is the trivial sum of the two wave functions [Eq. (A. 4a)] or it is not consistently good in defining both the approximate singlet and triplet wave functions: from a single trial function it is not reasonable to obtain two good solutions to the Schrödinger equation, even solutions of different symmetry.

In Löwdin's generalized Hartree–Fock scheme[56] which utilizes different orbitals for different spins, projection operators of the form

$$ {}^{(2S+1)}\mathfrak{O}=\prod_{k}^{k\neq S}\frac{[\mathbf{S}^2-k(k+1)]}{[S(S+1)-k(k+1)]} \qquad \text{(A. 6)} $$

are used to project from a single determinant, which is not a spin eigenfunction itself, the spin eigenfunction of multiplicity $2S+1$. As with the two-electron example just given, a single determinant D will not give equally valid wave functions for different S from the relationship

$$ {}^{(2S+1)}\Psi={}^{(2S+1)}\mathfrak{O}D \qquad \text{(A. 7)} $$

but instead a new D must be defined as the sum of determinants

$$ D=\sum_{S}{}^{(2S+1)}\mathfrak{O}D_S \qquad \text{(A. 8)} $$

such that

$$ {}^{(2S+1)}\Psi={}^{(2S+1)}\mathfrak{O}D={}^{(2S+1)}\mathfrak{O}D_S. \qquad \text{(A. 9)} $$

For a particular S, ${}^{(2S+1)}\Psi$ is given by Eq. (A. 7) for a single determinant D[i.e., $D=D_S$ of Eq. (A. 9)] but

---

[55] See p. 82 of Ref 35(a).

[56] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

by the present arguments the same equation does not adequately define $(2S'+1)$ for $S'\neq S$.[57]

APPENDIX B. ZEROTH-ORDER ELECTRIC AND MAGNETIC PROPERTIES FOR ψ_0(NS)

The zeroth-order electric polarizability α_0, magnetic susceptibility, χ_0, and nuclear magnetic shielding σ_0, for ψ_0(NS) of the hydrogen molecule can be obtained exactly from the solutions to

$$[h_0(i)-\tfrac{1}{2}E_0]f_\epsilon(i)\phi_N(i)=-z_i\phi_N(i) \qquad \text{(B.1)}$$

and

$$[h_0(i)-\tfrac{1}{2}E_0]f_H(i)\phi_N(i)=i(\mathbf{r}_i-\mathbf{R}_i)\times\boldsymbol{\nabla}_i\phi_N(i). \qquad \text{(B. 2)}$$

Thus $f_\epsilon(i)$ are the same as for hydrogen atoms and the zeroth-order electric polarizability is

$$\begin{aligned}\alpha_0&=\langle 0\mid(z_1+z_2)[f_\epsilon(1)+f_\epsilon(2)]\mid 0\rangle\\&=2\langle 0\mid z_1f_\epsilon(1)\mid 0\rangle=9Z^{-4}\end{aligned} \qquad \text{(B. 3)}$$

or the sum of the polarizabilities of two H atoms of screening parameters, Z. If the arbitrary constants R_1 and R_2 are taken as R_A and R_B, respectively, then both $f_H(i)$ vanish identically, and the zeroth-order magnetic susceptibility is[58]

$$\chi_0=\tfrac{1}{6}\langle 0\mid r_{1A}{}^2+r_{2B}{}^2\mid 0\rangle=Z^{-2} \qquad \text{(B. 4)}$$

or the sum of the susceptibilities of two H atoms of screening Z. The scalar nuclear magnetic shielding for the nucleus at A is

$$\begin{aligned}\sigma_0{}^A&=\frac{1}{3}\left\langle 0\left| r_{1A}{}^{-1}+\frac{r_{2A}{}^2-z_{2A}R}{r_{2A}{}^3}\right| 0\right\rangle\\&=\tfrac{1}{3}Z[1+\exp(-2ZR)(1+2ZR)]\end{aligned} \qquad \text{(B. 5)}$$

or the sum of the shielding due to an H atom at A plus the long range shielding due to a second H atom.

The spin-rotational interaction at a given nucleus, c_w, has been shown by Ramsey[59] to be related to an expression which can be written formally as part of the nuclear magnetic shielding σ. This relationship is

$$\sigma_N{}^{\mathrm{HF}}=-\frac{K'}{6\mu_N}\left[\frac{\mu_N}{R_0}-\frac{2\pi(\mu' R_0)^2c_w}{M\gamma_N}\right] \qquad \text{(B. 6)}$$

in Ramsey's notation where K' is a vibrational correction and $\sigma_N{}^{\mathrm{HF}}$ at nucleus N, which is simpler to treat than c_w itself, is that part of σ_N defined by

$$\sigma_N{}^{\mathrm{HF}}=\sigma_N-\tfrac{1}{3}\langle 0\mid \sum_i r_{iN}{}^{-1}\mid 0\rangle \qquad \text{(B. 7)}$$

with $r_{iN}=\mid r_i-R_N\mid$, a radial coordinate centered on N. $\sigma_A{}^{0,\mathrm{HF}}$ is easily seen to be

$$\begin{aligned}\sigma_A{}^{0,\mathrm{HF}}-&=\tfrac{1}{3}\langle 0\mid Rz_{2A}/r_{2A}{}^3\mid 0\rangle\\&=-\tfrac{1}{3}[R^{-1}-(R^{-1}+2Z+2Z^2R)\exp(-2ZR)]\end{aligned} \qquad \text{(B. 8)}$$

and it is clearly negative as found experimentally.

The rotational magnetic moment μ_J/J has been shown by Wick[59,60] to be related to an expression which can be written formally as part of the magnetic susceptibility χ. This relationship is

$$\chi^{\mathrm{HF}}=\frac{e^2R_0{}^2K}{12mc^2}\left(1-\frac{2\mu'}{M\mu_N}\frac{\mu_J}{J}\right) \qquad \text{(B. 9)}$$

in Ramsey's notation[59] where K is a vibrational correction and χ^{HF}, which is simpler to treat than μ_J/J itself is that part of χ defined by

$$\chi^{\mathrm{HF}}=\chi+\tfrac{1}{6}\langle 0\mid \sum_i r_{i0}{}^2\mid 0\rangle \qquad \text{(B. 10)}$$

with $r_{i0}=\mid r_i-R_0\mid$ a radial coordinate centered at the electronic center of charge—the midpoint of the H_2 bond. $\chi_0{}^{\mathrm{HF}}$ is easily seen to be

$$\chi_0{}^{\mathrm{HF}}=R^2/12 \qquad \text{(B. 11)}$$

and thus independent of Z.

The calculated values for these properties are presented in Table II and agreement with experiment is certainly good despite the strong Z dependence of the results. Note that $\chi_0{}^{\mathrm{HF}}$ is ten times larger than experiment and shows no Z dependence, but contrast this with the only other really accurate value, that for ψ_0(GMO), which is five times smaller than experiment.

We had hoped that ψ_0(NS) could be used to give an exact value for the Fermi-contact term (and the other terms) of the electron-coupled proton–deuteron interaction in the HD molecule.[61] The problem requires solution of the equation

$$\begin{aligned}&[h_0(1)+h_0(2)-E_0]\Psi_{01}{}^H\\&\qquad=-\tfrac{8}{3}\pi I_z{}^H[S_z(1)\delta(r_{1H})+S_z(2)\delta(r_{2H})]\Psi_0(\mathrm{NS})\end{aligned} \qquad \text{(B. 12)}$$

where the spin is included in Ψ_0(NS) and in $\Psi_{01}{}^H$, and there is a similar equation involving $I_z{}^D$ and $S\delta(r_D)$'s. It can be seen that $\Psi_{01}{}^H$ can be written as

$$\Psi_{01}{}^H=\tfrac{8}{3}\pi I_z(H)2^{-\frac{1}{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]\psi_{01}{}^H, \qquad \text{(B. 13)}$$

where $\psi_{01}{}^H$ is a linear combination of the spatial part of triplet functions and is the solution to

$$\begin{aligned}&[h_0(1)+h_0(2)-E_0]\psi_{01}\\&\qquad=-[\delta(r_{1H})-\delta(r_{2H})]\psi_0(\mathrm{NS})\end{aligned} \qquad \text{(B. 14)}$$

---

[57] A series of papers by A. T. Amos and L. C. Snyder [J. Chem. Phys. **41**, 1773 (1964); **43**, 3670 (1965), *et seq.*] discusses the utility of wave functions which are not eigenfunctions of S^2. These authors use spin projections in the reverse sense, to subtract off the unwanted spin components.

[58] This is described in a somewhat different way in J. I. Musher, Advan. Mag. Resonance **2** (to be published in 1967). This article also gives a few corrections to Ref. 4 above.

[59] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956).

[60] G-C. Wick, Z. Physik **85**, 25 (1933).

[61] J. I. Musher, Phys. Rev. Letters **15**, 1015 (1965).

This equation, as it stands, has no solution because the inhomogeneous term is not orthogonal to $\psi_0(\text{NS})$, the solution to the homogeneous equation on the left-hand side. This is due explicitly to the nonsymmetrical nature of $\psi_0(\text{NS})$ since the right-hand side would automatically be orthogonal for any symmetrical ψ_0. In our calculation[61] we wrote $\psi_{01}{}^{H}$ as the sum of two terms and in doing so we added and subtracted constants to the square brackets on the right-hand side of (B. 14). Had ψ_0 been symmetrical these constants would have been equal and there would have been no problem. Here, however, the constants were not equal and it was as if (B. 14) had the additional constant that would have enabled its solution. We do not really appreciate the significance of the error in adding this constant, but it seems likely that there is no way to justify it or correct for it.

APPENDIX C. TIGHT-BINDING THEORY VERSUS BAND THEORY

It is well known that for a crystal containing atoms in closed shells (or such that $|m_S|=S$), a localized or tight-binding description as given in Sec. IV is exactly equivalent to a delocalized description such as in the band theory of Bloch. The purpose here is to emphasize a rather obvious point which is sometimes not appreciated: these delocalized tight-binding states, constructed in terms of atomic functions by

$$\psi_{\mathbf{k}}(r)=\sum_{\mathbf{R}}\exp(i\mathbf{k}\cdot\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r}-\mathbf{R}), \qquad (\text{C. 1a})$$

where the $\phi_{\mathbf{R}}$ are, e.g., the $1s$-hydrogen atom orbitals on center R in the parallel spin example of Sec. IV, are not the same as the usual Bloch wave functions which are eigenfunctions of the equation

$$[-\tfrac{1}{2}\nabla^2+V(\mathbf{r})]\phi_k(\mathbf{r})=\epsilon_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r}) \qquad (\text{C. 1b})$$

in which $V(\mathbf{r})$ possesses the periodicity of the lattice. This is easily seen explicitly by considering the functions $v_{\mathbf{k}}$ and $u_{\mathbf{k}}$ which possess the periodicity of the lattice and are defined by

$$\psi_k(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})\sum_{\mathbf{R}}\exp[i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})]\phi(\mathbf{r}-\mathbf{R})$$

$$\equiv\exp(i\mathbf{k}\cdot\mathbf{r})v_{\mathbf{k}}(\mathbf{r}) \qquad (\text{C. 2a})$$

and

$$\phi_{\mathbf{k}}(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \qquad (\text{C. 2b})$$

and which satisfy the equations

$$[\tfrac{1}{2}(-i\nabla+\mathbf{k})^2+V_v]v_{\mathbf{k}}=\epsilon_{\mathbf{k}}{}^{v}v_{\mathbf{k}} \qquad (\text{C. 3a})$$

and

$$[\tfrac{1}{2}(-i\nabla+k)^2+V_u]u_{\mathbf{k}}=\epsilon_{\mathbf{k}}{}^{u}u_{\mathbf{k}}. \qquad (\text{C. 3b})$$

An obvious although arbitrary choice for the Bloch potential V_u would be the one-electron Coulomb attraction to each center

$$V_u=-\sum_{R}(1/|r-R|), \qquad (\text{C. 4a})$$

whereas V_v which is defined by the explicit form of ψ_k can be written symbolically as

$$V_v=-\sum_{R'}(1/|r-R'|)\exp[-i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{r})]\delta_{RR'}, \qquad (\text{C. 4b})$$

where the $\delta_{RR'}$ is to operate *inside* the sum of v_k. Thus clearly the true Bloch functions ϕ_k and the delocalized (or Bloch) tight-binding functions are different. The fact that for large systems the crystal Hartree–Fock solutions approach the Bloch functions is irrelevant to this problem since we are discussing here Slater determinants made up of free-atom Hartree–Fock solutions as in Sec. IV and not Hartree–Fock solutions for the entire crystal.

The problem can be inverted by comparing the Wannier functions

$$a_{\mathbf{R}}=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{R})\phi_{\mathbf{k}}(\mathbf{r}) \qquad (\text{C. 5})$$

with the tight binding function ϕ_R. While it is true that the $a_{\mathbf{R}}$ are localized, they are of course not necessarily—even in any limit—equal to the ϕ_R. The nonequivalence of these two functions cannot be attributed to the lack of orthogonality of the ϕ_R's and thus the use of Löwdin-orthogonalization, although simplifying the expression for the energy, cannot affect the inherent difference between tight-binding theory and band theory. It is true that a given $a_{\mathbf{R}}$ can be expanded in the complete set of functions $\phi_{\mathbf{R}}{}^{i}$, on a single nucleus $\mathbf{R}'$ not necessarily equal to $\mathbf{R}$

$$a_{\mathbf{R}}=\sum_{i}c^{i}{}_{\mathbf{RR}'}\phi^{i}{}_{\mathbf{R}'} \qquad (\text{C. 6})$$

but it is not true that it can be expanded in terms of a single orbital, one on each center, i.e.,

$$a_{\mathbf{R}}\neq\sum_{\mathbf{R}'}c_{\mathbf{RR}'}\phi_{\mathbf{R}'}. \qquad (\text{C. 7})$$

APPENDIX D. EXAMPLE OF NONCONVERGENT EXPANSION FOR H_0 OF EQ. (4.47)

In Sec. IV the perturbation theory expansion with

$$H_0=E_0|0\rangle\langle 0| \qquad (\text{D. 1})$$

was shown to be exactly soluble for all ψ_0's, a fact which alone should make it suspect. Actually, this is a legitimate expansion, but it is probably only convergent in exceptional cases and at best ψ and E show the properties of an asymptotic expansion and a semiconvergent series, respectively.

To illustrate this procedure we try to obtain the known exact solution for the $1s$-hydrogen atom from a zeroth-order wave function which would be exact for a screened nuclear change. Thus we take

$$\psi_0(Z)=(Z^3/\pi)^{\frac{1}{2}}\exp(-Zr) \qquad (\text{D. 2})$$

Table III. Approximate hydrogen atom energies.

Z	$-E_0$	$-E^{(2)}$
1/8	15/128	421/1920
1/4	7/32	85/224
1/3	5/18	41/90
1/2	3/8	13/24
2/3	4/9	5/9
3/4	15/32	87/160
4/5	12/25	8/15
1[a]	1/2[a]	1/2[a]
6/5	12/25	3/5
5/4	15/32	65/96
3/2	3/8	15/8

[a] For $Z=1$ $\psi_0=\psi$ and $E_0=E$, the exact solutions.

for an arbitrary value of $Z\neq 1$ which has energy of

$$E_0(Z)=\langle 0\,|\,H\,|\,0\rangle=\tfrac{1}{2}[Z(Z-2)]Ry, \qquad (\text{D. }3)$$

where H is the exact Hamiltonian of the hydrogen atom. From (4. 49) ψ_1 is found to be

$$\psi_1=[2(Z-1)/Z(Z-2)](Z^3/\pi)^{\frac{1}{2}}(r^{-1}-Z)\exp(-Zr) \qquad (\text{D. }4)$$

which gives the second-order partial sum ($E_1=0$)

$$E^{(2)}=E_0+E_2=[Z(5Z^2-12Z+8)/2(Z-2)]. \qquad (\text{D. }5)$$

The third-order energies, however, contain divergent terms which arise from the cube of the Coulomb potential and also from the product $(1/r)\nabla^2(1/r)$. One can speculate that this deceptively attractive perturbation theory expansion gives divergent results for all $E^{(n)}$ with n finite for all values of the parameter λ in the artificial Hamiltonian

$$H'=E_0\,|\,0\rangle\langle 0\,|+\lambda(H-E_0\,|\,0\rangle\langle 0\,|\,) \qquad (\text{D. }6)$$

so that the problem has zero radius of convergence in the usual sense of the term, unless $Z=1$, for which ψ_1 and all higher corrections vanish identically. It might however be possible to obtain a finite result by formally summing the entire infinite series.

It is still possible that $E^{(2)}$ give a fair approximation to the exact energy E and this is seen in Table III where E_0 and $E^{(2)}$ are tabulated for a number of values of Z. For all values within the range

$$0\lesssim Z\lesssim 1 \qquad (\text{D. }7)$$

$E^{(2)}$ is a very good approximation to the exact result, and is a considerable improvement over E_0 except when E_0 is not a bad approximation itself. Values of $Z\gtrsim 2$ are excluded since it is seen from (C. 5) that the energy $E^{(2)}$ is positive (nonbinding) in that region, while values of $Z\gtrsim 1$ are excluded since $E^{(2)}$ decreases monotonically and rapidly for Z between 1 and 2. One can say that the procedure works well in the range that it does because $E^{(2)}$ has turning points at $Z=1$ and $Z\sim\frac{2}{3}$, but this is in a sense tautological. This procedure can also be applied to other problems, such as that of the London–van der Waals interaction.

APPENDIX E. THE GENERALIZED SEPARABLE H_0

The most general separable, or independent particle, approximate Hamiltonian for an N-electron closed-shell molecule, containing nuclei A of charge Z_A, is

$$H_0(V)=\sum_i h_0(V,i)=\sum_i[-\tfrac{1}{2}\nabla_i^2-\sum_A(Z_A/r_{iA})+V(i)], \qquad (\text{E. }1)$$

where $V(i)$ is an arbitrary one electron operator. The lowest eigenfunction of $H_0(V)$ is the single-determinant

$$\Psi_0(V)=\mathcal{A}\alpha(V,1)\beta(V,2)\cdots \qquad (\text{E. }2)$$

constructed from the N spin orbitals of lowest energy, $\mu(V,i)$, which are eigenfunctions of $h_0(V,i)$ of energy $\epsilon_\mu(V)$, satisfying

$$[h_0(V,i)-\epsilon_\mu(V)]\mu(V,i)=0. \qquad (\text{E. }3)$$

The corrections to Ψ_0 are found by solving the equations of perturbation theory with $\lambda_v H_1(V)$ defined by

$$\lambda_v H_1(V)\equiv H-H_0(V)=\sum_{i<j}(1/r_{ij})-\sum_i V(i) \qquad (\text{E. }4)$$

and, as is well-known, the corrections to first-order in λ involve only the solutions to a series of two-electron inhomogeneous partial differential equations.

It is significant that the formal solution to the perturbation theoretic problem is independent of the particular choice of the one-electron potential, $V(i)$, since whatever terms introduced into $H_0(V)$ are identically subtracted out in $\lambda_V H_1(V)$. The convergence of the expansion will depend critically on the particular choice of $V(i)$ but if the expansion converges for one choice of $V(i)$ it should converge as well for a wide variety of $V(i)$'s which are in some sense similar. Thus a criterion such as "best possible" Ψ_0, has little meaning when a perturbation expansion is envisaged, and the choice of $V(i)$ should be based on expediency rather than on an arbitrary criterion such as minimizing the total energy. [Kelly (Ref. 23 and earlier papers cited therein) has described and used procedures which amount to choosing an expedient $V(i)$ for the perturbative part of the calculation, *after* Ψ_0 is determined. Kelly shows that this is equivalent to partially summing certain sets of diagrams while neglecting others. The author has related a similar procedure to a Taylor series expansion (Ref. 68 below).]

The various schemes for choosing $V(i)$ discussed in the literature are: (1) the Hartree–Fock scheme in which the potential $V(i)$ contains integral operators as well as functions of position; (2) the bare nucleus scheme discussed by Sinanoğlu,[31] Dalgarno[32] and others in which $V(i)=0$; (3) the screened bare nucleus scheme in which

$$V_s(i)=\sum_A(s_A/r_{iA})$$

with the s_A chosen as discussed in the text above; (4) Slater's[62] approximation to the Hartree–Fock potential in which the "exchange" or integral potential is "approximated" by an effective exchange potential; (5) Gaspar's[63] and Kohn and Sham's[64] approximation and improvement to the Hartree–Fock potential in which the "exchange" potential is replaced by an effective exchange potential differing from Slater's[65] by a numerical factor of $\frac{2}{3}$, and in which an additional "correlation" potential is added.[66]

Therefore as long as $\Psi_0(V)$ will be improved upon using perturbation theory, there are no inherent advantages to a self-consistent-field solution, and therefore the fully-iterated solutions to the coupled equations of schemes (1), (4), and (5) are not significantly better than, say the first-iteration, to justify the additional computing time. Since the simplest scheme with a reasonable $V(i)$ will be the most practicable, both the first-iterated Slater or Kohn and Sham schemes—and it makes little difference which of the two—will be chosen over the Hartree–Fock scheme. The bare nucleus scheme (2) will probably not converge, but a reasonably screened nucleus scheme (3) should, as would also a scheme based on any reasonable guessed-at $V(i)$ such as the sum of Thomas–Fermi atomic potentials.

We feel that the simplest and most accurate procedure would take as $V(i)$ that obtained by the first-iteration of the Hartree–Fock procedure *without including the exchange term at all.* [Since the Slater and Tong and Sham[67] results (excluding correlation) differed by less than 0.1%, leaving out the entire exchange term in H_0 can only change the total energy by $\sim$0.2%, and the convergence should certainly not be affected. Notice, however, that the total "exchange energy" will not be significantly affected—it will still be large—as there will only be a small change in the orbitals. It might be necessary to multiply the Coulomb term by $(N-1)/N$ in order not to "over-screen" the nucleus so that there are at least N bound spin orbitals.] The absence of nonlocal potentials in H_0, besides simplifying the calculation of Ψ_0, Ψ_1, etc. will also simplify the calculation of molecular electric and magnetic properties. We have discussed elsewhere[68] the fact that there is no advantage in obtaining approximate self-consistent molecular properties, where the self-consistency refers to the interaction with the external field since the self-consistency corrections identically vanish to all orders. The present discussion shows that the only advantage of self-consistent calculations of atomic and molecular wave functions is that more rapid convergence might thereby be afforded. No general proof exists, however, that the Hartree–Fock scheme provides the most rapid convergence of all possible independent particle schemes.[69] (See also Ref. 14 above.)

We have discussed the problem of separable H_0's from the point of view of the molecular theorist for whom first-order perturbation theory corrections are a practicable possibility. The solid-state theorist, who is in general only interested in the "best possible" Ψ_0 and corresponding energy, should, however, appreciate the observation that there is no "higher virtue" whatever to a self-consistent procedure. Thus, for example, a sophisticated theory which would be rendered impracticable by making it self-consistent is nevertheless to be preferred over a simple-minded theory which is constructed from the start to be self-consistent.

---

[62] J. C. Slater, Phys. Rev. **81,** 385 (1951).

[63] R. Gaspar, Acta Phys. Hung. **3,** 263 (1954), *et seq.*

[64] W. Kohn and C. J. Sham, Phys. Rev. **140,** A1133 (1965).

[65] See J. C. Slater, M. I. T. Solid-State and Molecular Theory Group Quarterly Progress Report, October 1965 (unpublished) for a critical discussion.

[66] This correlation potential cannot be considered an improvement on the Hartree–Fock H_0 in the sense of making ψ_0 contain some "correlation" since according, at least, to the accepted criterion of minimum energy, the "best possible" single-determinant ψ_0 is the Hartree–Fock ψ_0. These authors do not consider as their total energy the expectation value of H but rather the expectation value of H plus a "correlation" potential. Thus even if the wave function were not to contain correlation the energy would, although in a somewhat *ad hoc* fashion. We feel it is certainly a reasonable possibility that the Kohn–Sham ψ_0 is "better" than the Hartree–Fock ψ_0 in the sense of being closer to the exact ψ, but that the comparison of the "energy," which includes the expectation value of the correlation potential, with the Hartree–Fock energy is misleading.

[67] B. Y. Tong and L. J. Sham, Phys. Rev. **144,** 1 (1966).

[68] J. I. Musher, J. Chem. Phys. **46,** 369 (1967).

[69] For a discussion of Hartree–Fock and "best possible" wave functions, see Refs. 17 and 65.