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General Formulation of the Variational Cellular Method for Molecules and Crystals

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ABSTRACT

A variational form of the cellular method is proposed as a new model to solve the one-electron Schrödinger equation for molecules and crystals. The model keeps the good features of the traditional cellular method, as the arbitrary partition of space, and eliminates its main drawback, the slow convergency of the cellular expansion series. With the aid of a criterion of precision on the trial wave functions, we discuss the possibilities offered by the method for more accurate calculations of the electronic structures of molecules and solids. As an example of the accuracy and fast convergency of the model, computation of the energy spectrum of the hydrogen molecular ion H_2^+ is presented.

I. Introduction

One of the earliest method to solve the problem of finding the one-electron solutions of the Schrödinger equation for crystals was the cellular model proposed by Wigner and Seitz[1]. An improved version of the method was suggested by Slater, in his classic study of metallic sodium[2]. In Slater's scheme, the crystal volume is first decomposed into space - filling atomic polyhedra (Wigner - Seitz cells). By reducing the crystal wave equation to a central field problem in each cell, the one electron solutions of the Schrödinger equation are obtained by imposing boundary conditions on the surfaces of the cells. Slater's cellular method has been applied in various forms to many metallic crystals[3], diamond lattice-type crystals[4] and insulators[5].

From the reported works we can conclude that the cellular method is an accurate technique for the calculation of the electronic structure of solids, even for loosely packed structures as diamond crystals. Furthermore, the theory of the method is extremely simple and has the advantage of discarding the muffin-tin approximation of the self-consistent potential, which is the main source of errors in methods like the augmented -plane-wave (APW) method[6] and Kohn - Korringa - Rostoker (K K R) method[7]. However, in order to obtain a realistic crystal electronic structure with the cellular method, the expansion of the wave function has to be carried to very large angular momenta[4]. This severe convergence problem has been pointed as one of the fundamental weakness of the method[8].

It has been shown previously[9] that this limitation can be overcome by reformulating the solution of the cellular boundary condition problem through a variational procedure. This promising variant of the cellular method was suggested as a new approach to the problem of finding the one-electron solutions of the Schrödinger equation for molecules and crystals, in preference to the methods which deal with muffin-tin potentials.

The aim of the present paper is to establish the full theoretical formulation of the variational cellular method as well give indications on how the self consistency in the method can be implemented. Under new lights the case of the hydrogen molecular ion H_2^+ is restudied. This molecule has been already calculated by several authors[10-12] and the exact solutions are available in the literature[13].

It is worth mentioning that other modified versions of the cellular method have been proposed recently as models of the molecular and crystal electronic structures[14-19].

II. Review of the Variational Cellular Method

According to the original formulation of the cellular method, one starts by decomposing the molecular or crystal space into cells. Although is common practice the partition of the crystal space into Wigner-Seitz atomic cells, in general the cells can have arbitrary shapes. The molecular or crystal potential can be expressed as the spacial superposition of spheric potentials, one centered at each atomic site. In the simplest form of the cellular method, the potential is approximated within each cell by its spherical average with respect to the center of the cell.

Within the cell i, the wave function ψ_i is expanded in spherical harmonics

$$\psi_i = \sum_\lambda A_{i\lambda} f_{i\lambda}(\vec{r}) \tag{1a}$$

where

$$f_{i\lambda}(\vec{r}) = R_\ell^{\varepsilon_0}(r_i)\, Y_\lambda(\hat{r}_i) \tag{1b}$$

In the equations above, λ stands for the pair (ℓ, m) specifying the angular momentum, and $R_\ell^{\varepsilon_0}$ is a solution of the radial Schrödinger equation for the energy ε_0. If the trial function is a propagating state in a periodic lattice, the coefficients $A_{i\lambda}$ in different cells are related by the Bloch theorem. Then, the unknown coefficients $A_{i\lambda}$ are determined by the following variational expression for the energy eigenvalue

$$\left[\sum_i \int d\Omega \, \psi_i^* \psi_i \right] \varepsilon = \sum_i \int d\Omega \, \psi_i^* \, (- \nabla^2 + V) \, \psi_i$$

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

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

The $d\Omega$ integrals are volume integrals in the cell space, while the dS integrals are integrals in the surfaces separating the cells. In (2), one must sum the volume integrals of all cells and the surface integrals of all cell boundaries. ∂_n is an outward normal derivative such that, when applied to ψ_j, means an outward derivative from the cell j, while when applied to ψ_i it is an outward derivative from i.

Varying the coefficients $A_{i\lambda}$ and imposing that the variation of the energy ε is null, one arrives at the following secular equation

$$\sum_{i'\lambda'} < i\lambda \mid H \mid i'\lambda' > A_{i'\lambda'} = 0 \tag{3}$$

where the matrix H is

$$<i\lambda| \, H \, |i'\lambda'> = (1 - \delta_{ii'}) \int dS_{ii'} \left[\partial_n f_{i\lambda}^* f_{i'\lambda'} + f_{i\lambda}^* \partial_n f_{i'\lambda'} \right] \tag{4}$$

Equations (3) and (4) are basic to the method. The energy eigenvalue determination becomes a simple matter of calculating the matrix H according to Eq. (4), for several energies ε, and finding the energy for which Eq. (3) has a non trivial solution.

The calculation of H according to Eq.(4) involves the making of surface integrals along the cell boundaries. In most instances, these integrals can only be made by establishing a net of points in the surfaces, and adding the values of the integrands at these points multiplied by properly chosen weights. Thus, before discussing some special features of the method, one must face the two problems of how to define the cells, and how to establish nets of points for the surface integrations.

III. A Guideline for Cell Construction

One important asset of the cellular method is the freedom one gains in the cell construction. By choosing the cells judiciously, one can span the whole space with cells where the potential is spherically symmetric, and obtain a realistic description of the true potential. In this respect, the cellular method is outstanding when compared with the multiple-scattering[10] methods. In the latter case, the cells are necessarily spheres, and these cannot be arranged without leaving much open space.

Despite of being an important asset, the enormous freedom for cell construction is confusing. One has so many possibilities that it is difficult to make a choice. In what follows, we intend to show a simple guideline, by which we loose a bit of freedom but become a lot less confused when constructing the cells.

To begin with, one may assume that, in each cell, the potential does not depend on how the cells are constructed. In other words, we assume that in a variation of the cell boundaries the potential of a cell does not vary. This assumption is arbitrary but not unreasonable. Indeed, one could expect that in a variation of the cell boundaries, the wave functions and charge distribution would be only negligibly varied. Now, if the spherically symmetric potential of the cell is forced to satisfy the Poisson equation, the potential in each cell becomes only negligibly dependent on the shape of the cell boundaries.

Thus consider the integrated square error in the potential

$$E = \int d\Omega \left[v(\vec{r}) - \bar{v}(\vec{r}) \right]^2 \qquad (5)$$

$v(\vec{r})$ is the true potential, while $\bar{v}(\vec{r})$ is the potential trimmed to become spherically symmetric in each cell. Consider an arbitrary variation in the surface separating cell i from cell j , according to Fig. 1. The resulting variation in E is

$$\delta E = \int d\Omega \, (\bar{v}_j - \bar{v}_i)(2\, v - \bar{v}_i - \bar{v}_j) \qquad (6)$$

where $\bar{v}_i$ and $\bar{v}_j$ are the spherically symmetric potentials of cells i and j , and the integration is performed just in the shaded region of Fig. 1.

<u>Insert Figure 1</u>

The cell boundaries should be chosen so that δE is null, or approximatively so. This is automatically satisfied at the planes of symmetry for which

$$\bar{v}_i = \bar{v}_j$$

In the general case, instead of calculating the surfaces determined by

$$\delta E = 0$$

one would find insulated points for which

$$\bar{v}_i = \bar{v}_j \qquad (7a)$$

or

$$v = \frac{\bar{v}_i + \bar{v}_j}{2} \qquad (7b)$$

and pass simple surfaces, such as planes or spheres, at these points. These surfaces would define the cell boundaries.

IV. Nets of Points for Surface Integration

The regular use of the variational cellular method would be seriously hindered if the surface integrations had to be made with much precision. In that case we would be forced to study the problem of establishing a net of points and their weights, in each surface, that would permit precise integrations. Since the very shape of the surfaces is not predetermined, this problem would be a very serious one.

In what follows we show that the surface integrations need no special cares, but can be made very naively. To prove this point, consider a situation where the integrations have been made with much precision. Let $H^{(true)}_{i\lambda,i'\lambda'}$ be the matrix H of Eq. (4) resulting from this precise calculation. Consider now a deliberate error in the integrations in the surface separating cell I and cell J. To the point $\vec{r}_o$ of this surface we add an extra weight w. Let $H^{(wrong)}$ be the resulting matrix H. According to Eq. (4) we write

$$H^{(wrong)}_{i\lambda,i'\lambda'} = H^{(true)}_{i\lambda,i'\lambda'} + w\, Z^{(IJ)}_{\lambda\lambda'}\, \delta_{Ii}\, \delta_{Ji'} + w\, Z^{(JI)}_{\lambda\lambda'}\, \delta_{Ji}\, \delta_{Ii'} \tag{8}$$

where

$$Z^{(IJ)}_{\lambda\lambda'} = \partial_n\, f^*_{I\lambda}(\vec{r}_o)\, f_{J\lambda'}(\vec{r}_o) + f^*_{I\lambda}(\vec{r}_o)\, \partial_n\, f_{J\lambda'}(\vec{r}_o) \tag{9}$$

Let ε be the solution of the true secular equation

$$\det \{ H^{(true)} \} = 0 \tag{10a}$$

and let $\varepsilon + \delta\varepsilon$ be the solution of the wrong equation

$$\det\{\,H^{(\mathrm{wrong})}\,\} = 0 \tag{10b}$$

Expanding $H^{(\mathrm{wrong})}$ linearly in $\delta\varepsilon$ and w we obtain

$$\begin{aligned}\det\{\,H^{(\mathrm{wrong})}\,\} &= \det\{\,H^{(\mathrm{true})}\,\} \\ &+ \delta\varepsilon \sum_{i\lambda}\sum_{i'\lambda'} \frac{d}{d\varepsilon} H^{(\mathrm{true})}_{i\lambda i'\lambda'} M_{i'\lambda' i\lambda} \\ &+ w \sum_{\lambda\lambda'} \left\{ Z^{(IJ)}_{\lambda\lambda'} M_{J\lambda' I\lambda} + Z^{(JI)}_{\lambda\lambda'} M_{I\lambda' J\lambda} \right\} = 0\end{aligned} \tag{11}$$

where M is the matrix of minors of the matrix $H^{(\mathrm{true})}$. But

$$M_{i'\lambda',i\lambda} = K A^{*}_{i\lambda} A_{i'\lambda'} \tag{12}$$

that is, the M are proportional to the products of the expansion coefficients. Then

$$\delta\varepsilon = -w \frac{\sum_{\lambda\lambda'} \left\{ A^{*}_{I\lambda} Z^{(IJ)}_{\lambda\lambda'} A_{J\lambda'} + A^{*}_{J\lambda} Z^{(JI)}_{\lambda\lambda'} A_{I\lambda'} \right\}}{\sum_{i\lambda}\sum_{i'\lambda'} A^{*}_{i\lambda} \frac{d}{d\varepsilon} (H^{(\mathrm{true})}_{i\lambda,i'\lambda'}) A_{i'\lambda'}} \tag{13}$$

According to Eqs. (9) and (1), the numerator of Eq. (13) is

$$\partial_n \psi^{*}_I(\vec{r}_o)\, \psi_J(\vec{r}_o) + \psi^{*}_I(\vec{r}_o)\, \partial_n \psi_J + \text{c.c.}$$

Now, if the angular momentum expansion in Eq. (1) has been carried out to sufficiently high angular momenta, ψ_I and ψ_J match at the cell boundaries, or

$$\psi_I(\vec{r}_o) = \psi_J(\vec{r}_o) \tag{14a}$$

and $$\partial_n \psi_I(\vec{r}_o) = -\,\partial_n \psi_J(\vec{r}_o) \tag{14b}$$

Then $\delta\varepsilon = 0$

This derivation proves that the present version of the cellular method is doubly variational, because the first-order variation in the energy is zero for a variation in the expansion coefficients and a variation in the net for the surface integrations. In this respect, it must be remarked that Leite et al.[4] had observed that, once the angular momentum convergence was reached, the net of points could be changed. In fact, they used those changes in the net of points as a criterion of convergence in the angular momentum series.

V. A Criterion of Precision

We turn now to the variational expression for ε, Eq. (2). Up till now we have made variations only in the expansion coefficients $A_{i\lambda}$. Now we will consider the variations in the energy ε_o which is used to define the basis functions of Eq. (1b). ε_o must not be confused with ε, because this is the eigenvalue while that is the energy one uses in the radial Schrödinger equation to calculate $R_\ell^{\varepsilon_o}$ of Eq. (1b). Thus, the first term in the r.h.s. of Eq. (2) becomes

$$\varepsilon_o \sum_i \int d\Omega\, \psi_i^* \psi_i$$

and since

$$\sum_{S_{ij}} \int dS \left[- \psi_i \partial_n \psi_i^* + \psi_i^* \partial_n \psi_i \right]$$
$$= \int_{\text{cell } i} dv \left[- \psi_i \nabla^2 \psi_i^* + \psi_i^* \nabla^2 \psi_i \right] = 0$$

Eq. (2) simplifies to

$$\varepsilon \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right) = \varepsilon_o \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right)$$
$$+ \frac{1}{2} \sum_{S_{ij}} \int dS \left[\psi_i \partial_n \psi_j^* + \psi_i^* \partial_n \psi_j + \psi_j \partial_n \psi_i^* + \psi_j^* \partial_n \psi_i \right] \qquad (15)$$

But the second term in the r.h.s. of Eq. (15) is simply related to the matrix H of Eq. (4), then

$$\varepsilon \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right) = \varepsilon_o \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right)$$
$$+ \frac{1}{2} \sum_{i\lambda} \sum_{i'\lambda'} A_{i\lambda}^* H_{i\lambda,i'\lambda'} A_{i'\lambda'} \qquad (16)$$

Now, making a variation $\delta\varepsilon_o$ in ε_o, but maintaining fixed the $A_{i\lambda}$ at their values which satisfy the secular equation (3), setting $\varepsilon_o = \varepsilon$, one obtains the following value for the variation $\delta\varepsilon$ in ε :

$$\delta\varepsilon \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right) = \delta\varepsilon_o \left(\sum_i \int d\Omega\, \psi_i^* \psi_i \right)$$

$$+ \delta\varepsilon_o \frac{1}{2} \sum_{i\lambda} \sum_{i'\lambda'} A_{i\lambda}^* \frac{d}{d\varepsilon_o} (H_{i\lambda,i'\lambda'}) A_{i'\lambda'} \qquad (17)$$

At the exact solution, the r.h.s. of Eq.(17) will be necessarily zero. On the other hand, if the angular momentum series has been cut at a not too high value, the r.h.s. will be small but not zero. Thus, the r.h.s. of Eq. (17) gives a good indication of how precise the calculation is.

In order to formulate a practical criterion of precision, one must write the volume integrals in Eqs. (17) as surface integrals. Considering the two equations

$$-\nabla^2 \psi_i(\varepsilon) + v\, \psi_i(\varepsilon) = \varepsilon\, \psi_i(\varepsilon)$$

and

$$-\nabla^2 \psi_i^*(\varepsilon + \delta\varepsilon) + v\, \psi_i^*(\varepsilon + \delta\varepsilon) = (\varepsilon + \delta\varepsilon)\, \psi_i^*(\varepsilon + \delta\varepsilon)$$

for the functions ψ_i and ψ_i^* in the cell i, satisfying the Schrödinger equation for energies ε and $\varepsilon + \delta\varepsilon$, it is a simple matter to prove that

$$\int d\Omega\, \psi_i^* \psi_i = \int dS \left[\frac{d}{d\varepsilon} (\psi_i^*)\, \partial_n \psi_i - \psi_i \frac{d}{d\varepsilon} (\partial_n \psi_i^*) \right]$$

Thus, letting

$$N^{(i)}_{\lambda\lambda'} = \int dS \left[\frac{d}{d\varepsilon} (f^{*}_{i\lambda})\, \partial_n f_{i\lambda'} - f_{i\lambda'} \frac{d}{d\varepsilon} (\partial_n f^{*}_{i\lambda}) \right] \tag{18}$$

one obtains

$$\int d\Omega\, \psi^{*}_{i}\, \psi_i = \sum_{\lambda\lambda'} A^{*}_{i\lambda}\, N^{(i)}_{\lambda\lambda'}\, A_{i\lambda'} \tag{19}$$

Then one uses for a criterion C of precision, the value of the following expression

$$C = 1 + \frac{A^{*}_{i\lambda} \frac{d}{d\varepsilon} (H_{i\lambda,i'\lambda'})\, A_{i'\lambda'}}{2\, A^{*}_{i\lambda}\, N^{(i)}_{\lambda\lambda'}\, A_{i\lambda'}} \tag{20}$$

In Eq. (20) we sum over repeated indices.

We reckon Eq. (20) as an important asset of the variational cellular method. In all methods for electronic calculations one can only guess the precision of the calculation by increasing the set of basis functions. On the other hand, in the present method one can calculate C and reach his conclusions on the precision, <u>without increasing the basis set</u>.

It is interesting to show that C is exactly zero when the function is continuous and has a continuous normal derivative at the surfaces. To see this, from Eqs. (15), (18) and (19), we derive the following expression

$$2\, A^{*}_{i\lambda}\, N^{(i)}_{\lambda\lambda'}\, A_{i\lambda'} + A^{*}_{i\lambda} \frac{d}{d\varepsilon} (H_{i\lambda,i'\lambda'})\, A_{i'\lambda'} =$$

$$= \sum_{S_{ij}} \int dS_{ij} \left\{ (\mathring{\psi}^{*}_{i} + \mathring{\psi}^{*}_{j})(\partial_n \psi_i + \partial_n \psi_j) + (\psi_i - \psi_j)(\partial_n \mathring{\psi}^{*}_{j} - \partial_n \mathring{\psi}^{*}_{i}) \right\} + \text{c.c.}$$

In the equation above, a dot over a function ψ implies an energy derivative with fixed values of the expansion coefficients $A_{i\lambda}$. Thus, for an exact match of the functions of the cell boundaries, or

$$\psi_i = \psi_j$$

$$\partial_n \psi_i = - \partial_n \psi_j$$

the value of C is exactly zero. Thus, the value of C is actually an integrated error of function mismatch at the surfaces. On the other hand, Eq. (17) tells that this error of mismatch is related to the derivative $d\varepsilon/d\varepsilon_0$ which says how much the eigenvalue is independent of the energy ε_0.

VI. Spurious Solutions

Eq. (3) has also non-trivial solutions which are not physical. To recognize a physical solution one can calculate the value of criterion C of Eq. (20) and see whether it is small, as it should at a true solution. On the other hand there is a simpler method to distinguish a physical solution.

First of all, it is being common practice among us to look for the solutions of Eq. (3) by searching the zeros of

$$(\mathrm{Tr}\ H^{-1})^{-1} = 0 \tag{21}$$

instead of

$$\det(H) = 0 \tag{22}$$

The inverse of the trace of the inverse matrix (ITIM) goes to zero when the determinant of the matrix goes to zero. On the other hand, for a degenerate energy level, the zero of the determinant is also degenerate while the zero of ITIM is simple. Practically this means that a doubly degenerate level can be easily recognized through Eq. (21) but is difficult to locate when one uses Eq. (22), because the determinant does not change its sign at the zero. An added advantage is that a determinant may have a fantastic order of magnitude if proper cares are not taken, while the ITIM has the order of magnitude of a matrix element. Of course one must pay a price for these advantages: the calculation of an inverse matrix is three times slower than the calculation of a determinant.

For our purposes, the use of Eq. (21) instead of Eq. (22) permits an easy recognition of the physical solutions.

Indeed, consider the derivative of ITIM with respect to the energy

$$\frac{d}{d\varepsilon}(\mathrm{Tr}\ H^{-1})^{-1} = -\frac{\frac{d}{d\varepsilon}\mathrm{Tr}\ H^{-1}}{(\mathrm{Tr}\ H^{-1})^2}$$

but

$$\frac{d}{d\varepsilon}H^{-1} = -H^{-1}\frac{dH}{d\varepsilon}H^{-1}$$

thus

$$\frac{d}{d\varepsilon}(\mathrm{Tr}\ H^{-1})^{-1} = \frac{\mathrm{Tr}\ (H^{-1}\frac{dH}{d\varepsilon}H^{-1})}{(\mathrm{Tr}\ H^{-1})^2} \tag{23}$$

Now, at an energy very near a zero of Eq. (21) one has

$$H^{-1}_{ij} = \gamma A^*_j A_i \tag{24}$$

Here, i and j are multiple indices and stand for the cell index and angular momentum indices. Eq. (24) is an imediate consequence of Eq. (12), and the A's are the expansion coefficients. Thus

$$\frac{d}{d\varepsilon}(\mathrm{Tr}\ H^{-1})^{-1} = \frac{\gamma^2}{(\mathrm{Tr}\ H^{-1})^2}\left(\sum_k A^*_k A_k\right)\left(\sum_{ij} A^*_i \frac{dH_{ij}}{d\varepsilon} A_j\right)$$

But, according to Eq. (20), near a true physical solution

$$\sum_{ij} A^*_i \frac{dH_{ij}}{d\varepsilon} A_j \simeq -2\sum_{ij} A^*_i N_{ij} A_j$$

and, as the matrix N is positive definite, one has

$$\frac{d}{d\varepsilon}(\mathrm{Tr}\ H^{-1})^{-1} < 0 \tag{25}$$

Or, in words, the ITIM goes to zero at the non trivial solutions of the secular equation (3), and, <u>at a true physical solution, the ITIM is decreasing with increasing energy</u>.

VII. Normalization of the Wave Function and the Probability of a Cell

The matrix N, defined by Eq. (19), could be used to normalize the wave function and to determine the probability P_i of the electron being in the cell i. Obviously

$$P_i = \frac{\sum_{\lambda\lambda'} A^*_{i\lambda} N^{(i)}_{\lambda\lambda'} A_{i\lambda'}}{\sum_j \sum_{\lambda\lambda'} A^*_{j\lambda} N^{(j)}_{\lambda\lambda'} A_{j\lambda'}} \qquad (26)$$

The normalization would be made by setting the denominator in Eq. (26) equal to 1.

This method of normalization can only be relied upon when the criterion C in Eq. (20) is very near zero. When this does not happen we must recur to the secular matrix H and its energy derivatives to determine P_i and the normalization. One must remember that it is H, and not N, the matrix which is determining the eigenvalue, and that it is H, and not N, the matrix that can be calculated with naively constructed nets of points in the boundary surfaces of the cells. Thus, to determine P_i we shift the potential in the cell i by a constant δV_i and recalculate the energy level. The consequent shift in the energy eigenvalue $\delta\varepsilon$ is related to P_i by

$$P_i = \lim_{\delta V_i \to 0} \frac{\delta\varepsilon}{\delta V_i} = \frac{d\varepsilon}{dV_i} \qquad (27)$$

In order to relate $\delta\varepsilon$ and δV_i we use

$$\begin{aligned} \mathrm{ITIM}(\varepsilon + \delta\varepsilon, \delta V_i) &= \mathrm{ITIM}(\varepsilon, 0) \\ &+ \delta\varepsilon \frac{\partial}{\partial\varepsilon} (\mathrm{ITIM}) + \delta V_i \frac{\partial}{\partial V_i} (\mathrm{ITIM}) = 0 \end{aligned}$$

Thus

$$P_i = - \frac{\frac{\partial}{\partial V_i}\,(\mathrm{ITIM})}{\frac{\partial}{\partial \varepsilon}\,(\mathrm{ITIM})} \tag{28}$$

Then, letting

$$\frac{\partial H}{\partial \varepsilon_i}$$

be the derivative of the matrix with respect to the energy with which the functions at cell i are calculated, and since

$$\frac{\partial}{\partial \varepsilon_i} = - \frac{\partial}{\partial V_i} \tag{29}$$

we obtain, from Eqs. (23) and (24)

$$P_i = \frac{\sum_{j\lambda} \sum_{k\lambda'} A^*_{j\lambda} \frac{\partial}{\partial \varepsilon_i} (H_{j\lambda,k\lambda'}) A_{k\lambda'}}{\sum_{j\lambda} \sum_{k\lambda'} A^*_{j\lambda} \frac{\partial}{\partial \varepsilon} (H_{j\lambda,k\lambda'}) A_{k\lambda'}} \tag{30}$$

These probabilities add up to 1 , this fact following from the relation

$$\frac{\partial}{\partial \varepsilon} = \sum_i \frac{\partial}{\partial \varepsilon_i} \tag{31}$$

VIII. The Spherical Electronic Density $n(r)$ in the Inscribed Sphere

In self-consistent calculations, one can only hope to integrate the Poisson equation if, in each cell, the electronic density is spherically symmetric. The spherical average $n_i(r)$ of the electronic density in the cell i can be simply calculated only in the inscribed sphere that just touch the boundary of the cell (see Fig. 2).

Insert Figure 2

Let r_o be a radius smaller than R, the radius of the inscribed sphere in the cell i. Let $v_i(r)$ be the spherically symmetric potential in the cell. Analogously to the development of the preceding section, we can write an expression for the electronic density at r_o, $n_i(r_o)$

$$4\pi\, r_o^2\, n_i(r_o) = - \frac{\sum\limits_{j\lambda} \sum\limits_{k\lambda'} A^*_{j\lambda} \dfrac{\delta}{\delta\, v_i(r_o)} (H_{j\lambda,k\lambda'})\, A_{k\lambda'}}{\sum\limits_{j\lambda} \sum\limits_{k\lambda'} A^*_{j\lambda} \dfrac{\partial}{\partial\varepsilon} (H_{j\lambda,k\lambda'})\, A_{k\lambda'}} \qquad (32)$$

where $$\frac{\delta}{\delta\, v_i(r_o)}$$

means a functional derivative with respect to $v_i(r)$ at r_o.

The calculation of the functional derivative in Eq. (32) can be made as follows. The radial functions $p_{i\ell}(r)$ in the cell i obey the equation

$$- \frac{d^2}{dr^2}\, p_{i\ell} + \frac{\ell(\ell+1)}{r^2}\, p_{i\ell} + v_i(r)\, p_{i\ell} = \varepsilon\, p_{i\ell} \qquad (33a)$$

This radial function $p_{i\ell}(r)$ is just r times $R_\ell^{\varepsilon_o}(r)$ of Eq.

(1b). At r_o we add a potential $\Delta\delta(r - r_o)$. With this addition, the radial function becomes $\tilde{p}_{i\ell}(r)$ and obeys

$$- \frac{d^2}{dr^2} \tilde{p}_{i\ell} + \frac{\ell(\ell+1)}{r^2} \tilde{p}_{i\ell} + \left[v_i(r) + \Delta\delta(r - r_o)\right] \tilde{p}_{i\ell} = \varepsilon \tilde{p}_{i\ell} \tag{33b}$$

Multiplying (33a) by $\tilde{p}_{i\ell}$ and subtracting it from (33b) multiplied by $p_{i\ell}$, and then integrating from the origin to the radius R of the inscribed sphere, we obtain

$$p_{i\ell}(R) \frac{d}{dR} \tilde{p}_{i\ell}(R) - \tilde{p}_{i\ell}(R) \frac{d}{dR} p_{i\ell}(R) = \Delta\, p_{i\ell}(r_o)\, \tilde{p}_{i\ell}(r_o) \tag{34}$$

When derivating the matrix H with respect to the energy we have overlooked the problem of how to normalize the radial functions. Till now, this normalization has been left completely arbitrary. But now we shall make a choice: we will always normalize the radial functions so that

$$p_{i\ell}(R) = 1 \; ; \quad \text{or} \quad R_\ell^{\varepsilon_o}(R) = 1/R \tag{35}$$

With this choice, the derivative of $\tilde{p}_{i\ell}$ differs from the derivative of $p_{i\ell}$ by

$$\frac{d}{dR} \tilde{p}_{i\ell}(R) - \frac{d}{dR} p_{i\ell}(R) = \Delta\, p_{i\ell}(r_o)\, \tilde{p}_{i\ell}(r_o) \tag{34a}$$

Now let $q_{i\ell}(r)$ be a solution of Eq.(33a) but such that

$$q_{i\ell}(R) = 0$$

$$\frac{d}{dR} q_{i\ell}(R) = 1$$

Then, in the limit when $\Delta \to 0$ and $\tilde{p}_{i\ell}$ and $p_{i\ell}$ almost coincide, we can write, for any radius r larger than R,

$$\tilde{p}_{i\ell}(r) = p_{i\ell}(r) + \Delta\, p_{i\ell}(r_o)^2\, q_{i\ell}(r) \qquad (35)$$

according to Eq. (34a).

Inserting $\tilde{p}_{i\ell}(r)$ instead of $p_{i\ell}(r)$ in the matrix elements of H, we obtain the matrix corresponding to the potential perturbed by

$$\Delta\delta(r - r_o)$$

But this is what we need to perform the functional derivative in Eq. (32). Thus

$$4\pi\, r_o^2\, n_i(r_o) = -\sum_{\ell} p_{i\ell}(r_o)^2 \frac{\sum_{j\lambda}\sum_{k\lambda'} A^*_{j\lambda}\, Q^{(i\,,\,\ell)}_{j\lambda,k\lambda'}\, A_{k\lambda'}}{\sum_{j\lambda}\sum_{k\lambda'} A^*_{j\lambda}\, \frac{\partial}{\partial\varepsilon}\,(H_{j\lambda,k\lambda'})\, A_{k\lambda'}} \qquad (36)$$

where the matrix $Q^{(i\,,\,\ell)}$ is obtained from H through the following:

1 - $q_{i\ell}(r)$ substitutes $p_{i\ell}(r)$.

2 - the matrix elements not containing $p_{i\ell}$ are made zero.

IX. Results for H_2^+

Having reported the theoretical framework of the variational cellular method, we consider now its application to the evaluation of the energy spectrum of the hydrogen molecular ion H_2^+. Instead of using the cells reported in Ref. 9, we now use cells constructed according to the prescriptions of section III. The new cells are described in Fig. 3.

Insert Figure 3

In table I is shown the behaviour of the $1\sigma_g$ energy level of H_2^+ (R = 2 a.u.) with the variation 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.

Insert Table I

The choice of the cells according with the prescription indicated in section III leads to a more accurate energy eigenvalues than the choice we have made in our previous work (ref. 9). According to table I we obtain the value -2.172 Ry for the $1\sigma_g$ energy level of H_2^+. This value is in better agreement with the exact result, - 2.205 Ry, than the value - 2.155 Ry reported by us in reference 9.

The entries quoted in table I show that the variational cellular method is accurate and of fast convergence. Since the energy eigenvalue was derived from a variational principle, the expansion of the cellular function did not have to be carried to large angular momenta. Table I also enphasizes the double variational character of the method. The same converged energy eigenvalue is obtained for different sets of points used to perform the integrations on the cell surfaces.

In table II we show the behaviour of the criterion of precision C as a function of the number of spherical harmonics in the cellular expansion and the number of points used to perform the surface integrations. C is defined in the text by Eq. (20). The entries correspond to the $1\sigma_g$ level, thus they are related with the entries in table I.

Insert Table II

Table II shows that the lack of precision in the calculation of the surface integrals is not critical in the method. In fact, for a converged energy eigenvalue, the value of C is almost insensitive to the number and location of the points for surface integrations. Another very interesting conclusion about the cellular method can be reached if we observe the behavior of the criterion C as a function of ℓ_{max}, for a fixed value of the number "points". There is an optimal value of ℓ_{max} which leads to a minimal C. If the number of basis functions is increased by including spherical harmonics with order higher than the optimal value, C increases. The entries in table I show that the $1\sigma_g$ energy level is fully convergent for $\ell_{max} = 4$. By extending the cellular expansion up to $\ell_{max} = 5$, C increases while the converged energy eigenvalue does not change. This has a straightforward interpretation. The number of points, 15 for example, is not enough to sample correctly a spherical harmonic whose angular momentum is 5 . The inclusion of this harmonic generates a mismatch at the cell boundaries, thus increasing the value of C . On the other hand, due to the variational character of the method, the mismatch has no first-order effect in the energy eigenvalue. However, if more and more basis elements are included in the cellular expansion, for a fixed number of points, the calculation looses its meaning and the solution disappears.

Our finding leads to one more argument in disfavour of the conventional cellular method based on the exact point matching. In that method, the number of matching points is related to the number of spherical harmonics in the trial function . Thus, frequently we are faced with the problem of sampling a high order spherical harmonic at few matching points. According to the conclusions taken from table II, the roots of the secular equation may not even be found. This limitation in the exact point matching method was already observed by Leite et al.[4] when dealing with the four-fold partitioning model of the diamond crystal.

Our results for the lowest electronic energy levels of H_2^+ for the internuclear distance 2 a.u. are listed in table III. The results of a multiple scattering calculation[10], the overlapping-spheres (OS) calculation[12] along with the exact solutions[13] are also shown.

Insert Table III

From the cellular calculation of the $1\sigma_g$ level as a function of the internuclear distance we obtained the value 2.0 a.u. for the H_2^+ bond length, in agreement with the exact result. According to table III, the energy obtained for the ground-state $1\sigma_g$ agrees with the exact result in 1.5% . The molecular excited states calculated with the variational cellular method agree with the exact values within 5% .

X. Conclusion

In this paper we have surveyed the possibility of the variational cellular method becoming a satisfactory tool for the solution of the Schrödinger equation in molecules and crystals. According to the theoretical framework of the method, no assumption is made about the shape of the cells. Thus, the motivation of the present work was to add to the flexibility of the cellular method a much faster convergency. It is just this flexibility that makes the method suitable to treat a wide range of problems.

It is already known from other calculations with the cellular method[4] that the resulting energy levels are insensitive to the choice of matching points, provided that a sufficiently large basis set is used. Our results for H_2^+ show that the statement above is valid as long as the number of points for surface integration is sufficiently larger than the maximum order of the angular momentum series. For high angular momenta and small number of points, the eigenvalues may even desappear. In all cases we verified that the value of C was a reliable criterion of precision of the calculation.

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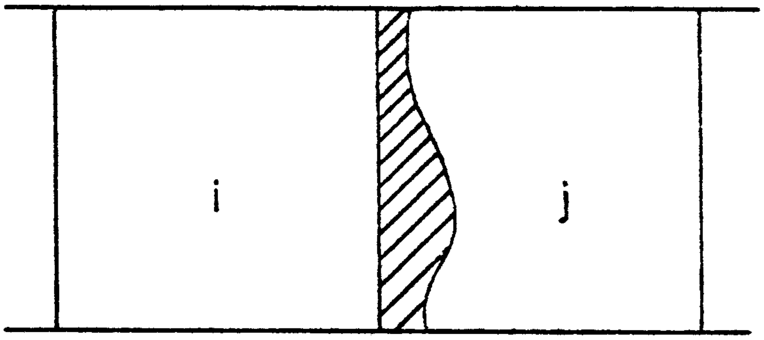

FIG. 1

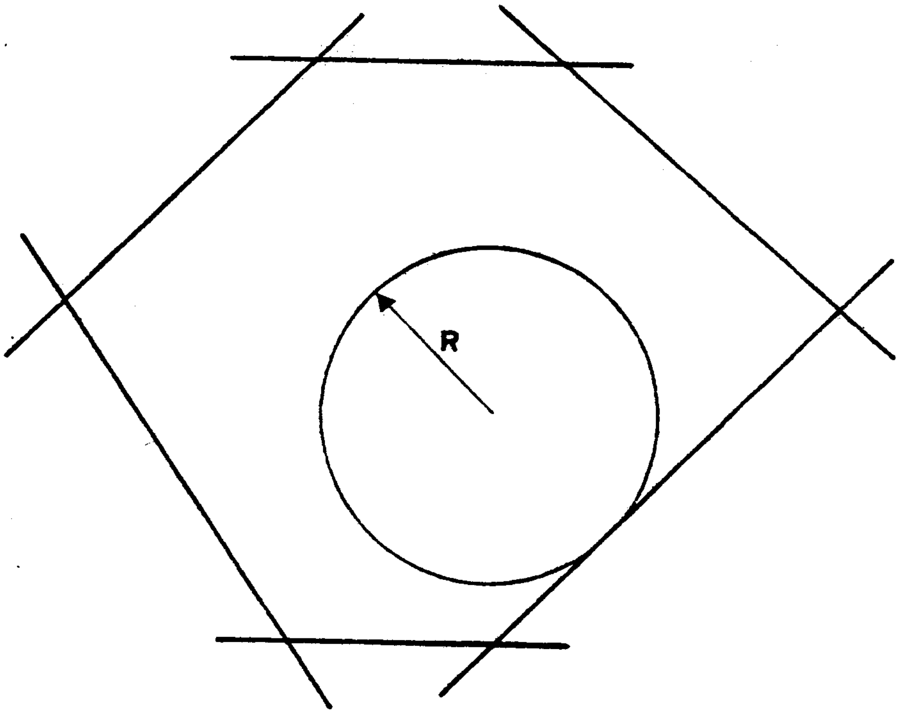

FIG. 2

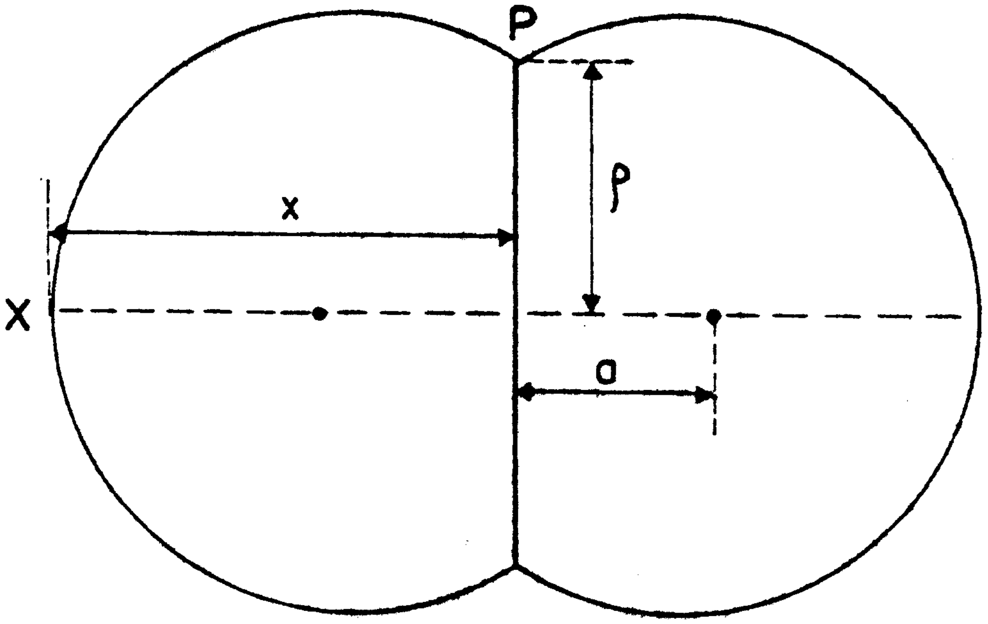

FIG. 3

FIGURE CAPTIONS

Figure 1 - Displacement of the boundary between two cells.

Figure 2 - Cell with the inscribed sphere with radius R .

Figure 3 - Partitioning of the molecular space for H_2^+ . The dots are the proton sites. The two atomic cells are spheres not centered at the protons and have a plane surface of contact. At the points P and X , Eqs. (7) are satisfied. The coordinates of these points are $\rho = 2.18\ a$ and $x = 2.31\ a$, where $2a$ is the interatomic distance. The outer cell extends from the atomic cells to infinity. The figure was not drawn to scale.

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 spherical surfaces and in the plane. The exact value of the $E_{1\sigma_g}$ level is 2.205 (Ref. 13).

ℓ_{max} POINTS	1	2	3	4	5
1	-2.12788				
2	-2.10705				
3	-2.09612	-2.16939			
4	-2.09279	-2.16140			
5	-2.09142	-2.15803	-2.15923	-2.18275	
7	-2.09031	-2.15523	-2.16075	-2.17621	
9	-2.08987	-2.15411	-2.16214	-2.17419	-2.21434
12	-2.08958	-2.15337	-2.16327	-2.17302	-2.18234
15	-2.08944	-2.15304	-2.16385	-2.17252	-2.17280
20	-2.08934	-2.15277	-2.16432	-2.17215	-2.17215

TABLE II

Behaviour of the criterion C of precision as a function of ℓ_{max} and "points". C is defined in the text by Eq. (20). The entries correspond to the $1\sigma_g$ level and this table should be compared with Table I.

ℓ_{max} POINTS	1	2	3	4	5
1	-0.21920				
2	-0.35569				
3	-0.36245	-0.06777			
4	-0.36509	-0.07643			
5	-0.36662	-0.08091	-0.06601	0.00880	
7	-0.36810	-0.08490	-0.04276	0.00134	
9	-0.36874	-0.08663	-0.03118	-0.00060	0.25710
12	-0.36919	-0.08781	-0.02285	-0.00158	0.08931
15	-0.36951	-0.08853	-0.01891	-0.00195	0.03114
20	-0.36968	-0.08879	-0.01580	-0.00221	0.00257

TABLE III

Lowest electronic energy levels of H_2^+ for the equilibrium internuclear distance $R = 2.0$ a.u.

ENERGY STATE	MULTIPLE SCATTERING MODEL[(a)] E (Ry)	OS MODEL[(b)] E (Ry)	CELLULAR MODEL E (Ry)	EXACT[(c)] E (Ry)
$1\sigma_g$	-2.0716	-2.155	-2.17215	-2.20525
$2\sigma_g$	-0.70738		-0.71108	-0.72173
$3\sigma_g$	-0.45574		-0.46451	-0.47155
$4\sigma_g$	-0.34859		-0.35128	-0.35536
$1\pi_g$	-0.44646		-0.45600	-0.45340
$1\sigma_u$	-1.2868	-1.366	-1.41200	-1.33507
$2\sigma_u$	-0.49722		-0.50483	-0.51083
$3\sigma_u$	-0.26979		-0.27204	-0.27463
$4\sigma_u$	-0.24997		-0.25017	-0.25329
$1\pi_u$	-0.88866	-0.860	-0.90525	-0.85755

(a) see Ref. 10

(b) see Ref. 12

(c) see Ref. 13