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Variational Cellular Model of the Molecular and Crystal Electronic Structure

Luiz G. Ferreira and José R. Leite
Instituto de Física, Universidade de São Paulo, São Paulo, Brazil
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A variational version of the cellular method is developed to calculate the electronic structure of molecules and crystals. Because of the simplicity of the secular equation, the method is easily implemented. Preliminary calculations on the hydrogen molecular ion suggest that it is also accurate and of fast convergence.

The multiple-scattering method has been applied successfully to a wide range of solids, molecules, and molecular clusters.[1,2] However, there are some molecular geometries where the muffin-tin potential has to be improved considerably if one wants to obtain an electronic structure with a reasonable degree of physical realism.[3] The unsatisfactory features of the muffin-tin approximation applied to open structures are already known from previous calculations of electronic structure of solids.[4] For open structures, the muffin-tin approximation is poor because of the large volume where the potential is constant. To circumvent this limitation, it is becoming common practice to overlap the spheres circumscribing the atoms,[5] thus minimizing the bad effects of a constant potential in a much extended region. This procedure improves the results considerably, as examplified by the case of the ion H_2^+ to be discussed below. The extension of the multiple-scattering method to non-muffin-tin potentials, that has been tried by some authors, is difficult and costly to implement.[6] In preference to the methods which deal with muffin-tin potentials, we suggest in this Letter a new approach to the problem of finding the one-electron solutions of the Schrödinger equation for molecules and crystals. Our starting point goes back to the Wigner-Seitz-Slater cellular method,[7] where the solution of the boundary condition problem is reformulated by us as a variational principle. A critical test of the model is made by carring out preliminary calculations of the hydrogen molecular ion H_2^+. As will be shortly seen, one important asset of the present method is the elimination of the constant-potential region of the multiple-scattering method. In this respect, the good features of the overlapping-spheres model can be also expected in the present case.

The present method has a resemblance to the one proposed by Antoci and Nardelli.[8] Their method and ours have a common starting point, which is a variational expression for the energy eigenvalue.[9] While Antoci and Nardelli use spherical cells centered at the nuclei, our cells can have any shape, which is an asset for open structures. On the other hand, in the interatomic region, Antoci and Nardelli expand the wave function in terms of functions which are regular at the origin and at infinity. Thus, in the interatomic region, the wave function is not an exact solution of the Schrödinger equation for the energy eigenvalue. In this respect, the method of Antoci and Nardelli is an extension for molecules of the augmented-plane-wave method for crystals, and one cannot expect rapidly converging wave functions. The method we present below is differently motivated: We attempt to formulate the cellular method in a variational way. Thus we add to the flexibility of the cellular method a much faster convergence.

According to the original idea of the cellular method, we start by decomposing the molecular or crystal space into cells, one surrounding each atom or interstitial region. In the simplest form of the cellular method, the true potential is approximated, within each cell, by its spherical average with respect to the center of the cell. In this Letter we will confine our attention to spherical cellular potentials. By solving a central-field problem within the cell i, we generate a trial function ψ_i, to be used in a fully variational expression[9] for the energy ϵ:

$$(\textstyle\sum_i \int d\Omega\, \psi_i{}^* \psi_i)\epsilon = \textstyle\sum_i \int d\Omega\, [\nabla\psi_i{}^* \cdot \nabla\psi_i + \psi_i{}^* V \psi_i]$$

$$+\tfrac{1}{2}\sum_{S_{ij}} \int dS\, [(\psi_i{}^* - \psi_j{}^*)(\partial_n\psi_j - \partial_n\psi_i) + (\psi_i - \psi_j)(\partial_n\psi_j{}^* - \partial_n\psi_i{}^*)], \tag{1}$$

where we are adding volume integrals in each cell i and surface integrals in each boundary S_{ij} between cells i and j. In Eq. (1), V is the potential and $\partial_n\psi_i$ means the normal derivative to the cell surface S_{ij}, outwards from the cell i. Thus, at S_{ij}, $\partial_n\psi_i$ and $\partial_n\psi_j$ have opposite directions. Equation (1) can be written as

$$(\textstyle\sum_i \int d\Omega\, \psi_i{}^* \psi_i)\epsilon = \textstyle\sum_i \int d\Omega\, \psi_i{}^*[-\nabla^2 + V]\psi_i + \tfrac{1}{2}\textstyle\sum_{S_{ij}} \int dS\, (\psi_i - \psi_j)(\partial_n\psi_j{}^* - \partial_n\psi_i{}^*)$$

$$+\tfrac{1}{2}\sum_{S_{ij}} \int dS\, (\psi_i{}^* + \psi_j{}^*)(\partial_n\psi_j + \partial_n\psi_i). \tag{2}$$

ϵ is always real for any trial wave function; thus we can vary $\psi_i{}^*$ to obtain the conditions for ϵ to be stationary:

$$[-\nabla^2 + V]\psi_i = \epsilon\psi_i, \tag{3}$$

$$\psi_i|_{S_{ij}} = \psi_j|_{S_{ij}}, \tag{3a}$$

$$\partial_n\psi_i|_{S_{ij}} = -\partial_n\psi_j|_{S_{ij}}, \tag{3b}$$

which imply that the wave function and its normal derivative have to be continuous through the cell boundaries. To proceed with the derivation of the secular equation, the usual spherical harmonic representation of the trial function ψ_i is assumed:

$$\psi_i = |i\lambda\rangle = \textstyle\sum_\lambda A_{i\lambda} f_{i\lambda}(\vec{r}), \tag{4}$$

where

$$f_{i\lambda}(\vec{r}) = R_l{}^{\epsilon_0}(r_i) Y_\lambda(\hat{r}_i), \tag{4a}$$

where $\lambda = (l, m)$ is the spherical harmonic angular momentum index. The functions $R_l{}^{\epsilon_0}(r)$ are the solutions of the radial Schrödinger equation for energy ϵ_0 and potential $V(r)$ which are regular at the origin or decrease exponentially at infinity. $Y_\lambda(\hat{r}_i)$ are spherical harmonics and the coefficients $A_{i\lambda}$ are to be determined. If the trial function is a propagating state in periodic lattice, the coefficients $A_{i\lambda}$ in different cells are related by the Bloch theorem. The variation of the trial function $\psi_i{}^*$ in Eq. (2), assuming the representation given by Eq. (4), leads to the following secular equation:

$$\sum_{i'\lambda'} \langle i\lambda|H|i'\lambda'\rangle A_{i'\lambda'} = 0, \tag{5}$$

where H is a matrix whose elements are

$$\langle i\lambda|H|i'\lambda'\rangle = (1 - \delta_{ii'}) \int dS_{ii'} [\partial_n f_{i\lambda}{}^* f_{i'\lambda'} + f_{i\lambda}{}^* \partial_n f_{i'\lambda'}]. \tag{6}$$

This is a Hermitian square matrix where the diagonal elements are all nulls.

As a test of the method we consider the hydrogen molecular ion $H_2{}^+$. This molecular geometry can be partitioned into cells, by first considering a sphere of radius R_0 enclosing the constituent nuclei and centered at the middle point between them. The outside region of this sphere defines a cell that extends out to infinity (outer cell). The inside region of this sphere can be divided in two equivalent cells by the inscribed portion of a plane perpendicular to the line joining the nuclei through the middle point between them (atomic cells). The averaged cellular potentials within these cells can be represented, in Rydberg units, as

$$V_a(r) = -2/r - 2/R \tag{7a}$$

within the atomic cells, and

$$V_0(r) = -4/r, \quad r > R_0, \tag{7b}$$

in the outer cell. R is the internuclear distance. In general R_0 will be an adjustable parameter. In order to improve the physical realism of our potential model we choose R_0 in a way that the averaged potential is continuous at the intersection of the outer sphere with the plane dividing the atomic cells. We generate the functions $R_l^{\epsilon_0}(r)$ by numerically integrating the radial Schrödinger equation. For each trial value ϵ_0, the outward and inward integrations are performed, respectively, for the potentials V_a and V_0. The surface integrations in Eq. (6) are performed according to the usual procedure of numerical integration, where the integrand is evaluated at a finite number of points and summed with appropriate weight factors. The secular matrix is parametrized in terms of ϵ_0. The one-electron energies are given by the zeros of the associated determinant.

In Table I is shown a convergence study of the $1\sigma_g$ level of H_2^+ ($R = 2.0$ a.u.) as function of the number of terms in the cellular expansion and the number of points used to perform the numerical surface integrations at the plane and at the hemispheres. The cellular representation includes, in each cell, spherical harmonics whose maximum angular momentum is $l_{\max}$.

Table I has two interesting features: First, our variational version of the cellular method shows fast convergence with respect to l. For $l_{\max} = 2$ the solution is already convergent within tenths of eV, being fully convergent for $l_{\max} = 4$. Secondly, for a fixed value of $l_{\max}$, the solution converges if enough points are used for the surface integrations. When this number of points is reached, the solution is no longer sensitive to the number and location of the points on the cell surfaces. It is well known that the Slater cellular method, based on exact point matching, is an accurate technique to determine one-electron eigenstates in crystals.[7] However, many authors have pointed out that the method is not practical,[10] since too high a value of $l_{\max}$ is needed in the cellular expansion to ensure a reasonable convergence. If the matching points sample only limited portions of the cell surfaces, as originally suggested, it is clear that the eigensolutions cannot be derived from a variational principle.[11] Energy eigenvalues not determined variationally demand wave functions with high-order spherical harmonics. On the other hand, Table I shows that, once the integrations in expression (6) are performed in an accurate way, the energy converges even for wave functions with just a few spherical harmonics.

In Fig. 1 we show the results of our calculation

TABLE I. Convergence of the lowest energy level, $E_{1\sigma_g}$, of H_2^+ for the equilibrium internuclear distance $R = 2.0$ a.u. $l_{\max}$ is the maximum spherical harmonic angular momentum in the cellular expansion. Values are in Rydbergs. "Points" is the number of points used for numerical integration in the hemispheres and in the plane.

Points \ $l_{\max}$	0	1	2	3	4	5
1	−1.900	−2.105				
2	−1.900	−2.097	−2.182	−2.438		
3	−1.900	−2.084	−2.150	−2.167	−2.240	
4	−1.900	−2.080	−2.142	−2.141	−2.181	−2.989
5	−1.900	−2.079	−2.139	−2.140	−2.167	−2.527
7	−1.900	−2.078	−2.136	−2.142	−2.159	−2.253
9	−1.900	−2.077	−2.135	−2.143	−2.157	−2.191
12	−1.900	−2.077	−2.134	−2.144	−2.155	−2.155
15	−1.900	−2.077	−2.134	−2.145	−2.155	−2.155
20	−1.900	−2.077	−2.134	−2.145	−2.155	−2.155

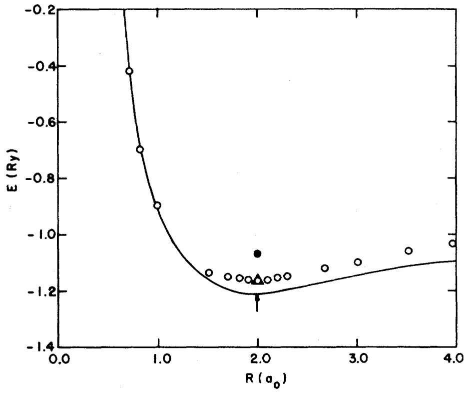

FIG. 1. Ground-state energy of H_2^+ as a function of the internuclear distance. The multiple-scattering calculation (full circle), the overlapping-spheres calculation (triangle), and the results of the cellular method (empty circles) are compared with the exact solution (solid curve).

for the ground-state energy of H_2^+, as a function of the internuclear distance (empty circles). The results of a multiple-scattering calculation[12] (full circle), an overlapping-sphere (OS) calculation[13] (triangle), and the exact solution[14] (solid curve) are also shown. For small internuclear distance the results of our variational cellular method are in perfect agreement with the exact solution. In this latter case, the averaged spherical potential within the atomic cells is a good approximation, since the cells have small size. Other authors, who have been applying different versions of the cellular method to crystals, have already pointed out the accuracy of the method for close-packed structures.[15] The arrow in Fig. 1 shows the exact equilibrium internuclear distance, which is in perfect agreement with our result. For internuclear distances greater than 1.5 a.u., our results agree with the exact solutions within 0.05 Ry. Our results presented here could be improved still further by going beyond the standard spherically averaged cellular potential model.[16-17] The deviation of the multiple-scattering result from the exact solution is due mainly to the failure of the muffin-tin potential approximation.

To conclude we point out that the proposed variational cellular method is suitable to deal with complicated structures, since no assumption is made *a priori* about the shape of the cells.

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