Localized Wave Functions and the Interaction Potential between Electronic Groups

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(Received 21 February 1974)

It is shown that the Schrödinger equation for electronic wave functions can be modified so that its solutions describe a molecule as a collection of interacting atoms or other units. The interaction potential between electrons localized in different units is the weakest one possible that is consistent with the constraint that the corresponding localized wave function yield upon symmetry projection one solution to the Schrödinger equation. The binding energy of the system can be calculated directly.

We understand the chemistry and physics of molecules in terms of "weakly" interacting units: atoms, ions, electronic shells, etc. If we wish to improve the quantitative predictions based on these physical models by including the interactions between the units, we must define the interaction potentials. The theorem proven here defines these potentials without introducing approximations. If we wish to calculate *ab initio* an electronic wave function, the units in a molecule are hidden by the indistinguishability of electrons. The theorem proven here allows us to calculate a wave function which is least distorted from a product of the wave functions of the noninteracting units. I believe the theorem offers a new starting point for formal and computational studies of electronic structure.

The published works most closely related to this paper are by Klein[1] and the author.[2] Neither's formulation involves approximations, but both have unnecessarily constrained their wave functions to be sums of a finite number of eigenfunctions of the molecular Hamiltonian.[3] In the present theory the wave function to be determined is the sum of an infinite number of such eigenfunctions. In other respects the present formulation parallels the author's previous work.[2]

The next most relevant works are those of Gilbert[4] and the author.[5,6] They based their works on the Hartree-Fock approximation to the many-electron theory and generalizations of that theory. I do not use such approximations in this paper.

Other theories of the interactions between units in molecules have involved approximations which are much less well understood than the Hartree-Fock approximation or have depended intrinsically upon the use of perturbation methods. I shall discuss these theories in detail elsewhere.[7-9]

Let H be the spin-independent, nonrelativistic Hamiltonian for an N-electron molecule in the Born-Oppenheimer approximation. Let $\Psi_{\alpha i}{}^{\mu}$ be an eigenfunction of H, where μ specifies the multiplicity, the irreducible representation (IR) of the symmetric group, and the IR of the molecular point group to which the eigenfunction belongs; i specifies the z component of the total spin and the rows of the IR's to which it belongs; and α specifies the different energy states having the same μ and i. Let $E_{\alpha}{}^{\mu}$ be the eigenvalue of H which belongs to $\Psi_{\alpha i}{}^{\mu}$.

Conceptually divide an N-electron molecule into units (atoms, ions, shells, etc.) and assign each electron to a specific unit. Let h_a be the Hamiltonian of the unit a when all interactions between units have been turned off. Define $H_1 = \sum_a h_a$. If $h_a\varphi_a = E_a\varphi_a$, then defining $F^0 = \Pi_a \varphi_a$ and $\epsilon^0 = \sum_a E_a$, one has $H_1 F^0 = \epsilon^0 F^0$. We assume that the φ_a depend on both the position and spin coordinates of the electrons assigned to a.

Let $\rho_{ii}{}^{\mu}$ be the projection operator which acting on any N-electron function gives a function having the properties specified by μ and i, or gives zero. We wish to determine a function G of the position and spin coordinates of the N electrons which is related to F^0 and, for one particular choice of μ and i, satisfies the constraint

$$M^{1/2}\rho_{ii}{}^{\mu}G = \Psi_{\alpha i}{}^{\mu} \tag{1}$$

for $M^{-1} = \langle G|\rho_{ii}{}^{\mu}|G\rangle \neq 0$. The most general form that G can have and satisfy (1) is

$$G = C_{\alpha i}{}^{\mu}\Psi_{\alpha i}{}^{\mu} + \sum_{\nu j \beta}(1 - \delta_{\mu\nu}\delta_{ij})C_{\beta j}{}^{\nu}\Psi_{\beta j}{}^{\nu}, \tag{2}$$

where the coefficients $C_{\gamma k}{}^{\lambda}$ are arbitrary except that $C_{\alpha i}{}^{\mu} \neq 0$. It is essential to extend the sum in (2) over *all* eigenfunctions of H including those which violate the Pauli principle.

We can choose the $C_{\gamma k}{}^{\lambda}$ in (2) as we wish and still satisfy (1). We choose them so that G will be least distorted[2] from F^0 in the sense that

$$\langle G|H_1|G\rangle / \langle G|G\rangle = \epsilon = \text{extremal}. \tag{3}$$

If the constraint (2) were not imposed, F^0 would

satisfy (3). We call a function which satisfies
(2) and (3) a *minimally distorted localized wave
function*. More restrictive constraints than (1)
can be imposed. They correspond to using fewer
$\Psi_{\beta j}{}^{\nu}$ in (2) and, by (3), defining a less well local-
ized wave function than G.[9]

One can derive from (3) and (2) a secular equa-
tion which determines the $C_{\gamma k}{}^{\lambda}$ and ϵ. We re-
write the secular equation using the projection
operator

$$Q = |\Psi_{\alpha i}{}^{\mu}\rangle\langle\Psi_{\alpha i}{}^{\mu}| + \sum_{\nu j \beta}(1 - \delta_{\mu\nu}\delta_{ij})|\Psi_{\beta j}{}^{\nu}\rangle\langle\Psi_{\beta j}{}^{\nu}|.$$

The sum over β, ν, and j includes *all* eigenfunc-
tions of H as in (2). Note that since the eigen-
functions of H form a complete set, $\sum_{\beta}|\Psi_{\beta j}{}^{\mu}\rangle$
$\times\langle\Psi_{\beta j}{}^{\nu}| = \rho_{jj}{}^{\nu}$. Since $\sum_{\nu j}\rho_{jj}{}^{\nu} = 1$, we have

$$Q = |\Psi_{\alpha i}{}^{\mu}\rangle\langle\Psi_{\alpha i}{}^{\mu}| + 1 - \rho_{ii}{}^{\mu}. \tag{4}$$

From (2) and (4) it follows that $QG = G$. From
(3) we find that

$$QH_1QG = \epsilon G. \tag{5}$$

Equation (5) can be used to determine G, how-
ever, only if $\Psi_{\alpha i}{}^{\mu}$ is known.

In stating the following theorem, we redefine
Q and G, then show that the new definitions im-
ply the old. We gain as a consequence the abili-
ty to determine G and Q without having first to
know $\Psi_{\alpha i}{}^{\mu}$.

Theorem: If $\rho_{ii}{}^{\mu}G \neq 0$ and if G satisfies for an
arbitrary operator U the equation

$$(H - QUQ)G = \epsilon G, \tag{6a}$$

where

$$Q = M\rho_{ii}{}^{\mu}|G\rangle\langle G|\rho_{ii}{}^{\mu} + 1 - \rho_{ii}{}^{\mu} \tag{6b}$$

and $M^{-1} = \langle G|\rho_{ii}{}^{\mu}|G\rangle$, then

$$M^{1/2}\rho_{ii}{}^{\mu}G = \Psi_{\alpha i}{}^{\mu}.$$

Furthermore, if $U = V_1 = H - H_1$, then G satisfies
(5) and is least distorted from F^0 in the sense of
Eq. (3).

Proof: Note that $QG = G$ follows from the defini-
tion of Q in (6b). Thus multiplication of (6a) by
$1 - Q$ gives

$$(1 - Q)HG = 0. \tag{7}$$

Since $\rho_{ii}{}^{\mu}H = H\rho_{ii}{}^{\mu}$ and $\rho_{ii}{}^{\mu}Q = M\rho_{ii}{}^{\mu}|G\rangle\langle G|\rho_{ii}{}^{\mu}$,
multiplication of (7) by $\rho_{ii}{}^{\mu}$ yields

$$H\rho_{ii}{}^{\mu}G = M\langle G|\rho_{ii}{}^{\mu}H|G\rangle\rho_{ii}{}^{\mu}G. \tag{8}$$

Thus $\rho_{ii}{}^{\mu}G$ is one of the eigenfunctions of H. It
follows that Eqs. (6b) and (4) define the same

operator. Multiplication of (6a) by Q and use of
$QG = G$ gives

$$Q(H - U)QG = \epsilon G.$$

Thus, if we set $U = V_1$, we obtain Eq. (5). There-
fore G satisfies Eqs. (1) and (3) if it satisfies
Eq. (6b), q.e.d.

There is nothing in the statement or proof of
the theorem which limits its applicability to the
lowest energy state belonging to μ. Whether or
not one can solve (6a) depends only on how accu-
rately F^0 approximates G.

I have solved Eq. (6a) approximately for H_2^+
and H_2 with $U = V_1$ by both a perturbation method[8]
and an iterative configuration-interaction meth-
od.[9,10] For H_2 the latter method has converged
for the equilibrium nuclear separation of 1.4 a.u.
Programming has begun to extend the calcula-
tions to three- and four-electron diatomic com-
plexes.

The effect of QV_1Q in Eq. (6a) is to screen V_1.
One can see this by considering the effect of add-
ing to Q as defined in (4) more projectors of the
form $|\Psi_{\beta i}{}^{\mu}\rangle\langle\Psi_{\beta i}{}^{\mu}|$. In the limit in which all $\Psi_{\beta i}{}^{\mu}$
have been included, we have $Q = 1$. Then QV_1Q
exactly cancels V_1 in (6a) and $G = F^0$. Thus for
$Q \neq 1$, the potential QV_1Q must partially cancel
V_1. The potential of interaction between elec-
trons in different units in a molecule, $V_1 - QV_1Q$,
is thus a weaker potential than V_1.

The theorem proven in this Letter is one of a
series of theorems concerning wave functions re-
lated to F^0 by condition (3), but upon which more
stringent constraints than (1) are imposed. These
constraints lead to wave functions which are less
accurate approximations to F^0 by the condition
(3) than is G.[9]

There are criteria other than (3) by which local-
ized wave functions may be defined.[9] They cor-
respond to choices of U different from V_1 and are
straightforward generalizations of the criteria
considered by Gilbert for localized orbitals.[3]

The solution of (6a) gives directly no physically
measurable quantities. The eigenvalue ϵ is the
energy of the molecule in no physical state. The
difference $\epsilon - \epsilon^0$ is useful when $U = V_1$. Then, it
is a quantitative measure of the distortion of G
from F^0 due to the interactions between the units
in a molecule. It can thus indicate how accurate-
ly our physical understanding of a molecule in
terms of atoms, shells, etc., approximates math-
ematical reality. Comparison of G and F^0 yields
more detailed information.

We can obtain measurable quantities from G in most cases only by first using (1) to obtain $\Psi_{\alpha i}{}^{\mu}$, then calculating matrix elements. An interesting special case is the energy $E_{\alpha}{}^{\mu}$. We can calculate the binding energy $E_{\alpha}{}^{\mu} - \epsilon^0$ of the units without having to calculate separately $E_{\alpha}{}^{\mu}$ and ϵ^0 and then take the difference between these potentially large numbers. Multiply (8) from the left by $\langle F^0|$ and use $H = H_1 + V_1$ and $H_1 F^0 = \epsilon^0 F^0$ to obtain

$$E_{\alpha}{}^{\mu} - \epsilon^0 = \langle F^0|V_1\rho_{ii}{}^{\mu}|G\rangle / \langle F^0|\rho_{ii}{}^{\mu}|G\rangle . \tag{9}$$

This equation is valid even when G and F^0 are approximated by expansions in terms of a finite set of N-electron functions.[9]

I have asserted that $V_1 - QV_1Q$ is the weakest possible interaction potential given the constraint (1) and a chosen resolution of the molecule into units. I reason as follows: Equation (2) shows the most general form G can have and satisfy (1). Equation (3) defines the arbitrary coefficients in (2) so that G differs minimally from F^0. Since G satisfies (6a), $V_1 - QV_1Q$ distorts F^0 into G. Since the distortion is minimal, $V_1 - QV_1Q$ must be the weakest potential consistent with (2) and the chosen resolution of the molecule into interacting units. We are free to choose the units so as to ensure that $V_1 - QV_1Q$ is weak.

The usefulness of Eq. (6a) as a practical starting point for *ab initio* calculations must be tested by calculation. We have only determined that it is possible to solve it. On the other hand, the usefulness of Eq. (6a) for formal studies should be obvious. It defines without resort to approximation the weakest potential by which the electrons of the different "physical" units in a molecule interact. The electronic wave function calculated using this potential is least distorted from a product of wave functions for the noninteracting units in a molecule, but yields upon symmetry projection one solution to the Schrödinger equation. Thus as a starting point for formal studies Eq. (6a) eliminates the need to infer or guess an interaction potantial which correctly accounts for the indistinguishability of electrons.

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[9] W. H. Adams, to be published.

[10] The details of the implementation of the present theory are quite similar to those for the theory of Ref. 2. The implementation and application of that theory to H_2 has been described by W. H. Adams, Int. J. Quantum Chem., Symp. **1973**, 127.