METHOD OF CALCULATING MOLECULAR WAVE FUNCTIONS AND BINDING ENERGIES

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A technique for adapting the quantum defect method to symmetrical diatomic molecules is derived and applied to Li_2 with reasonable success.

Methods of calculating electronic wave functions and energies in solids, especially metals, are more highly developed and more successful than those used in the harder problem of molecules. Perhaps the most important components of this success have been, first, the use of wave functions which are approximate eigenfunctions of the Hamiltonian in all parts of space, internal and external to the atoms; and second, the use of unperturbed, spherically symmetric potentials in the core regions, the properties of which can often be accurately inferred—or, in the case of the quantum defect method, avoided entirely—by the use of atomic term values.[1] We present here the first use of such a method for molecular problems, specifically a method based on the quantum defect method[2] and applicable to symmetrical diatomic, monovalent molecules (we do Li_2).

Our approximation to the potential is an adaptation of that of Wigner and Seitz.[3] We divide space symmetrically into two halves, with one atom in each. When the electron under consideration is in the left half, we assume that the other electron is spherically arranged about the right-hand atom and screens it perfectly, so that the potential is just the spherically symmetrical potential of the left-hand atom. Thus the potential is spherically symmetric in each half-space but has a discontinuous gradient at the boundary plane. The experience of Wigner and Seitz and later authors is that this approximation to the correlation is quite good in metals; since in molecules correlation effects are smaller, we expect to overestimate them somewhat. We emphasize that at large r the assumption becomes exact, especially near the boundary plane.

The exact wave function in each half-space may be written

$$\psi(r,\theta,\varphi)=\frac{1}{r}\sum_{l,m} Y_{lm}(\theta,\varphi)A_{lm}U_l(r), \tag{1}$$

where Y_{lm} is a spherical harmonic and U_l is the radial wave function satisfying

$$\frac{d^2U_l}{dr^2}+\left(E-V(r)-\frac{l(l+1)}{r^2}\right)U_l=0. \tag{2}$$

We specialize to the σ wave function with $m=0$. The coefficients $A_{lm}=A_l\delta(m,0)$ must be chosen to satisfy the boundary conditions $\psi(r\to\infty)\to 0$ and $d\psi/dn=0$ at the boundary plane.

The surprising thing about the method is that the former boundary condition supplies a very great deal of information about the wave function. At any energy not an eigenvalue for that particular l,

$$U_l(r)\sim C_l(E)(r/n)^{-n}e^{(r/n)} \times [1+O(1/r)+\cdots] \tag{3}$$

where $1/n^2=-E$. We define C_l by (3); its value is available from the quantum defect method.[2] It goes through zero at an energy eigenvalue for the relevant l. Since the molecular orbital energy will seldom be an eigenvalue, and never for all l, most of the components of (1) explode rapidly as $r\to\infty$. The only way to satisfy the boundary condition then, is to make

$$f(\cos\theta)=\sum_l C_l(E)P_l(\cos\theta)A_l=0 \tag{4}$$

<u>for all</u> $-1\leq\cos\theta\leq 0$. But even more information can be gained by studying the boundary plane. On this plane,

$$r\cong R/\cos\theta,$$

where R is $\frac{1}{2}$ the internuclear distance. Only if

$$f(\cos\theta)\sim\exp\left(-\frac{2R}{n\cos\theta}\right) \quad \text{as } \cos\theta\to 0 \tag{5}$$

will the wave function converge sufficiently rapidly along this plane. (A weaker condition, that all derivatives of f vanish at $\cos\theta=0$, is obtained by the requirement that <u>all</u> exponentially growing terms of the asymptotic series vanish.) This suggests attempting to match the boundary conditions along this plane with a function in which the coefficients A_l are determined by (5); more generally, we could attempt a Laurent expansion of $f(\cos\theta)$ in terms of functions all of which satisfy (5), e.g.,

$$f_0 = \exp\left(-\frac{2R}{n\cos\theta}\right);$$

$$f_1 = \frac{1}{\cos\theta}\exp\left(-\frac{2R}{n\cos\theta}\right); \cdots. \qquad (6)$$

The coefficients of as many of these functions will be determined as we place conditions at the boundary plane. [We reject discontinuous functions for f because the spherical harmonic series (1) would then converge slowly.] For the present, we have used only the condition at the central point of the boundary plane and assumed that only the component f_0 is present:

$$\sum_l A_l \frac{d}{dr}\left[\frac{1}{r}U_l(r)\right]\bigg|_R = 0, \qquad (7)$$

$$\sum_l C_l(E)P_l(\cos\theta)A_l$$

$$= \exp\left[-\frac{2R}{n}\left(\frac{1}{\cos\theta}-1\right)\right], \quad \cos\theta > 0,$$

$$= 0, \quad \cos\theta < 0, \qquad (8)$$

The wave functions U_l and the coefficients C_l of the asymptotic expansion are fortunately available from the mathematical apparatus of the quantum defect method[2]: C_l explicitly in terms of the quantum defects ν_l,

$$C_l(E) = -\frac{1}{\pi n^l}\Gamma(n+l)\sin\pi(n-l+\nu_l), \qquad (9)$$

and

$$U_l(r) = -\frac{\Gamma(n+l+1)}{n^{2l+1}\Gamma(n-l)}\cos(\pi\nu_l)\,{}^0U^l(r,E)$$

$$+ \sin(\pi\nu_l)\,{}^1U^l(r,E) \qquad (10)$$

in terms of the functions ${}^0U^l$ and ${}^1U^l$ tabulated by Blume, Briggs, and Brooks.[4] Equation (10), of course, uses the standard assumption of the quantum defect method that there exists a radius R_c outside of which the potential is purely Coulombic, and which is less than R, so that for $r > R_c$ the Coulomb wave functions with quantum defect ν_l are valid. Ham's paper[2] gives interpolation formulas for the ν_l as a function of energy for all alkalies.

Our preliminary calculation for Li_2 at a radius $2R = 5.00$ close to the equilibrium value 5.05 gives an energy for the molecular orbital of −0.486 Ry as compared to −0.396 in the free atom. The resulting binding energy for the molecule is 2.44 eV as compared to the experimental 1.14 eV. In the metal an accurate calculation of the net Coulomb, exchange, and correlation corrections to the Wigner-Seitz scheme leads to a correction of +0.125 eV per electron, which would give 2.19 eV binding energy; but that is very much too low for the molecule. If we assume, as is usual, that the correlation correction in the molecule is $\frac{1}{2}$ to $\frac{3}{4}$ of that in the metal, we get a binding energy of 1 to 1.5 eV which is in excellent agreement with experiment. It is hard to see how to avoid overcorrelating with this method, but Li_2 is probably the worst possible case; and in any case there is no reason why correlation corrections should be more difficult than in other Wigner-Seitz calculations. A very rough preliminary calculation gives about 0.7 eV binding energy.

The details of our wave function may be summarized by giving the "asymptotic" and "boundary condition" or "bonding" contributions of each angular momentum, i.e., the contribution C_lA_l of each to the asymptotic behavior [using (3) and (8)] and to the derivative of the wave function [the l'th term of (7)]:

l	Asymptotic (C_lA_l)	Bonding $\left[A_l\frac{d}{dr}\left(\frac{U_l}{r}\right)\right]$
0	0.191	0.095
1	0.170	−0.015
2	0.110	−0.054
3	0.075	−0.026

Note that a very appreciable contribution is made by d and f states, though we believe $l = 4$ will be truly negligible in its effect on the boundary condition, since $l \geq 4$ electrons do not penetrate the centrifugal barrier. The last column of the table illustrates the importance to the phenomenon of chemical bonding of $l > 1$ states even for first-row elements. This possibility has been occasionally mentioned in the chemical literature.

This preliminary calculation, accurate as it is, was carried out rather easily by hand in a few hours. Plots of the resulting wave function, and improvements on it by fitting over a larger region of the boundary plane, would require simple machine work and extensive use of Ham's numerical algorithms and tables for Coulomb functions, but are very much simpler and more transparent than direct methods for the corresponding problems. More important, however, are the many avenues for generalization which are opened up by it, as well as the fact that for the first time a wave function accurate in all regions of space, and especially in regions exterior to the bonded atoms, is available with little effort for a molecular valence bond.

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[1] These are the common features of the orthogonalized plane-wave method and its descendants (including the augmented plane wave), the Korringa-Kohn-Rostoker method, and the quantum defect method and its ancestor, the cellular method. The two former use plane waves fitted to match realistic wave functions in the atom cores, the two latter Coulomb functions. A good review of the older literature on these methods is given by John R. Reitz, Solid State Phys. 1, 2 (1955), and of later work by W. A. Harrison, Pseudopotentials (W. A. Benjamin, Inc., New York, 1966).

[2] The most complete article, with references to all early work, is that of F. S. Ham, Solid State Phys. 1, 127 (1955). We also draw on formulas quoted in F. S. Ham, U. S. Office of Naval Research Technical Report No 204, September, 1955 (unpublished).

[3] E. P. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

[4] M. Blume, N. Briggs, and H. Brooks, U. S. Office of Naval Research Technical Report No. 260, 1959 (unpublished). These functions are equal numerically to $z/2$ times the functions (J) and (N) used in the older work following Wannier.

SOME EFFECTS OF QUANTIZATION OF INTERNAL ROTATION ON SPIN-LATTICE RELAXATION AND HYPERFINE STRUCTURE*

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The temperature dependence of the spin-lattice relaxation time of the oriented H_3C-$\dot{C}R_1R_2$ radical in x-irradiated single crystals of acetyl-(d,l)-alanine has been observed to be dominated by "spin-flip" transitions between the rotational states of the methyl group. The energy separation of these levels has been confirmed by an analysis of the ESR spectra of the radical. The low-temperature ESR spectra show quantum effects also not previously observed.

Several papers have appeared recently both on the effects of rotations on spin-lattice relaxation and on hyperfine structure.[1-6] In most cases, rotations in magnetic resonance have been treated "semiclassically" using a classical Brownian diffusion model for the rotational motion while treating the spins quantum mechanically as in the pioneering work of Bloembergen, Purcell, and Pound.[7] This Letter is to report what we believe to be the first observed case in which the effects of quantization of the rotational motion dominate the electron spin-lattice relaxation, as well as the first observation of some effects of the quantization of the rotational motion of the ESR spectra.

Both the spin-lattice relaxation time (T_1) and the ESR spectra of the H_3C-$\dot{C}R_1R_2$ radical[8] in x-irradiated single crystals of acetyl-(d,l)-alanine as well as the T_1 of the H_3C-$\dot{C}HR$ radical[6] in x-irradiated single crystals of l-alanine were observed at 9 kMc/sec as a function of T from 1.2 to 300°K. R, R_1, and R_2 denote the remaining groups of the molecules. They make no significant contribution to the hyperfine structure. The T_1's were measured by observation of recovery from pulsed saturation.

In Fig. 1, second-derivative traces of the ESR spectrum of H_3C-$\dot{C}R_1R_2$ are shown for several values of the temperature (T). As can be seen, the spectrum consists of four lines of intensity ratio 1:3:3:1 at high temperatures and of seven equally spaced lines at low temperatures. One can account for this by assuming either of the following: (1) that the magnitudes of the three proton coupling constants have the ratios 1:2:3, and are tunneling or rotating sufficiently slowly at low temperatures so as to be distinguishable, or (2) that the ro-