

SCATTERING MODEL OF MOLECULAR ELECTRONIC STRUCTURE*

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A multiple-scattering model for calculating molecular orbitals has been applied with reasonable success to several elementary diatomic molecules. These results, together with the flexibility and computational simplicity of the model, suggest that it will be a practical new approach to the theoretical electronic structures of complex, polyatomic molecules.

Recently there has been some interest expressed in adapting certain methods of theoretical solid-state physics to the theory of the chemical bond. For example, Anderson¹ has discussed the application of the quantum-defect method to the molecular-orbital theory of simple diatomic molecules, and Phillips² has proposed an *a posteriori* dielectric model of covalent bonding, based, in part, on pseudopotential formalism. In previous papers by one of the authors (K.H.J.),^{3,4} it has been shown how a multiple-scattering model, similar in many respects to the scattering method of energy band theory,⁵⁻⁷ can be developed for the calculation of the bound one-electron orbitals of molecules. Even earlier suggestions that such a theoretical approach to molecules might be useful can be found in the literature.⁸⁻¹⁰ We feel that the calculation technique proposed in Refs. 3 and 4 is particularly well suited for the molecular-orbital theory of polyatomic molecules where more conventional methods based on linear combinations of atomic orbitals (LCAO methods)¹¹ are difficult and costly to implement. The present method leads to an exact solution of a model Hartree-Fock (HF) Hamiltonian for molecules of arbitrary stereochemical structure, without further approximation and without undue computational effort. This Hamiltonian is based on the partitioning of molecule space into regions of average potential, including a local approximation to the exchange potential. The possible adoption of such a potential for the theory of polyatomic molecules was first suggested by Slater.¹⁰ There are no multicenter integrals to compute or to estimate, as there are in LCAO methods.

So that we can more quantitatively assess the potentialities of the scattering approach, as well as its limitations, we have carried out preliminary calculations on several elementary diatom-

ic molecules, including the hydrogen molecular ion (H_2^+), carbon (C_2), and lithium hydride (LiH). These systems are a critical test of the model because it is least appropriate for small molecules. H_2^+ , C_2 , and LiH also exemplify types of chemical bonding (molecular-ionic, covalent, and covalent-charge-transfer) found in more complex molecules. LCAO methods are relatively easy to apply to these diatomics, and the results of several such calculations can be found in the literature for comparison. In the case of H_2^+ , the exact solutions are available.

To illustrate how the scattering model is set up, we first consider the case of H_2^+ . The partitioning of molecule space into three basic regions is shown in Fig. 1. The H_2^+ potential is expanded in spherical harmonics around each atomic site and with respect to the center of the molecule. Within each atomic or "inner" sphere (I) and in region III beyond the periphery of the "outer" sphere (II), the model potential is taken to be the first (spherically averaged) term of the corresponding expansion. These potentials there-

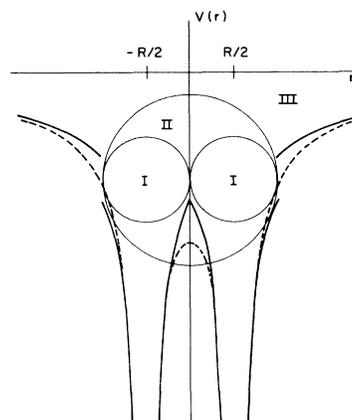


FIG. 1. Comparison of the model potential (solid curves) with the true potential (dashed curves) for H_2^+ .

fore include a large portion of the true overlapping potentials in regions I and III. For H_2^+ the averages can be represented in Rydberg units as

$$V_I(r) = -2/r - 1/R_I, \quad r < R_I; \quad (1)$$

$$V_{III}(r) = -4/r, \quad r > R_{II}. \quad (2)$$

The intersphere potential V_{II} is taken to be a constant. In general, V_{II} and the sphere radii R_I and R_{II} will be adjustable parameters. We have chosen the particular values, V_{II} equal to the average value of the potential over the intersphere region, $R_{II} = R$ (the internuclear distance), and $R_I = \frac{1}{2}R$.

The one-electron wave functions for region II are expanded in three-center, partial-wave solutions of the ordinary stationary wave equation containing the energy parameter E . In regions I and III we expand in partial-wave solutions of the stationary Schrödinger equation for potentials (1) and (2), respectively, and as a function of E . The radial parts of these solutions must be finite near the origin of each atomic sphere, and they should decay exponentially in region III at large distance from the molecule. They are generated by numerically integrating the radial Schrödinger equation outward and inward, respectively, for potentials (1) and (2) and for each trial value of E . The wave functions and their first derivatives are required to be continuous at the sphere radii. This is accomplished via the scattering formalism of Refs. 3 and 4. The "amplitude" of scattering at each sphere j ($j = 1, 2, 3$) for each partial wave l of energy E is described by a quantity $T_l^j(E)$, which, in turn, can be written in terms of the radial function and its first derivative at the sphere radius R_j . The "propagation" of the

partial waves within the intersphere region II is described by matrix elements, $G_{ll'}^{jj'}(R; E)$, of an appropriate single-particle Green's function. These quantities are structure factors in the sense that, other than their dependence on E , they are functions only of the internuclear distance R . The one-electron energies are given by zeros of the determinant

$$|\delta_{jj'} \delta_{ll'} [T_l^j(E)]^{-1} - G_{ll'}^{jj'}(R; E)|. \quad (3)$$

We have set up the above determinant in double precision for the occupied and first few excited states of H_2^+ at the exact equilibrium internuclear distance $R = 2$ a.u. Exploiting the symmetry of the molecule, we have found that only one partial wave ($l = 0$ or $l = 1$) per atom and two partial waves ($l = 0, 2$ or $l = 1, 3$) for region III are required for convergence of the energies. This leads to 4×4 determinants, which require only a small amount of time to evaluate on a conventional electronic computer. The resulting energy levels are listed in Table I, along with the exact energies obtained by Bates, Ledsham, and Stewart¹² for the H_2^+ problem separated in spheroidal coordinates. Although not of chemical accuracy, the agreement with the exact results is reasonably good. Another critical test of the scattering model is to determine the variation of the sum of the electronic and internuclear repulsive energies with internuclear distance. We have therefore calculated the ground-state $1\sigma_g$ and the first excited level $1\sigma_u$ over a wide range of R . The "attractive" nature of the $1\sigma_g$ energy profile as a function of R is clearly reproduced by the scattering approach, with a minimum at 2.2 a.u. (close to the exact equilibrium value, $R = 2.0$

Table I. Lowest electronic energy levels of H_2^+ for the equilibrium internuclear distance $R = 2$ a.u.

Energy state	Scattering-model	Exact ^a	Energy state	Scattering-model	Exact ^a
	E (Ry)	E (Ry)		E (Ry)	E (Ry)
$1\sigma_g$	-2.0716	-2.205 25	$1\sigma_u$	-1.2868	-1.335 07
$2\sigma_g$	-0.707 38	-0.721 73	$2\sigma_u$	-0.497 22	-0.510 83
$3\sigma_g$	-0.455 74	-0.471 55	$3\sigma_u$	-0.269 79	-0.274 63
$4\sigma_g$	-0.348 59	-0.355 36	$4\sigma_u$	-0.249 97	-0.253 29
$1\pi_g$	-0.446 46	-0.453 40	$1\pi_u$	-0.888 66	-0.857 55

^aSee Ref. 12.

a.u.). The "repulsive" behavior of the $1\sigma_u$ state is also reproduced quite well by the model.

In the case of the molecule C_2 , we divide space in a fashion similar to that illustrated in Fig. 1 for H_2^+ . The model potential is now of the HF type, thus including an exchange contribution. In place of the full, nonlocal exchange, however, we adopt the approximate, local exchange potential proposed originally by Slater.¹³ This exchange has been used with considerable success in both atoms and solids. The electrostatic and exchange potentials have been generated by the alpha-expansion method¹⁴ from a superposition of Hartree-Fock-Slater (HFS) charge densities for the carbon atom.¹⁵ We have set up and evaluated a series of determinants of form (3) for the occupied one-electron energies of C_2 at the equilibrium internuclear distance $R = 2.3475$ a.u. These energies are compared with the results of a full self-consistent-field (SCF), HF-LCAO calculation¹⁶ in Table II. In view of the non-self-consistent nature of our preliminary calculations, the agreement with the SCF-LCAO energies is remarkably good.

The partitioning of space and potentials in the case of LiH is not as straightforward as it is for H_2^+ and C_2 , because it is a heteronuclear molecule. For these exploratory calculations, however, a possible choice of atomic sphere radii R_{Li} and R_H (consistent with our model for homonuclear diatomics) is one which sets the ratio R_{Li}/R_H equal to 5.8, the ratio of Slater's¹⁷ values for the atomic radii. With the sum of the radii equal to the approximate equilibrium internuclear distance $R = 3$ a.u., we arrive at the values $R_{Li} = 2.56$ a.u. and $R_H = 0.44$ a.u. The radius of the "outer" sphere is again chosen to be equal to R .

Table II. Occupied one-electron energy levels of C_2 for the internuclear distance $R = 2.3475$ a.u.

Energy state	Scattering-model	SCF-LCAO ^a
	E (Ry)	E (Ry)
$1\sigma_g$	-21.344	-22.6775
$1\sigma_u$	-21.341	-22.6739
$2\sigma_g$	- 1.5630	- 2.0567
$2\sigma_u$	- 0.826 26	- 0.9662
$1\pi_u$	- 0.859 06	- 0.8407

^aSee Ref. 16.

The model potential has been generated from a superposition of HFS free-atom charge densities,¹⁵ and the Slater¹³ exchange has been used. We have calculated the two occupied one-electron energy levels of LiH to be $E(1\sigma) = -4.3766$ Ry and $E(2\sigma) = -0.410 48$ Ry. The SCF-LCAO calculation of Ransil¹⁶ yielded corresponding orbital energies of $E(1\sigma) = -4.8514$ Ry and $E(2\sigma) = -0.5972$ Ry. An independent SCF-LCAO calculation by Karo¹⁸ gave $E(1\sigma) = -4.9590$ Ry and $E(2\sigma) = -0.6109$ Ry. Our results, while being of the right order of magnitude, do not compare as well with either of the SCF-LCAO results as they do in the example of C_2 . This is not unexpected, when we consider the rather arbitrary choice of sphere radii and the lack of self-consistency of our calculations. In heteronuclear diatomics such as LiH, there is a mixture of charge-transfer and covalent contributions to the chemical bond. We might just as arbitrarily have started with potentials based on the ions Li^+ and H^- , using the appropriate ionic sphere radii. In order to account more properly for charge-transfer effects in the scattering approach, it is necessary to carry out the calculations self-consistently within the framework of the HFS model Hamiltonian. Although we have not discussed, thus far, the actual computation of the one-electron wave functions, our preliminary studies indicate that the partial-wave orbitals obtained by the scattering technique should be an excellent starting point for an SCF calculation.

We have adopted an oversimplified physical model, in order to make practicable not just the molecular-orbital theory of simple diatomics, but also the quantitative theory of considerably more complex molecules. Before treating larger systems, however, further attention should be directed to the choice of exchange potential and to the effects of screening due to electron-electron correlation. Variants of the Slater¹³ exchange, which may better describe the one-electron behavior of atoms, molecules, and solids, have recently been proposed.¹⁹⁻²¹ We plan to extend the scattering formalism to truly overlapping potentials, but hopefully without significantly sacrificing the computational advantages of the method. Separable, nonlocal model potentials²² may be useful as a basis for such an extension, although low-order perturbation theory may suffice for some molecules.

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FEEDBACK STABILIZATION OF A DRIFT-TYPE INSTABILITY*

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Low-frequency electrostatic waves in a reflex discharge are stabilized by feeding an amplified and phase-shifted probe signal to a pair of plates at the discharge walls. The plates couple electrostatically to the $k_{\parallel} \approx 0$ drift-type modes and stabilize them, giving a modest increase in density. A root-locus diagram is devised to explain the observed features of the system response.

This Letter reports a successful attempt to stabilize a low-frequency electrostatic instability by feedback in a plasma created by a hot-cathode reflex discharge. The modes are essentially drift-type waves as manifested in a weakly ionized plasma. The radial electric fields at the anodes probably have an influence on the stability of the discharge, but since the measured plasma potential of the column is only a few volts, the rotational velocity is several times smaller than the diamagnetic drift velocity. A study of these modes and their importance in this discharge relative to cross-field transport has been made earlier.^{1,2} Theories describing these modes³⁻⁶ are largely inadequate, but recent work by Ewald, Crawford, and Self⁷ accounts well for the considerable difference between the characteristics of drift waves in weakly ionized gases and those in highly ionized alkali-metal plasmas. Yet, without looking in too much detail at the instability, we can establish the salient features of the feedback method for stabilizing the modes.

The discharge and plasma parameters differ

little from an earlier device.² Densities are several times 10^{10} cm^{-3} , electron temperatures 5-8 eV, pressure $\frac{1}{2}$ -2 $\mu \text{ H}_2$, magnetic field 75-150 G, column size 2 in. diam and 24 in. long, current 200-400 mA, and voltage 50 V. This voltage drop is largely at the cathode sheath, and is not manifested in a large radial electric field in the column. Neutral collision frequencies for electrons and ions are 5 MHz and 100 kHz, while mean free paths for collisions with neutrals are $\frac{1}{2}$ and 2 m, respectively. The ion gyroradius is on the order of the tube radius.

The modes lie in the range 10-100 kHz, have no detectable parallel wavelength, and occur in azimuthal modes $m = 1, 2,$ and 3 traveling around the magnetic field in the right-hand sense. This is the direction of the electron diamagnetic velocity (v_{De}), and $v_{\text{phase}} \ll v_{De}$ as expected for this range of collision frequencies.² There is little amplitude change with radius for these modes except near the cathode radius, where the amplitude drops rapidly and the phase changes more than 90°.