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LCAO Molecular Orbitals in One Dimension

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(Received 30 March 1973)

A one-dimensional model with δ-function potentials is used to investigate the accuracy of approximations commonly used in the linear combination of atomic orbitals (LCAO) method for constructing molecular wavefunctions and determining molecular energies. Numerical evaluations of the errors are obtained for the one-dimensional analogue of butadiene.

I. INTRODUCTION

A common method of approximation for calculating molecular wave functions and energy levels makes use of a linear combination of atomic orbitals (LCAO) to construct the molecular wave functions. The correct linear combinations are determined by variational calculations which also yield the energies. In carrying out such calculations a number of "small" terms are often dropped to simplify the manipulations.

For students who are being introduced to the LCAO method the justification for dropping various terms is often obscure. Unfortunately, it is difficult to justify these approximations without carrying out extensive numerical calculations. Nonetheless, it would be useful to demonstrate the accuracy of the approximations in detail.

The purpose of this paper is to carry out a complete LCAO calculation using a one-dimensional model of a molecule containing four atoms—the analogue of butadiene. In this model all matrix elements of the Hamiltonian may be computed

as well as all overlap integrals. These may be expressed in terms of the distances between atoms and the magnitude of each of the terms may be determined explicitly. Thus, it is possible to obtain a quantitative evaluation of the accuracy of the approximations used in neglecting any terms.

The one-dimensional model has been found to be extremely convenient for discussing a number of simple systems.[1] Electrons are attracted to nuclei by a potential of the form $V(x) = -e^2\delta(x-x_n)$, where x_n is the coordinate of the nucleus. The electron–electron repulsion has the form $V(x) = e^2\delta(x_1-x_2)$. Energies are expressed in terms of $E_0 = -e^2/2a_0$, where $a_0 = me^2/\hbar^2$.

II. LCAO CALCULATION FOR "BUTADIENE"

The one-dimensional analogue of butadiene consists of four atoms located at $x = -(a+b)$, $-a$, a, and $(a+b)$. The Hamiltonian for an electron interacting with these atoms is given by

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - e^2\delta(x+a+b) - e^2\delta(x+a)$$
$$- e^2\delta(x-a) - e^2\delta(x-a-b). \quad (1)$$

Approximate solutions of the Schrödinger equation,

$$H\psi_i = E_i\psi_i, \quad (2)$$

are obtained by assuming that the ψ_i have the form

$$\psi_i = \sum_{j=1}^{4} c_{ij}\phi_j, \quad (3)$$

where the c_{ij} are a set of constants which are to be determined and the ϕ_j are atomic orbitals. The energies are given by

$$E_i = \int\psi_i H\psi_i dx / \int\psi_i\psi_i dx$$
$$= \sum_{j,k} c_{ij}c_{ik}\int\psi_j H\psi_k dx / \sum_{j,k} c_{ij}c_{ik}\int\psi_j\psi_k dx \quad (4)$$
$$= \sum_{j,k} c_{ij}c_{ik}H_{jk} / \sum_{j,k} c_{ij}c_{ik}S_{jk}$$

where $H_{jk} = \int\psi_j H\psi_k dx$ and $S_{jk} = \int\psi_j\psi_k dx$.

Since the Hamiltonian (1) is symmetric for $x \rightarrow -x$, a number of the integrals are equal:

$$H_{11} = H_{44} \equiv \zeta_1, \qquad (5a)$$

$$H_{22} = H_{33} \equiv \zeta_2, \qquad (5b)$$

$$H_{12} = H_{21} = H_{34} = H_{43} \equiv \eta_1, \qquad (6a)$$

$$H_{23} = H_{32} \equiv \eta_2, \qquad (6b)$$

$$H_{13} = H_{31} = H_{24} = H_{42} \equiv \eta_3, \qquad (6c)$$

$$H_{14} = H_{41} \equiv \eta_4, \qquad (6d)$$

$$S_{11} = S_{22} = S_{33} = S_{44} = 1, \qquad (7a)$$

$$S_{12} = S_{21} = S_{34} = S_{43} \equiv S_1, \qquad (7b)$$

$$S_{23} = S_{32} \equiv S_2, \qquad (7c)$$

$$S_{13} = S_{31} = S_{24} = S_{42} \equiv S_3, \qquad (7d)$$

$$S_{14} = S_{41} \equiv S_4. \qquad (7e)$$

In addition, the ψ_i are also symmetric or anti-symmetric for $x \rightarrow -x$:

$$c_{11} = c_{14} \equiv c_1, \qquad (8a)$$

$$c_{12} = c_{13} \equiv c_2, \qquad (8b)$$

for the symmetric case, and

$$c_{21} = -c_{24} \equiv c_1, \qquad (9a)$$

$$c_{22} = -c_{23} \equiv c_2, \qquad (9b)$$

for the anti-symmetric case. The two other sets of coefficients satisfy the same conditions.

The energies are then given by

$$E_i = \langle H \rangle_i$$

$$= \frac{c_1^2(\zeta_1 \pm \eta_4) + 2c_1c_2(\eta_1 \pm \eta_3) + c_2^2(\zeta_2 \pm \eta_2)}{c_1^2(1 \pm S_4) + 2c_1c_2(S_1 \pm S_3) + c_2^2(1 \pm S_2)} . \qquad (10)$$

Imposing the variational conditions

$$\partial E_i / \partial c_1 = 0 \quad \text{and} \quad \partial E_i / \partial c_2 = 0 \qquad (11)$$

yields

$$[c_1(1 \pm S_4) + c_2(S_1 \pm S_3)]E_i$$
$$= c_1(\zeta_1 \pm \eta_4) + c_2(\eta_1 \pm \eta_3), \qquad (12a)$$

$$[c_1(S_1 \pm S_3) + c_2(1 \pm S_2)]E_i$$
$$= c_1(\eta_1 \pm \eta_3) + c_2(\zeta_2 \pm \eta_2), \qquad (12b)$$

where

$$2c_1^2(1 \pm S_4) + 2c_2^2(1 \pm S_2) + 4c_1c_2(S_1 \pm S_3) = 1.$$

Equations (12) may be solved directly to obtain E_i, c_1, and c_2.

In the usual applications of the LCAO method a number of simplifications are made:

$$H_{ij} = \zeta \delta_{ij} + \eta \delta_{ij \pm 1}, \qquad (13)$$

$$S_{ij} = \delta_{ij} + S \delta_{ij \pm 1}. \qquad (14)$$

(In the simplest Hückel approximation S equals 0.)

In order to determine the accuracy of these approximations it is necessary to evaluate all the integrals in Eqs. (5), (6), and (7).

Noting that[1]

$$\phi_1 = a_0^{-1/2} \exp(-|x + a + b|/a_0), \qquad (15a)$$

$$\phi_2 = a_0^{-1/2} \exp(-|x + a|/a_0), \qquad (15b)$$

$$\phi_3 = a_0^{-1/2} \exp(-|x - a|/a_0), \qquad (15c)$$

$$\phi_4 = a_0^{-1/2} \exp(-|x - a - b|/a_0), \qquad (15d)$$

the integrals are

$$\zeta_1 = E_0(1 + 2e^{-2\gamma} + 2e^{-2\gamma - 2\beta} + 2e^{-4\gamma - 2\beta}), \qquad (16a)$$

$$\zeta_2 = E_0(1 + 2e^{-2\gamma} + 2e^{-2\gamma - 2\beta} + 2e^{-2\beta}), \qquad (16b)$$

$$\eta_1 = E_0(S_1 + 2e^{-\gamma} + 2e^{-\gamma - 2\beta} + 2e^{-3\gamma - 2\beta}), \qquad (17a)$$

$$\eta_2 = E_0(S_2 + 4e^{-2\gamma - \beta} + 2e^{-\beta}), \qquad (17b)$$

$$\eta_3 = E_0(S_3 + 4e^{-\gamma - \beta} + 2e^{-3\gamma - \beta}), \qquad (17c)$$

$$\eta_4 = E_0(S_4 + 6e^{-2\gamma - \beta}), \qquad (17d)$$

$$S_1 = (1 + \gamma)e^{-\gamma}, \qquad (18a)$$

$$S_2 = (1 + \beta)e^{-\beta}, \qquad (18b)$$

$$S_3 = (1 + \beta + \gamma)e^{-(\beta + \gamma)}, \qquad (18c)$$

$$S_4 = (1 + \beta + 2\gamma)e^{-(\beta + 2\gamma)}, \qquad (18d)$$

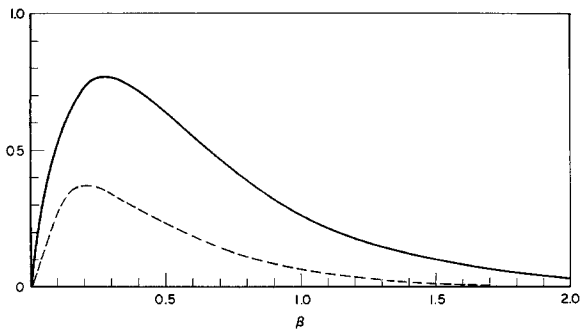where β equals $2a/a_0$, and γ equals b/a_0.

FIG. 1. Plots of $(\zeta_2-\zeta_1)/E_0$ vs β (—) and $(\eta_2-\eta_1)/E_0$ vs β (- - -).

In order to examine the magnitude of the terms in Eqs. (16), (17), and (18) it is convenient to simplify the problem by assuming that the four atoms are equally spaced, i.e., $\gamma = \beta$. Then the quantities in Eqs. (16), (17), and (18) may be expressed as functions of a single variable:

$$\zeta_1 = E_0(1+2e^{-2\beta}+2e^{-4\beta}+2e^{-6\beta}), \qquad (16a')$$

$$\zeta_2 = E_0(1+4e^{-2\beta}+2e^{-4\beta}), \qquad (16b')$$

$$\eta_1 = E_0 e^{-\beta}[(3+\beta)+2e^{-2\beta}+2e^{-4\beta}], \qquad (17a')$$

$$\eta_2 = E_0 e^{-\beta}[(3+\beta)+4e^{-2\beta}], \qquad (17b')$$

$$\eta_3 = E_0 e^{-2\beta}[(5+2\beta)+2e^{-2\beta}], \qquad (17c')$$

$$\eta_4 = E_0 e^{-3\beta}(7+3\beta). \qquad (17d')$$

$$S_1 = (1+\beta)e^{-\beta}, \qquad (18a')$$

$$S_2 = (1+\beta)e^{-\beta}, \qquad (18b')$$

$$S_3 = (1+2\beta)e^{-2\beta}, \qquad (18c')$$

$$S_4 = (1+3\beta)e^{-3\beta}. \qquad (18d')$$

In the usual approximations which are made using the LCAO method, $\zeta_2 = \zeta_1$. It is clear from Eqs. (16') that the error in this approximation is proportional to $e^{-2\beta}$. A plot of $(\zeta_2-\zeta_1)/E_0$ is shown in Fig. 1. Similarly, to illustrate the error in the approximation $\eta_2 = \eta_1$, a plot of $(\eta_2-\eta_1)/E_0$ is also shown in Fig. 1. In this case the error is proportional to $e^{-3\beta}$. The errors in the approximations $\eta_3 = 0$ and $\eta_4 = 0$ are proportional to $e^{-2\beta}$ and $e^{-3\beta}$, respectively.

It is also of interest to compare the exact LCAO energies with the approximate ones obtained by replacing Eqs. (12) by

$$(c_1+c_2 S)E_i = c_1\zeta + c_2\eta, \qquad (19a)$$

$$[c_1 S+c_2(1\pm S)]E_i = c_1\eta + c_2(\zeta \pm \eta), \qquad (19b)$$

where ζ, η, and S are evaluated neglecting terms proportional to $e^{-2\beta}$, $e^{-3\beta}$, and $e^{-4\beta}$.

Plots of the energies vs β are shown in Fig. 2.

For small values of β the approximate solutions for the energies are very inaccurate. However, for $\beta > 1$ the agreement improves rapidly. At large distances the four energy levels correspond to the familiar solutions with zero, one, two, and three nodes in order of increasing E_B.

It is especially interesting to note the peculiar behavior of the energy for the solution with three nodes for small values of β. For $0.6 \lesssim \beta \lesssim 1.3$, the
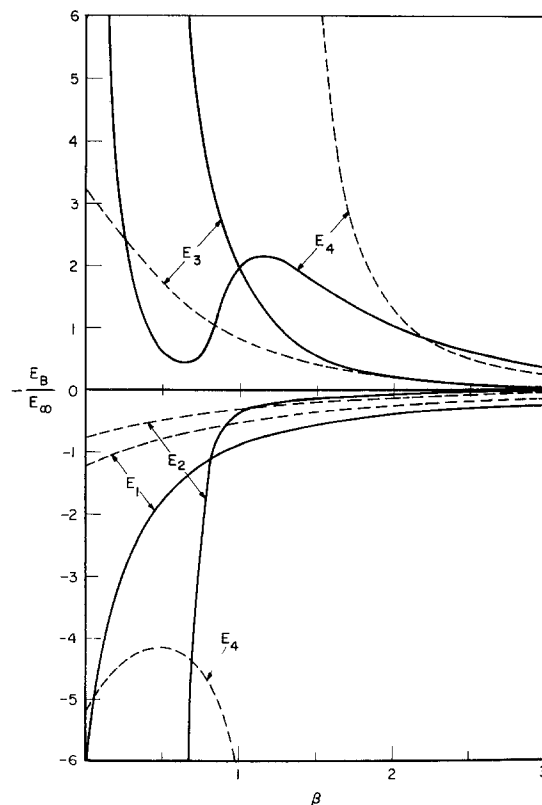

FIG. 2. Plots of exact LCAO energies vs β (—) and approximate LCAO energies vs β (- - -).

slope of the energy vs β curve is positive for the exact LCAO solution while for the approximate solution the energy is actually negative for $\beta \lesssim 1.3$ (where there is a discontinuity).

This result is a peculiarity of the LCAO solution since for $\beta \rightarrow 0$ there cannot be any solutions of the exact Schrödinger equation which are antisymmetric.

III. CONCLUSIONS

In this paper the approximations used to simplify LCAO calculations have been examined quantitatively using a one-dimensional analogue of butadiene in which the atomic potentials are represented as δ functions. If the separation of the atoms is large compared to their size, the approximations are excellent, but this is not generally the case so that the magnitude of the errors may not be negligible.

These considerations neglect electron–electron interactions which are significant as well as modifications of the simple LCAO wave functions which can improve the results.

Because of the simplicity of the model and the ease of carrying out detailed numerical evaluations, these calculations are useful pedagogical tools to illustrate the general methods used in more complicated computations.

[1] I. R. Lapidus, Am. J. Phys. **38**, 905 (1970).