PHYSICAL REVIEW VOLUME 181, NUMBER 1 5 MAY 1969

Localized Orbitals for Molecular Quantum Theory. I. The Hückel Theory

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(Received 23 August 1968)

An equation for calculating localized orbitals for use in molecular and solid-state chemical bonding problems is applied to a typical conjugated system to obtain an estimate of the one-electron Hückel parameter and a partial justification of Hückel theory and of methods involving linear combinations of atomic orbitals.

I. INTRODUCTION

Some of the simple theories of molecular electronic structure proposed in the early years of quantum mechanics have been more successful than the sophisticated attempts at exact solutions which followed them, at least until the present era of giant computer calculations which virtually reproduce nature's solutions of Schrödinger's equation. This is particularly true in the case of large, chemically interesting molecules (anything containing more than ten atoms or 10^2 electrons), for which even a correct one-electron theory should in principle involve wave functions and interactions extending over the entire molecule, and a properly correlated theory would be even worse. As a result, attempts at exact calculation tend to get bogged down in large numbers of "many-center integrals" involving several wave functions or atomic potentials.

All of this contradicts the empirical fact that the chemistry of covalently bonded compounds is, on the whole, a science in which action at a distance does not play any great role. Correspondingly, the most successful semiempirical theories of chemical bonding have a surprisingly local aspect to them. Saturated covalent bonds, for instance, are described very well by Pauling's valence-bond theory[1] using hybridized bond orbitals, an approximation which appears meaningful *a priori* only if correlation effects for such molecules are much larger than they really are. They are in fact much smaller than in metals and semiconductors, where band theory, which is equivalent to the method of molecular orbitals, has its greatest successes. The correlation energy itself is known to be about half as big in molecules as in metals, and is to be compared to greater binding energies.

The Pauling theory will be the subject of a later paper using similar methods to this one[2]; but for the time being we concentrate on the other successful theory, the Hückel theory of π electrons in unsaturated molecules.[3] Here undoubtedly great successes have been achieved by treating the π orbitals as running throughout the molecule, and nonlocal effects are observed and well predicted. The strange fact, however, is that the Hamiltonian matrix elements which are used are unexpectedly local and simple: nearest-neighbor matrix elements only are used and are usually in rough correspondence with those calculated from the simplest treatment of linear combinations of atomic orbitals (LCAO); and even more surprisingly, the undoubtedly large overlap elements that should appear in the secular equation using nonorthogonal atomic orbitals:

$$|\mathcal{H}-E(1+S)|=0 \qquad (1)$$

cannot successfully be included, even though all estimates agree that, for benzene, for instance, $S_{12}\sim 0.25$ for nearest-neighbor π orbitals, ~ 0.04–0.05 for next-nearest neighbors. The secular equation which *works* is then

$$|\mathcal{H}_{ij}-E\delta_{ij}|=0. \qquad (2)$$

Justifications of (2) which are, within their frames of reference, undoubtedly correct, have appeared in the literature. For a sufficiently small molecule one can simply use a sufficiently complete basis set of wave functions and calculate energy dependences of matrix elements and next-nearest-neighbor effects, and show that they all tend to cancel out leaving (2).[4] Even more naively, the validity of LCAO is assumed *a priori* ignoring the possibility of its providing an insufficient basis set, and numerical cancellation is demonstrated. So far as I know, no critical general discussion of why LCAO has tended to give correct answers for the Hückel theory – though it is known to fail in many metal and semiconductor band structures – has ever appeared.[5] This is the general problem which we attack here. We will show that (1) There is a set of wave functions which represent the *exact* solution of the one-electron problem and for which (2) is correct; (2) A definite prescription can be found for constructing these wave functions; (3) This prescription converges to functions which are for practical purposes the π atomic orbitals in the Hückel problem, but in any case converges and can be followed through by use of rather simple perturbation-theory techniques. (4) Using this prescription it is possible to calculate the one-electron approximations to the Hückel parameters and total ionization energy. What we find is a value of 2.43 eV for the Hückel parameter β (sometimes called "γ") in fair agreement with accepted semiempirical estimates.[6] In our opinion, our treatment of correlation corrections to *this* parameter is adequate, so that this numerical agreement is to be expected. Discussion of the rather full literature on this subject we leave until we can discuss our numerical treatment as well. In any case, the basic point is that the method is feasible and can be carried to a reasonably successful numerical conclusion.

We should emphasize that our method makes no attempt to treat the many-electron correlation problem with any sophistication at all, and that the π-electron problem, and benzene in particular, are cases in which correlation effects are non-negligible energetically, as well as of controlling importance to the spectrum. The so-called "extended Hückel" theory[7] has had some success in treating these effects, and it may be hoped that our methods will also provide a stronger basis for that theory eventually. Our method does not at all obviate present arguments for it, at least.

Unfortunately, it is not as common or as easy in the case of these molecules as it is in many solid-state problems, especially metals, to separate the two problems of solution of a one-electron potential to obtain a correct set of wave functions and energy parameters, and of solution of the correlation problem for electrons in this potential. I would like to emphasize here the great advantages of doing the two separately: of solving the one-electron problem well, once for all, for some suitably chosen mean potential (which with our method is extremely simple) and then treating correlation corrections and configurational changes in the self-consistent field on an identical basis (the so-called "Fermi liquid" point of view, that is). Our method contributes not at all to this second problem, but merely sets the stage properly for it.

Our method is a cousin of the pseudopotential method which has been successful in the quantitative theory of electronic structure of metals and semiconductors.[8] The new feature is that it is a "self-consistent" pseudopotential theory. (To avoid confusion: not self-consistent in the sense of being a Hartree-Fock theory, but self-consistent in the sense that the wave functions for a given, fixed *physical* potential are determined from a *pseudo*potential which depends on the wave functions themselves.) Some of the formal basis of the theory has been given in a previous publication.[9] A series of papers[2, 10] have appeared on the formal construction of localized orbitals using a self-consistent pseudopotential equation. These authors have confined themselves unnecessarily – and fatally for the case of conjugated molecules – to recombining the constituents of a single Hartree-Fock determinant, using the density matrix as a projector for their pseudopotential. By the usual Wannier function theorems,[9] in the case of the π-electron "band" no such local function can be found: only if the band is treated as a whole, empty and full states together, will the technique work. The much greater simplicity of our approach may also recommend itself. As far as we can see, it also appears that the use of ρ as a projector leads to nonlocalities almost as severe as does the use of Wannier functions.

II. FORMAL PSEUDOPOTENTIAL THEORY FOR LOCALIZED ORBITALS

Consider any grouping of atoms: ring, chain, solid, or molecule; the same formalism is applicable to all systems from diatomic molecules to solids. For simplicity in presenting the theory we proceed on the assumption that the atomic potentials are additive:

$$\mathcal{H} = T + \sum_n V_n(r) , \tag{3}$$

[but V_n need not be local or nonoverlapping; T is the kinetic energy $= -\nabla^2$ in our units (energy in Ry and distances in units of a_H). If any Madelung-type long-range Coulomb potentials due to charged groups are important, they probably should not be included in V_n so that the latter can be treated as fairly short-range].

Perhaps it would be well to discuss (3) a bit. Of course any potential may be written in this form, but our further development really assumes that the V_n are pretty similar to the atomic potentials, and in fact that any change to them in achieving self-consistency could be treated perturbationally. There are two aspects to our work here: First we are trying to show that the effect of neighbor potentials on the localized orbitals is very small and easily handled by perturbation theory. For this, the most important aspect, it is adequate to use any model potentials and AO's which are reasonably close to the real ones, in that we are merely testing convergences, not seriously calculating. But actually it is amusing, if not as important, to try to achieve some realism in the calculation, and the actual choice of the V_n was dictated by this. It is convenient, and makes the result far less sensitive to detailed assumptions about V_n and φ_n, to use the identity $(T + V_n)\varphi_n = E_n\varphi_n$, where E_n is the atomic eigenvalue. The innate flexibility of the pseudopotential method allows us to do this for each atom in turn, even though we know the potential – if only because of exchange terms – is quite far from the sum of atomic potentials. In particular, the atomic potential at large radii goes as $-2/r$, while the electron actually sees neutral atoms at all distant sites in the molecule. But it is perfectly within our power to choose $V_{m\neq n}$ to be the difference, whatever it may be, from the atomic potential V_n due to the presence of m. We feel this "Wigner trick" is a highly accurate device, unused so far as we know in molecular physics, which at a stroke makes the entire calculation sensitive only to the overlap regions of the wave functions (for which Slater functions are quite accurate) and insensitive to fine details of the potential. Thus our actual treatment is considerably better than (3).

Let me assume that there is an isolated "energy band" of this system. This appears to be the crucial assumption of the method, and restricts it entirely to nonmetallic binding. By "energy band" we mean a well-defined group of energy levels per atom, such as the σ bonds in a carbon framework. We define localized orbitals on each atom representing this "band" by means of an effective Hamiltonian containing a non-Hermitian pseudopotential term:

$$\mathcal{H}^{(n)}\varphi_n(r) = (T+V_n)\varphi_n(r) + \sum\nolimits_m{}'\Big[V_m(r)\varphi_n(r) - \int \varphi_m(r')\mathcal{H}_{\text{out}}^{(n,m)}(r')\,\varphi_n(r')\,d^3r'\,\varphi_m(r)\Big] = E_n\varphi_n(r)\,. \tag{4}$$

$\mathcal{H}_{\text{out}}^{(n,m)}$ is for the moment completely arbitrary, formally, though we should like it to depend on the difference $n-m$ for simplicity in a regular system. No matter what the choice of H_{out} we can make up eigenfunctions of $\mathcal{H}$ from the φ_n:

$$\psi_i = \sum\nolimits_n \alpha_n\varphi_n\ , \tag{5}$$

then (for generality we insert formally a diagonal matrix element for H_{out}, which will in most applications be zero)

$$\mathcal{H}\psi_i = \sum_n \alpha_n E_n\varphi_n + \sum_{n,m}(m|H_{\text{out}}^{(n,m)}|n)\,\varphi_m\alpha_n = \epsilon_i\psi_i\ , \tag{6}$$

if ϵ_i satisfies the secular equation

$$|(E_n-\epsilon_i)\delta_{nm} + H_{\text{out}}^{(n,m)}| = 0\,. \tag{7}$$

(This is just the set of linear equations for the α_n.) If H_{out} is the full Hamiltonian then φ_n are the Wannier functions (symmetry orbitals) and this is the usual Wannier equation. If $H_{\text{out}}=0$ the φ_n are eigenfunctions: molecular orbitals.

In both of these cases we can see that an iterative procedure for the solution of (4) starting from atomic orbitals would fail to converge. This is evident if $H_{\text{out}}=0$, since the whole assumption of localization breaks down there; but also in the Wannier case we know that the Wannier functions are not unique, because of the possibility of arbitrary phase factors for each k in their expansion in Bloch functions. Thus (4) has in that case no unique solution, since any set of Wannier functions no matter how nonlocalized would solve it. It can, however, be shown that if we use the full generality of $H_{\text{out}}^{(n,m)}$, and in particular if this operator is *local* to the neighborhood of m, uniqueness of the solutions is at least possible.

A much more useful choice of the pseudopotential is

$$H_{\text{out}}^{(n,m)} = V_m(r)\ , \tag{8}$$

in which case

$$H^n = T + V_n + \sum\nolimits_m{}' V_m(r')\times[\delta(r-r') - \varphi_m(r')\varphi_m(r)]\ , \tag{9}$$

and the effective Hamiltonian is still of the Hückel form, with $E_n=\alpha_n$ and $(n|V_m|m)=\beta_{nm}$. Note that although in every case but $H_{\text{out}}=0$ or the Wannier case, the orbitals are nonorthogonal, the secular equation is *not* of the form (1):

$$|\mathcal{H} - E(1+S)| = 0\,,$$

but of the Hückel form. This is the basic reason for the success of that theory. In fact, the secular equation is necessarily always just the Wannier equation.

The orbitals, at least for the special choice above, are more localized than Wannier functions, and in fact considerably so; they approximate atomic orbitals. The reason for this is that the pseudopotential term as written here is rather a strong repulsive term localized on all the atoms other than the one n under consideration. To see that it is repulsive, note that the total pseudopotential due to atom m obeys:

$$(\varphi_m|V_{ps}{}^n|\varphi_m) \cong (\varphi_m|V_m|\varphi_m) - (m|m)(\varphi_m|V_m|\varphi_m) = 0\ ,$$

so that the potential energy cancels approximately for a wave function φ_m localized on atom m. Thus the pseudo-Hamiltonian has actually a net positive value for φ_m, from the kinetic energy. Another way to estimate the strength of the repulsive term is to sum all the energies over the band:

$$\sum_i \epsilon_i = \sum_n E_n = \sum_n (\varphi_n | H^n | \varphi_n) . \qquad (10)$$

If φ_n is approximately an atomic orbital, this is then

$$\begin{aligned}\sum_i \epsilon_i &= \sum_n (\varphi_n | T + V_n | \varphi_n) \\ &\quad - \sum_{n,m}{}' S_{nm}(n|V_m|m) + \sum_{n,m}{}'(n|V_m|n), \\ &= \sum_n E_n{}^0 + \sum_{m,n}{}'(n|V_m|n) - \sum_{n,m}{}' S_{nm}(n|V_m|m).\end{aligned} \qquad (11)$$

V is negative; thus the second term is the mean potential of each atom on other wave functions, the last the overlap repulsion term which we know predominates for filled-shell situations. The degree to which it predominates may be estimated by approximating φ_n by an exponential $e^{-\kappa r}$. It is easy to show that the last term is approximately of order (κR) relative to the second, because the integrand of S extends over the volume between the atoms with roughly constant value, whereas $V_m(r)$ falls off rapidly with distance at a rate $\sim \kappa$ or faster. (We assume that long-range Coulomb potentials are either absent or treated separately.) Thus in the limit of well-separated atoms repulsion dominates.

Thus the situation is not quite the same as for the metallic pseudopotential where the two terms roughly cancel; the repulsive term here can predominate. However, we shall see that the actual effect on the wave function is very small; in determining the wave function the usual "cancellation theorem" holds.[11]

Because of the form of the pseudopotential, the equation contains an intrinsically small term and may be solved by perturbation theory based on the atomic eigenfunctions and eigenvalues. That is, the pseudopotential is finite only where V_m or φ_m are finite, and thus acting on a localized function φ_n at n its effect is intrinsically small. The pseudopotential depends on the functions φ_m which we are to calculate. Thus the computation procedure is intrinsically a self-consistent iteration, in which one approximates φ_m by $\varphi_m{}^0$, the unperturbed atomic function, in the pseudopotential equation for φ_n; this enters only a small term, so including the perturbation on $\varphi_m{}^0$ should have little effect, etc. The convergence of this procedure is quite fast, as we shall show; in practice probably no iteration is actually necessary.

This self-consistency feature is the new feature of our method relative to previous pseudopotential methods. They in general are concerned with core functions which do not change in bonded situations; in principle of course they too are to be found self-consistently but the perturbation there is so negligible it has not been previously noticed. It is the fact that this self-consistency can be handled even here by perturbation methods which now allows us to reduce molecular chemistry to perturbation theory starting from atomic orbitals, as those methods have reduced metallic chemistry to perturbation theory starting from plane waves.

We will not discuss here the more complicated procedures which are necessary in case φ_n is a bond function (as for σ bonds) not an atomic one.

III. COMPUTATIONAL METHOD AND RESULTS

Let us then consider π electrons on a ring or infinite chain of carbon atoms. Here every V_n, φ_n, and E is the same, and the eigenfunctions

$$\psi_i = \sum_n e^{i\vec{k}\cdot\vec{n}} \varphi_n(r)$$

have eigenenergies

$$E_k = E + \sum_m e^{i\vec{k}\cdot(\vec{n}-\vec{m})}(n|V_m|m) .$$

What we hope to do is to calculate φ_n and E by solving the pseudopotential equation

$$\mathcal{H}^n \varphi_n = E\varphi_n;$$

and thus to calculate $(n|V|n+1)$, which is the Hückel parameter, as well as E, the mean energy of the π band. The equation to be solved, then is (let $n = 0$ for simplicity)

$$E\varphi_0(r) = [T + V_0(r)]\varphi_0(r) + V_{ps}\varphi_0 , \qquad (12)$$

where

$$V_{ps}\varphi_0 = \sum_m \left[V_m(r)\varphi_0(r) - \int V_m \varphi_0 \varphi_m d^3r' \times \varphi_m(r) \right] . \qquad (13)$$

This term is small, we argue, both because V_m is centered at another atom, and because the two parts roughly cancel. Thus it is correct to treat $(V_{ps}\varphi_0)$ as a perturbation, so we do perturbation theory using the eigenfunctions of $(T + V_0)$ – the atomic eigenfunctions – as an unperturbed theory. We set $\varphi_m = \varphi_m{}^0$, the appropriate atomic eigenfunction, in the perturbation term. Having made that assumption, our scheme is to solve the resulting linear equation for φ_0. That solution might then have to be corrected by reinserting the correction to $\varphi_m{}^0$ on the right, etc.; in fact far from the atoms such corrections are probably not terribly small. But the parameters are all determined by behavior near the atoms, where actual computation will show the corrections are indeed very small. Let us carry out the whole computation schematically in order to sort out what is essential, and then do a very rough sample calculation to demonstrate that corrections are indeed small.

Write

$$\varphi_0 = \varphi_0{}^0 + \delta\varphi_0, \quad \varphi_m = \varphi_m{}^0 + \delta\varphi_m, \tag{14}$$

where $$\delta\varphi_0 = \sum_{j\neq 0} \alpha_j \varphi_0^j \tag{15}$$

j labels the different eigenstates of the atomic potential. Thus $\delta\varphi$ is orthogonal to φ; and to first order in $\delta\varphi$ we may neglect all normalization corrections, in which case the contributions of all neighbors are additive, and we may treat them one at a time. The workability of the method depends on the fact that V_m is chosen to be reasonably well localized near atom m. Any long-range potentials such as Madelung terms should, as stated below (3), be left in the unperturbed part of $\mathcal{H}$, "T". Then the perturbation $\delta\varphi_0$ due to $V_{ps}{}^m$ is localized near m, also, and we see that terms in $\delta\varphi_m$ are unimportant because $\delta\varphi_m$ is localized away from V_m. For instance, the most important correction is that to the Hückel parameter:

$$\begin{aligned}(m|V_m|0) &= \int \varphi_m{}^0 \varphi_0{}^0 V_m \\ &\quad + \int \varphi_m{}^0 \delta\varphi_0 V_m + \int \delta\varphi_m V_m \varphi_0{}^0 , \\ &\simeq \int \varphi_m{}^0 \varphi_0{}^0 V_m + \int \varphi_m{}^0 \delta\varphi_0 V_m , \\ &= V_{m0}{}^0 + \delta V_{m0} . \end{aligned} \tag{16}$$

It is δV_{m0} we use as a measure of the perturbation; note that it is an average of $V_m \delta\varphi_0$, which is the non-negligible first-order effect in the first term of the pseudopotential.

Also resolving $V_{ps}\varphi_0$ into components according to the atomic potential eigenstates

$$V_{ps}\varphi_0{}^0 = \beta_0 \varphi_0{}^0 + \sum_{j\neq 0} \beta_j \varphi_0^j , \tag{17}$$

we see that our first-order estimate of $\delta\varphi_0$ is

$$\delta\varphi_0 = \sum_{j\neq 0} \varphi_0^j \frac{\beta_j}{E - E_j} ,$$

$$\begin{aligned}\delta\varphi_0(r) &= \sum_{j\neq 0} \frac{\varphi_0^j(r)}{E - E_j} \\ &\quad \times \int d^3r' \, \varphi_0^j(r') [V_{ps}\varphi_0{}^0(r')] \\ &= \int G_0{}^0(r, r') d^3r' [V_{ps}\varphi_0{}^0(r')] . \end{aligned} \tag{18}$$

Here $G_0{}^0$ is the "Green's function" of the Hamiltonian $T + V_0$ with the state $\varphi_0{}^0$ projected out of it:

$$G_0{}^0(r, r') = \sum_{j\neq 0} \frac{\varphi_0^j(r)\varphi_0^j(r')}{E - E_j} . \tag{19}$$

Our actual calculation depends on the well-known fact that outside of the core region of the atom the wave functions and energies for the single free-atom problem can be approximated extremely well by plane waves, so that for the corrections near atom m we can simply use the plane wave G

$$\begin{aligned} G_0{}^0 \simeq G^{\text{free}} &= -(4\pi)^{-1} e^{-\kappa|r - r'|} / |r - r'| \\ &= -\sum_k e^{i\vec{k}\cdot(\vec{r} - \vec{r}\,')} / (k^2 + \kappa^2) , \end{aligned} \tag{20}$$

where $\kappa^2 = -E$. To very high accuracy, (19) could be approximated by orthogonalizing G^{free} to $\varphi_0{}^0$. but that degree of accuracy is unnecessary here and we use (20). Thus our final expression for $\delta\varphi_0$ is

$$\begin{aligned}\delta\varphi_0(r) &= -(\kappa/4\pi) \int d^3r' \left(e^{-\kappa|r - r'|} / |r - r'|\right) \\ &\quad \times \sum_m [V_m(r')\varphi_0{}^0(r) - V_{m0}\varphi_m{}^0(r')] . \end{aligned} \tag{21}$$

We now outline the specific calculation we carried out, which was meant to apply to the case of benzene and similar aromatic ring molecules. Simple Slater orbitals were used for the π electrons:

$$\varphi_m{}^0 = Nz \exp[-1.625(r - R_m)] , \tag{22}$$

where z is the coordinate perpendicular to the molecular plane. For V_m we used the core Coulomb potential screened a la Hartree and including exchange and correlation corrections as discussed in the introduction (the Wigner approximation). That is the effective potential V_m, which is the change in potential relative to V_n which an electron in φ_n sees, is the fully (4-electron) screened V_m when the electron is near atom n, but

$$\begin{aligned} V_m = \tfrac{3}{4} (V_{\text{screened}}) + e^2/r \\ - (\text{exchange-correlation hole on atom } n) \end{aligned}$$

when the electron is on atom m, which is to say for virtually the whole of all integrals we do. Using this potential,

$$V_{0m}{}^0 = \beta^0 = -0.177 \text{ Ry} = -2.43 \text{ eV} \tag{23}$$

at $R = 1.40$ Å.

$\delta\varphi_0$ could be easily programmed by expanding G^{free} in spherical harmonics, as well as φ^0, using the standard spherical Bessel function series for imaginary argument:

$$G^{\text{free}}(r,r') = -\kappa \sum_l (2l+1) j_l(i\kappa r) \times h_l(i\kappa r') P_l(\cos\theta). \tag{24}$$

Only the $l=1$ term is of interest in the calculation of energies in this problem. In Fig. (1) we plot the coefficient of $\cos\theta$ as a function of $|r-R_m|$ for φ^0 and $\delta\varphi^0$. This graph demonstrates both the fact that the wave-function correction is not entirely negligible, and the tendency for it to be small and change sign. It is interesting also to plot (in Fig. 2) the pseudopotential term ($V\varphi_0{}^0 - V_{12}\varphi_m{}^0$), which demonstrates the cancellation also. The total computing time necessary for Figs. 1 and 2 was less than 1 min. Two different energies E, 0.9 and 1.0 Ry, were used in G_0 to check that these results are not fortuitous.

Integrating (22) against the potential to get δV_{0m} as defined in (17) is a mistake, because this is very sensitive to whether $\varphi_m{}^0$ is an exact eigenfunction of the assumed potential. Instead, we transform V to an insensitive form; here as everywhere in this method the trick in achieving accuracy is to avoid doing one-center integrals where possible, because these are very sensitive to small errors. (For the derivation I am indebted to E. I. Blount.) We write the pseudopotential equation for φ_0

$$(T+V_0+\textstyle\sum'_m V_m - E)(\varphi_0+\delta\varphi_0) = \sum_m V_{0m}(\varphi_m+\delta\varphi_m). \tag{25}$$

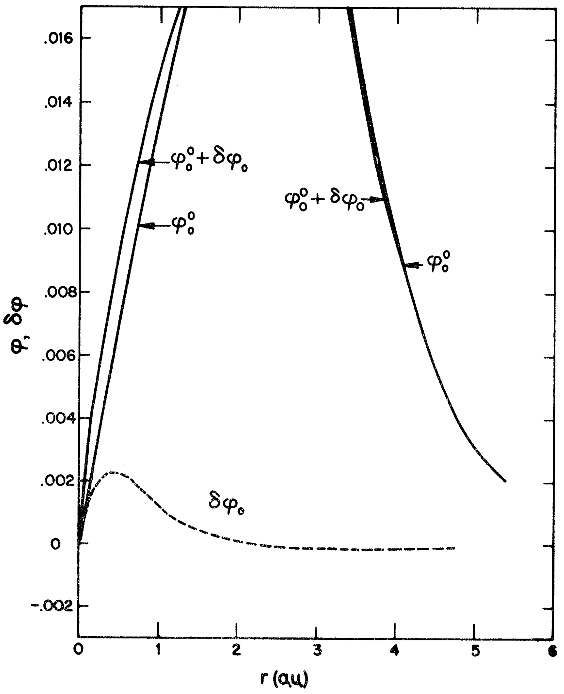

FIG. 1. The unperturbed Slater orbital $\varphi_0{}^0$ near the neighbor atom (spherical average of coefficient of $\cos\theta$) and the first-order correction $\delta\varphi_0$, compared.

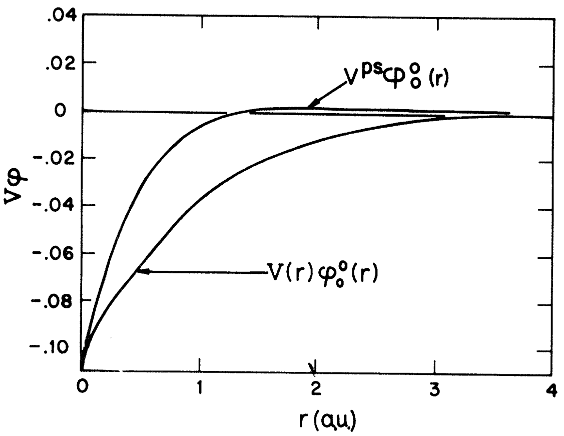

FIG. 2. The true potential of the neighboring atom, acting on $\varphi_0{}^0$, and the pseudopotential compared. In both cases the region of sign change near ~1.8 a.u. is heavily weighted.

Now we multiply by $\varphi_m{}^0$ and integrate. We assume normalization such that the coefficient α_0 is unity, and using the fact that $\delta\varphi$ is orthogonal to φ^0 and assuming the different neighbors m do not overlap each other appreciably, we get

$$\int \varphi_m{}^0 (T+V_0+V_m-E)(\varphi_0{}^0+\delta\varphi_0) = V_{0m}. \tag{26}$$

Using the fact that $\varphi_m{}^0$ is an eigenvalue of $T+V_m$, this may be written

$$(E_m{}^0-E)\left(S_{m0}{}^0+\int\varphi_m{}^0\delta\varphi_0\right)+\int\varphi_m{}^0 V_0\delta\varphi_0 = (\delta V)_{0m}. \tag{27}$$

The major term on the left is the unperturbed atomic overlap integral term; both the others were computed and found to be less than 0.01 eV. For instance, the overlap was computed to be $S_m{}^0 \simeq 0.218$, the correction to this due to $\delta\varphi$ being $\delta S = 0.0027$. Because there are two neighbors,

$$\begin{aligned} E_m{}^0 - E &= 2\left(-S_{m0}V_{m0}{}^0+\int\varphi_0{}^0 V_m\varphi_0{}^0\right) \\ &= 2\,(0.039-0.038) \end{aligned} \tag{28}$$

and the net correction is negligible for either value of E. Thus the LCAO wave functions give extraordinarily accurate parameter values if properly used; the final result of our refined procedures is to show conclusively that they were unnecessary in this case.

IV. CONCLUSIONS

The purpose of this paper has been to justify, rather than to recompute the parameters for, the Hückel method, which has been very successful in understanding the electronic structure of π-bonded molecules. In every case our prescriptions for calculation of physical parameters – bond orders, wave functions, etc., – would be identical with those already being used, and which work.

Our energy shift was rather small, and our Hückel parameter agrees with present estimates. That is a bit surprising; the "Hückel band" is comparable in width with the d band of transition metals, where "mass renormalizations," due to Coulomb effects, of 1.5 are not unheard of, and we would expect similar changes here. But the situation with regard to experimental comparison is quite different: the semiempirical value of β[6] comes from a Goeppert-Mayer-Sklar configuration interaction treatment for the excited states, which is already perhaps as good as a random phase approximation (RPA) treatment of correlation – i.e., we are not simply comparing with the lowest one-electron excitation but with the centroid of the whole singly excited configuration. For the moment, the point here is that the one-electron result is essentially exact and that, therefore, we can arrive at a fairly precise empirical estimate of the effect of higher correlations on β. It is clear that the large effects estimated by Linderberg[12] cannot be correct.

The one approximation we have made which requires discussion is the "Wigner" approximation of using a potential including an exchange and correlation hole of one full electron, which means the potential is slightly more attractive than a Hartree-Fock SCF would be, i.e., slightly over correlated if anything. This is in the opposite direction from any discrepancy from Linderberg and Öhrn, but is I suspect the reason for the good experimental agreement, since the potential makes good physical sense.

As for actually doing the correlation problem, the usual argument for "neglect of differential overlap" which makes it manageable and seems to work reasonably well rests on using Wannier (orthogonalized) functions to calculate Coulomb integrals; then the overlap charge $\varphi_i\varphi_j$ is a rapidly varying, though not small, quantity, and the integrals do tend to be small. In spite of the fact that our pseudopotential equation is for highly localized nonorthogonal functions, the secular equation – which is quite distinct in principle – is that appropriate to orthogonalized, Wannier functions. Thus it is in fact correct to insert interaction terms appropriate to Wannier functions: the true Hamiltonian is

$$\mathcal{H}=\sum_{n} E_n N_n + \sum_{n,m} V_{nm} C_n{}^* C_m + \sum_{nmlp} (nm\,|\,lp)\, C_n{}^* C_m{}^* C_l C_p \,,$$

where $(nm\,|\,lp)$ are calculated with orthogonalized functions.

It is clear that we can go ahead to do similar calculations for heteropolar systems, getting one-electron α values, for instance, and so on through the whole apparatus of the Hückel theory. Spin densities and effects on structure and spectra must await further improvements: correlation, especially, and a good treatment of the σ bonds, which last is now in progress.

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[1] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1960), 3rd ed., Chap. 4.

[2] It has already been pointed out by W. H. Adams, J. Chem. Phys. 37, 2009 (1962), and T. L. Gilbert, Molecular Orbitals, a Tribute to Mulliken, edited by P. O. Lowdin and B. Pullman (Academic Press Inc., New York, 1964), that saturated valence bonds can be described in terms of a set of localized orbitals which are the solutions of a pseudo-wave-equation.

[3] Some typical papers are collected in R. G. Parr, Quantum Theory of Molecular Electronic Structure (W. A. Benjamin, Inc., New York, 1963). See also Ref. 12.

[4] K. Rudenberg, J. Chem. Phys. 34, 1861 (1961).

[5] Since preparation of this article, my attention has been called to an unpublished note by T. L. Gilbert (to appear in the "Proceedings of the Yale Conference on Orbitals," edited by O. Sinanoğlu) in which the techniques of Ref. 2 are applied formally to the Hückel theory. There is some overlap between those ideas and the present ones, although numerical calculations to check the vital question of the size of the wave function distortion are not attempted there, and as explained in Ref. 9 the methods are by no means identical.

[6] K. Rudenberg, J. Chem. Phys. 34, 1897 (1961).

[7] See R. G. Parr, Ref. 3, Sec. 10.

[8] See, e.g., B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962); W. A. Harrison, Pseudopotentials (W. A. Benjamin, Inc., New York, 1966).

[9] P. W. Anderson, Phys. Rev. Letters 21, 13 (1968).

[10] C. Edmiston and K. Rudenberg, Rev. Mod. Phys. 35, 457 (1963).

[11] M. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

[12] J. Linderberg and Y. Öhrn, Proc. Roy. Soc. (London) A285, 445 (1965); Phys. Rev. 139, A1063 (1965).

PHYSICAL REVIEW VOLUME 181, NUMBER 1 5 MAY 1969

Transition Operators in Radiative Damping Theory

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(Received 18 November 1968)

The application of transition operators $\mathcal{P}_{m,m'}(t) = \exp(iHt)\,|m\rangle\langle m'|\exp(-iHt)$ is studied for the problem of an atomic system S with eigenstates $\{m\}$ interacting with one or more damping reservoirs R. The average value of these operators gives the reduced density matrix $\rho_{m',m}{}^{(S)}(t)$ for S. If R consists of broad-band distributions of harmonic oscillators, (e.g., radiative damping), then damped equations of motion can be derived for all $\mathcal{P}_{m,m'}(t)$, even if S is a multilevel system. One need not specify the initial states of R, nor restrict the treatment to second order in the S-R coupling. The formalism is illustrated for the case where S consists of (i) a four-level atom in a resonant cavity (with broad-band modes also present), and (ii) a collection of atoms that can be treated as a multilevel spin system. Density-matrix equations are obtained for the case where no damping radiation is present initially. In (ii), the formalism is used to derive a two-time correlation function without the aid of the fluctuation-regression theorem.

I. INTRODUCTION

Dissipation is ordinarily treated quantum mechanically by coupling the appropriate atomic or spin system S to a loss mechanism or damping reservoir R. Most treatments assume that (i) R has a broad continuum of modes coupled more or less uniformly to S; (ii) the initial density operator can be written as $\rho^{(S)}(0)\rho^{(R)}(0)$, where $\rho^{(S)}(0)$ describes the initial states of S, and $\rho^{(R)}(0)$ is a thermal equilibrium distribution for R; (iii) R is only slightly affected by its interaction with S. The usual procedure is to write equations of motion for the reduced density operator $\rho^{(S)}(t)$[1,2] (or for reservoir-averaged amplitude operators[3]) to second order in the coupling constant. Assumption (iii) is then implemented by an approximation equivalent to replacing the actual density operator $\rho(t')$ in the second-order terms by the factored expression $\rho^{(S)}(t')\rho^{(R)}(0)$.

If R is a collection of harmonic oscillators, then one can derive damped equations of motion for the amplitude operators of S, without explicitly using assumptions (ii) or (iii). Only the unperturbed reservoir coordinates appear in these equations, the perturbation due to S being entirely absorbed in the damping constant and frequency shift. (A well-known example of this would be the case where S is itself a harmonic oscillator.[4]) If similar damped equations could be derived for the reduced density-matrix elements of a multilevel atom, it would provide a convenient and nearly exact starting point for studying its interaction with a known radiation field. These can, in principle, be obtained from the amplitude operator equations[5,6]; however, the procedure is rather tedious to apply to multilevel atoms.

In this article, we define a set of operators that enable one to obtain the reduced density-matrix equations by a straightforward, yet rigorous, derivation. Two examples will be presented. In the first, the system S consists of a four-level atom in a resonant cavity; in the second, S is a collection of atoms that can be treated as a multilevel spin system. We show in the second example that the formalism can be used to calculate two time correlation functions, without using the fluctuation-regression theorem[6–8] required in an ordinary density operator treatment.

If H and $\rho(t)$ are the complete Hamiltonian and density operator, respectively, and S is described by basis states $|m\rangle$, then the components of the reduced density operator can be written as