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Self-consistent calculation of the electronic structure of N_2 and CO by the variational cellular method

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In this paper the variational cellular method is extended to the self-consistent calculation of diatomic molecules. This extension is based on a new variational expression for the total molecular energy the extremum of which defines the one-electron potential of the Schrödinger equation. The method was tested in the calculation of N_2 and CO and the results are very good: the binding energy and the equilibrium interatomic distances were calculated to be within less than 10% of the known experimental results.

I. INTRODUCTION

In a previous paper,[1] which will be referred to as I, we proposed a general formulation of the variational cellular method (VCM) for molecules and crystals. As an example of the accuracy and fast convergence of the method, computation of the energy spectrum of the molecular hydrogen ion H_2^+ was shown. Now we present the continuation of our investigations of the cellular model as applied to the study of molecular electronic structure of diatomic molecules. The aim of this paper is to show the advantages of the VCM in calculating self-consistent potential curves and ionization energies for the lowest states of N_2 and CO.

The two major virtues of the cellular theory are removal of the muffin-tin approximation, which is inherent to the multiple-scattering-$X\alpha$ (MS) technique,[2] and an arbitrary partition of the molecular space. Diatomic molecules are particularly well suited to guide our first self-consistent calculations, since they are small systems and the non-muffin-tin corrections to the molecular potential are expected to be large.[3]

The paper is organized as follows: In Sec. II we show how one can construct an accurate self-consistent potential within the cells and evaluate the molecular total energy. The details of the mathematical development are left to the Appendix. In Sec. III we return to the problem of choosing the cells, but now aiming at making the total energy stationary, and discuss some principles for the choice of the basis sets for wave-function expansion.[4] The results for the ground-state potential curves of N_2 and CO and the ionization spectrum of N_2 computed by the VCM are reported in Sec. IV. Our conclusions are summarized in Sec. V.

II. VARIATIONAL EXPRESSION FOR TOTAL MOLECULAR ENERGY

A. Total-energy functional

In our general formulation of the variational cellular method in I two important items are missing: that of the definition of the potential for the Schrödinger equation and that of calculating the total energy. At the time of writing that paper our only experience was with the H_2^+ molecular ion, for which both questions are irrelevant. When we came to the problem of applying the cellular method to other molecules, we had to face these two questions for which we had no ready answer.

The two questions of how to define the potential and how to calculate the total energy are actually a single question. Indeed, the total energy should be calculated according to a variational expression whose extremum defines the potential. Thus the real question is what should be the variational expression for the energy? There is not a unique answer to this problem. For instance, in the MS method one adopts an expression which has built-in approximations of the charge density and potential in the muffin-tin form.[5] In the cellular method we could proceed analogously and make averages for fixed radii r in the cell. As a matter of fact, we tried this procedure, and with results much better than those of the MS method for the N_2 molecule, but worse than those obtained with the procedure to be explained below.

The variational expression we adopted is the following:

$$E = \sum_i K[\psi_i, \psi_i^*] + E_x[n] + U[n - p, c] - S[p] + \int v(\rho - n) . \tag{1}$$

The terms of which require explanation. First of all, $p(\vec{r})$ is the proton density, that is, a collection of δ functions at the nuclei. Second, one distinguishes the *real* electronic density

$$\rho = \sum_i \psi_i^* \psi_i , \tag{2}$$

which is a sum over the occupied states of the squared wave functions ψ_i, from the *assumed* electronic density $n(\vec{r})$. In any method for electronic-structure calculation, when integrating the Poisson equation one cannot avoid simplifying the charge density. That is the reason why we assume a density $n(\vec{r})$ possibly different from the real density $\rho(\vec{r})$.

The terms in Eq. (1) are defined as follows: (i) The first term

$$\sum_i K[\psi_i, \psi_i^*] ,$$

is the kinetic energy functional, normally written

$$-\sum_i \int \psi_i^* \nabla^2 \psi_i ,$$

but which, in the cellular method, has surface-integral contributions as in Eq. (2) of I. (ii) The second term, $E_x[n]$, is the exchange functional. The existence of such a functional was proved by Hohenberg and Kohn.[6] Normally, this functional would be written as a local approximation. (iii) The third term, $U[n-p, c]$, is an electrostatic Coulomb energy functional; c is the Coulomb potential, which, if written

$$c(\vec{r}) = 2 \int \frac{n(\vec{r}\,') - p(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' , \tag{3}$$

reduces U to the form

$$U = \tfrac{1}{2} \int [n(\vec{r}) - p(\vec{r})]\, c(\vec{r})\, d\vec{r} . \tag{4}$$

The electrostatic energy functional in the MS method is simplified to a version with a muffin-tin average of $n(\vec{r})$. This simplification is a possible source of uncontrollable errors in the MS method. In our case we chose a different policy: we adopted a functional which reduced to Eq. (4) if the real potential of Eq. (3) was used. But in this functional we used a potential suited to the needs of the cellular method instead of the exact potential of Eq. (3). (iv) The fourth term, $S[p]$, is the self-energy of the nuclei, which must be discounted from the electrostatic energy of the distribution $n-p$. (v) The last term, $\int v(\rho - n)$, makes it possible to deal with two densities: the real density ρ and the assumed density n. Instead of satisfying the equation

$$n = \rho \tag{5}$$

everywhere, we introduce the Lagrange multiplier function v, and Eq. (5) is incorporated into the variational expression, Eq. (1).

The expression for the total energy is stationary for arbitrary variations in ψ_i, ψ_i^*, n, v, and c.

a. Variations in ψ_i. An arbitrary variation in ψ_i leads to the Schrödinger equation, or Eq. (3) of I. In each cell the wave function that makes E stationary satisfies

$$-\nabla^2 \psi_i + v\psi_i = \epsilon_i \psi_i . \tag{6}$$

In other words, the Lagrange multiplier function v is none other than the one-electron potential.

b. Variations in v. An arbitrary variation in v leads to

$$\rho - n = 0 .$$

Thus E is stationary when the assumed and real electronic densities coincide.

c. Variations in n. Variations in n lead to the equation

$$\frac{\delta E_x}{\delta n} + \frac{\delta U}{\delta n} - v = 0 .$$

The first term is the exchange potential. Since v is the one-electron potential, $\delta U/\delta n$ must be the Coulomb potential c. Thus the electrostatic energy functional U must be such that

$$\frac{\delta U}{\delta n} = c . \tag{7}$$

d. Variations in c. Since E is extreme, the functional U must be extreme at the true solution, or

$$\frac{\delta U}{\delta c} = 0 , \tag{8}$$

when c equals the expression given by Eq. (3). In that case U must equal the expression of Eq. (4).

B. Electrostatic-energy functional

As seen above, the electrostatic energy U must be a functional of

$$q = n - p$$

and c, such that its extreme in c coincides with the true value [Eq. (4)], c coinciding with the expression given by Eq. (3). Second, the functional U must be such that

$$\frac{\delta U}{\delta q} = c . \tag{7a}$$

Restricting ourselves to functionals that are quadratic in q and c in the sense that, for any given number x,

$$U[xq, xc] = x^2 U[q, c] ,$$

then the above requisites become mutually dependent. Indeed, letting x be a small positive number ($x \ll 1$) then

$$U[(1+x)q,(1+x)c]=(1+x)^2U[q,c]$$

$$=U[q,c]+x\int q\frac{\delta U}{\delta q}+x\int c\frac{\delta U}{\delta c}.$$

But

$$\frac{\delta U}{\delta q}=c \tag{7b}$$

and

$$\frac{\delta U}{\delta c}=0 \tag{8a}$$

at the extreme. Thus

$$U[q,c]=\tfrac{1}{2}\int qc.$$

The requisites described above are still insufficient to define U completely. From now on we cannot proceed without a definite choice of the form for the functional. In Fig. 1 we show a partition of a diatomic molecule in cells. For each cell we draw an inscribed sphere. For the atomic cells, these spheres are centered at the nuclei. For the outer cell, the sphere is centered at any chosen point. We choose different expressions for c within each cell and within each inscribed sphere. Letting c_i denote the Coulomb potential at a cell i outside the inscribed sphere (or inside the inscribed sphere for the outer cell) and c_i' the Coulomb potential inside the inscribed sphere of cell i (or outside, in the case of the outer cell), we choose the following functional:

$$U[q,c]=\int qc-\frac{1}{16\pi}\int\nabla c\cdot\nabla c+\frac{1}{16\pi}\sum_{\text{cells}}\int dS(c_i-c_j)(\partial_n c_i-\partial_n c_j)+\frac{1}{8\pi}\sum_{\text{spheres}}\int dS(c_i'-c_i)\partial_n c_i', \tag{9}$$

which resembles the functional we used to define the variational cellular method in I. The first two terms in Eq. (9) are volume integrals in the whole space. The last two terms are surface integrals. The third term are integrals in the cell surfaces, while the fourth are integrals in the inscribed spheres. The meaning of the normal derivatives ∂_n has been explained in I.

Equation (9) satisfies all the requisites for U. First, Eq. (7a) is obviously satisfied. Second, when finding the extreme of U we must consider arbitrary variations in c_i and c_i'. From Eq. (9) one readily sees that the variation in U is null if

$$\nabla^2 c=-8\pi q \tag{10}$$

everywhere, and c is continuous and has normal continuous derivatives at the cell surfaces and at the spheres. Equation (10) is the Poisson equation the unique solution of which in the unlimited space is given by Eq. (3).

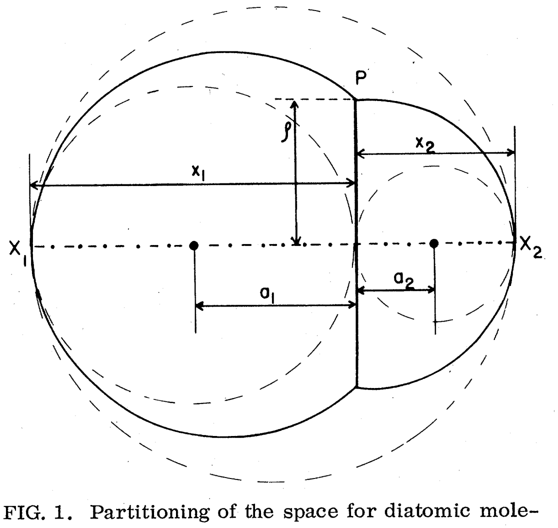

FIG. 1. Partitioning of the space for diatomic molecule. The dots are the proton sites. The two atomic cells are spheres not centered at the protons and have a plane surface of contact.

C. Choice of *n*, *v*, and *c*

As explained in I, in the cellular method, it is easy to determine the spherical average of the electronic density $n_i(r)$ in the inscribed sphere of cell i. Further, without much computational effort, one can determine the total electronic occupation for each cell, and thus one determines an average density $\bar{n}_i$ in the space of cell i outside its inscribed sphere. Thus, without any special techniques of space integration, one can define a function which is spherical inside the inscribed spheres and flat outside, but with the constant value $\bar{n}_i$ depending on the cell. The first question to answer is how this choice of $n(\vec{r})$ limits the precision of the calculation and the quality of the results. According to Eq. (1), a deviation $\delta n(\vec{r})$ from the exact value $\rho(\vec{r})$ produces a first-order change in the energy given by

$$\delta E=\int\delta n\left(\frac{\delta E_x}{\delta n}+c-v\right).$$

When one reaches self-consistency

$$v=c+\frac{\delta E_x}{\delta n}, \tag{11}$$

showing that the error in $n(\vec{r})$ has no first-order effect on the total energy E.

The exchange potential $\delta E_x/\delta n$ we used was the $X\alpha$ exchange[7] with the parameter $\alpha = 0.75$ in each cell. This value is slightly different from the atomic Hartree-Fock values, 0.751 97 for N, 0.759 28 for C, and 0.744 47 for O.[8] However, the modifications in the calculated results introduced by the use of more accurate values of α do not change the conclusions of this work. More elaborate forms of the local approximation[9,10] could have been used but the $X\alpha$ exchange is convenient for purposes of comparison with Hartree-Fock results.

We chose a Coulomb potential c satisfying the Poisson equation [Eq. (10)] everywhere and, in each cell, direction independent. Inside the inscribed sphere we use

$$c_i'(r) = A_i' - \frac{2Z_i}{r} + \frac{8\pi}{r}\int_0^r r^2 n_i(r)dr - 8\pi\int_0^r r n_i(r)dr\,, \tag{12a}$$

but for the outer cell

$$c_0'(r) = -\frac{8\pi}{r}\int_r^\infty r^2 n_0(r)dr + 8\pi\int_r^\infty r n_0(r)dr\,. \tag{12b}$$

Outside the spheres we use

$$c_i(r) = A_{i,0} + A_{i,1}/r - \tfrac{4}{3}\pi\bar{n}_i r^2\,. \tag{13}$$

In the above equations A_i', $A_{i,0}$, and $A_{i,1}$ can assume any values and Eq. (10) will remain valid. Their values will be determined by making $U[n-p, c]$ extreme. Now the form adopted for the functional U[Eq. (9)] has the special feature that

$$1 - \frac{\partial U}{\partial A_i'} = 0 \tag{14}$$

independently of the values of A_i', $A_{i,0}$, $A_{i,1}$. That is to say, the potential c inside the inscribed spheres can be shifted at will without affecting the value of U. This permits us to force the continuity of c at the inscribed spheres, except at the sphere of the outer cell, for there we have no freedom to shift the potential, as one sees from Eq. (12b). It is intuitive that, whenever possible, forcing continuity should be better than not forcing it. Mathematically, one sees from Eq. (9) that, if c_i' satisfies the Poisson equation and is continuous with c_i, U is extreme with respect to *any* variation in c_i', that

$$2 - \sum_i \frac{\partial U}{\partial A_{i,0}} = 0 \tag{15}$$

for any values of $A_{i,0}$, $A_{i,1}$, A_i'. This means that the constants $A_{i,0}$ can be shifted equally without affecting the value of U. Thus we choose to shift these constants so that at the sphere of the outer cell the potential is continuous.

Summarizing, we can say that the constants A_i', $A_{i,0}$, $A_{i,1}$ are chosen so that U is extreme and c is continuous at the inscribed spheres, even for the outer cell. These conditions determine the values of the constants uniquely. The potential outside the spheres is shifted so that one obtains continuity at the outer sphere, and the potential inside the inner spheres is shifted so that the continuity at these spheres is assured. We leave to the Appendix the details of the mathematical development.

To conclude this section, we return to the problem of calculating the total energy. Now, the calculation of all terms in Eq. (1) has been explained. When one inserts the Coulomb potential, defined above, in U we obtain

$$U[n-p, c] \neq \tfrac{1}{2}\int (n-p)c\,.$$

This is a logical consequence of assuming a potential c suited for the solution of the Schrödinger equation by the cellular method. The fact that Eq. (4) does not hold should not matter as long the total energy and the one-electron energy spectrum are calculated well. We must also add that the energy thus calculated is not necessarily a minimum for the ground state but just an extreme. Because of the last term in Eq. (1) and the second term in Eq. (9), one cannot prove that the ground state is a minimum.

III. CELL SHAPES AND BASIS SETS

In Fig. 1 we show the shape of the cells for diatomic molecules. The surfaces are two calottes, not necessarily centered at the nuclei, and one plane. In each cell we draw an inscribed sphere (dashed lines). Here a_1 and a_2 are the coordinates of the nuclei. The points x_1 and x_2 of the calottes were chosen so that

$$x_1 = 2a_1\,, \quad x_2 = 2a_2\,.$$

In the case of N_2 the plane is obviously in the middle of the segment joining the nuclei. Thus the only cell parameter that can be varied is the coordinate ρ of point P. In the case of CO, the position of the plane should also be chosen.

In Sec. III of I we presented a proposal for cell construction. In this paper, after obtaining the variational expression for the total molecular energy, we can do better than following the guideline established in I, for we can vary the cells to make the energy extreme. This new policy was used for N_2, where we varied the value of the coordinate ρ. The results of this study are reported in the Sec. IV. In the case of CO we found that obtaining the energy extreme was very time consuming, for we had to play with two cell parameters: the position of the plane and the parameter ρ. Thus we decided to construct the cells putting the plane in such a way that the interatomic distance was divided proportionaly to the covalent radii of the atoms. As for ρ, we chose to make the surface bounding the outer cell coincident with the inscribed sphere. Thus the C and O cells were limited by a single sphere. The fact that this simple recipe works informs us that cell construction can be made based on such simple procedures of the muffin-tin methods as the multiple-scattering and augmented-plane-wave techniques.

A word must also be said regarding the charge density. In Sec. II we have distinguished between the *assumed* density $n(\vec{r})$ and the true density

$$\rho(\vec{r})=\sum_i \psi_i^* \psi_i .$$

We have developed the theory by assuming $n(\vec{r})$ muffin tins per cell, that is, $n(\vec{r})$ is spherical in the inscribed spheres and constant outside the spheres but inside the cell boundaries. The values $\bar{n}_i$ of these constants may be cell dependent. Coming to the actual calculation of CO, we found that permitting $\bar{n}_i$ to be cell dependent leads to slow self-consistent convergences. Thus for CO we made the charge density muffin tin.

Regarding the choice of a basis set for the cellular method we must report the following results. First of all, the secular matrix [Eq. (4) of I] is such that it has zero along the diagonal. In the case of a diatomic molecule AB with three cells, namely A, B, and the external cell E, the form of the matrix is sketched in Fig. 2. When inverting the matrix to find I_{TIM} (see Sec. VI of I) or when calculating the determinant, one verifies that it is identically zero if the number of degrees of freedom in a certain cell (the number of basis functions in that cell) is larger than the sum of the degrees of freedom of neighboring cells. For instance, when the blocks *EA* and *EB* in Fig. 2 form a rectangle with a height larger than the base, the determinant of the matrix is null. In this example the height of the rectangle is the number of basis functions in the cell E, while the base is the number of functions of A plus that of B. Furthermore, if the two blocks *EA* and *EB* form a square matrix, the determinant of the total matrix becomes the square of the determinant of the blocks. This determinant does not depend on the matrix elements of blocks *AB* and the zeros of the determinant are double. Of course, this is an unfavorable situation that must be avoided. Thus the basis set must be such that

$$F_i<\sum_j F_j , \tag{16}$$

where F_i is the number of degrees of freedom (number of functions in the basis) in the cell i and the sum extends over the cells bounding cell i.

Equation (16) needs reinterpretation when one considers the reflexion symmetry in a molecule such as N_2. After reduction of the secular matrix by symmetry, it acquires the form sketched in Fig. 3. Now the block *AA* at the diagonal is no longer null and Eq. (16) is not necessary for $i=A$. On the other hand, for $i=E$, Eq. (16) becomes

$$F_E<F_A . \tag{16a}$$

In the case of N_2, adopting the policy of using in the external cell the maximum basis compatible with Eq. (16a), we constructed the following bases for the many irreducible representations presented in Table I. In the actual calculation we used the bases with five degrees of freedom.

In the case of CO, we construct bases with equal numbers of functions in the two atomic cells and, in the external cell, a number which is the maximum allowed by Eq. (16). Such bases are in Table II. In the actual calculation we started from the bases with eleven degrees of freedom and reduced the number of functions in the external cell, aiming at minimizing the value of the criterion C of Eq. (20) of I. We were contented when we found a value of C on the order of ± 0.1 or less, because, from our experience, a further reduction of C below this value has negligible consequences for the the calculated values of the energy. Table III illustrates that experience.

In a calculation by the VCM the criterion C seems to be a safe guide for the choice of the basis set. In the cellular method it is not enough to have a large basis set but it is also necessary to balance the number of functions in each cell. To see this point, consider expanding C in cell

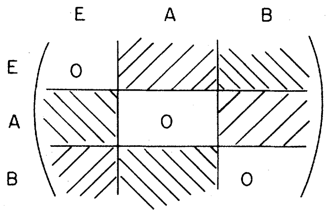

FIG. 2. Secular matrix for a molecule AB with three cells A, B, and E. There are nine blocks, the three lying along the diagonal being null.

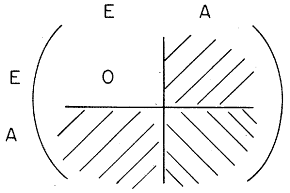

FIG. 3. Secular matrix for a homonuclear diatomic molecule after reduction of the matrix sketched in Fig. 2 by reflexion symmetry.

components

$$C=\sum_i C_i\,, \tag{17}$$

where

$$C_i=\Bigl(\sum_{j}\int dS_{ij}\,[\overset{0}{\psi}{}_i^*(\partial_n\psi_i+\partial_n\psi_j)+\partial_n\overset{0}{\psi}{}_i^*(\psi_j-\psi_i)]+\text{c.c.}\Bigr)\Big/2\sum_k\int d\Omega\,\psi_k^*\psi_k\,. \tag{18}$$

After a bit of algebra one obtains

$$C_i=(C-1)P_i+\sum_{\lambda\lambda'}A_{i\lambda}^*N_{\lambda\lambda'}^{(i)}A_{i\lambda'}\Big/\sum_j\sum_{\lambda\lambda'}A_{j\lambda}^*N_{\lambda\lambda'}^{(j)}A_{j\lambda'}\,, \tag{19}$$

where the symbols in the right-hand side are explained in I. Now assume that cell i has a small number of degrees of freedom and the neighbors have huge numbers. Then it is very likely that $\partial_n\psi_i+\partial_n\psi_j$ and $\psi_j-\psi_i$ are very small for the simple reason that there are enough degrees of freedom in the neighboring cells j to guarantee the smallness of these differences. In this case, according to Eq. (18), C_i is small. On the other hand, there are no guarantees that the other C_j are equally small for they correspond to surface integrals where one has competing degrees of freedom. Thus, when one of the C_i is much smaller than the others, it is likely that we will lack basis functions in the corresponding cell. Analogously, a C_i much larger than the others very likely indicates an excess of basis functions in that cell because the functions of neighboring cells are unable to match the wave function of cell i at the cell surfaces.

TABLE I. Bases for N_2 with the maximum number of angular momenta in the external cell, compatible with Eq. (16a).

Symmetry	Total degrees of freedom	Angular momenta l Atomic cells	External cell
σ_g	3	0,1	0
	5	0,1,2	0,2
	7	0,1,2,3	0,2,4
σ_u	3	0,1	1
	5	0,1,2	1,3
	7	0,1,2,3	1,3,5
π_g	3	1,2	2
	5	1,2,3	2,4
	7	1,2,3,4	2,4,6
π_u	3	1,2	1
	5	1,2,3	1,3
	7	1,2,3,4	1,3,5

Thus the components C_i of criterion C may orient the search for a well-balanced basis set for which C would be minimum.

IV. RESULTS

This Section gives the results for our VCM self-consistent calculations for N_2 and CO. We are interested in the ground-state potential curves, and therefore in the lowest energy-dissociation limit.

Near equilibrium N_2 in the ground state has paired spins in a molecular closed-shell configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$. According to Hartree-Fock calculations,[11] the molecule will dissociate into two neutral atoms at infinite separation with total energy −217.60 Ry. A free nitrogen atom in its lowest energy state is an open-shell system which has a ^4S configuration. In Fig. 4 the curve of the total energy E of N_2 as a function of the interatomic distance R, obtained by using Eq. (1) to define the energy, is shown. This curve is labeled VCM and lies

TABLE II. Bases for CO with equal number of functions in the atomic cells, and the maximum number in the external cell compatible with Eq. (16).

Symmetry	Total degrees of freedom	Angular momenta l C	O	External
σ	7	0,1	0,1	0,1,2
	11	0,1,2	0,1,2	0,1,2,3,4
	15	0,1,2,3	0,1,2,3	0,1,2,3,4,5,6
π	7	1,2	1,2	1,2,3
	11	1,2,3	1,2,3	1,2,3,4,5
	15	1,2,3,4	1,2,3,4	1,2,3,4,5,6,7

TABLE III. Self-consistent one-electron energies and total molecular energy (Rydbergs) for N_2 calculated with different bases and/or different number of points for the surface integrations. The interatomic distance was $2.04a_0$.

Basis	5 degrees of freedom		7 degrees of freedom		7 degrees of freedom	
Number of points	5		5		10	
Electron state	Eigenvalue	c	Eigenvalue	c	Eigenvalue	c
$2\sigma_g$	−1.832	−0.147	−1.851	−0.094	−1.851	−0.091
$3\sigma_g$	−0.562	−0.104	−0.597	−0.011	−0.581	−0.029
$2\sigma_u$	−0.950	0.022	−0.971	−0.029	−0.954	0.004
$1\pi_u$	−0.865	−0.076	−0.865	−0.066	−0.864	−0.071
Total energy	−217.959		−218.109		−218.015	

below the dashed line, which denotes the atomic dissociation limit. For comparison, the results of a MS-$X\alpha$ calculation (labeled MS) are also shown.[12] Our results were obtained by partitioning the molecular space into three cells (see Fig. 1), assuming that the atomic ones are equal and $x = \rho = 2a$, where $2a$ is the interatomic distance. The computations were performed using the bases with five degrees of freedom in Table I.

It is well known that the MS method, within the framework of the standard muffin-tin potential approximation, is unreliable for predicting the equilibrium conformation of diatomic molecules.[12] The non-muffin-tin corrections to the potential play a fundamental role in these cases.[3] On the other hand, the cellular method leads to a ground-state potential curve, shown in Fig. 4, which displays a minimum very close to the experimental bond length, $2.073\,a_0$.[13] The arrow in the figure denotes the location of the minimum, at $2.10a_0$. In order to obtain a more accurate value for the N_2 dissociation energy, we performed a study of the molecular total energy as a function of the cell parameter ρ (see Fig. 1). In this study we suppose that the atomic cells are equal, where $X = 2a = 2.10a_0$. The calculations were carried out assuming that the constant values of the averaged charge density outside the inscribed spheres

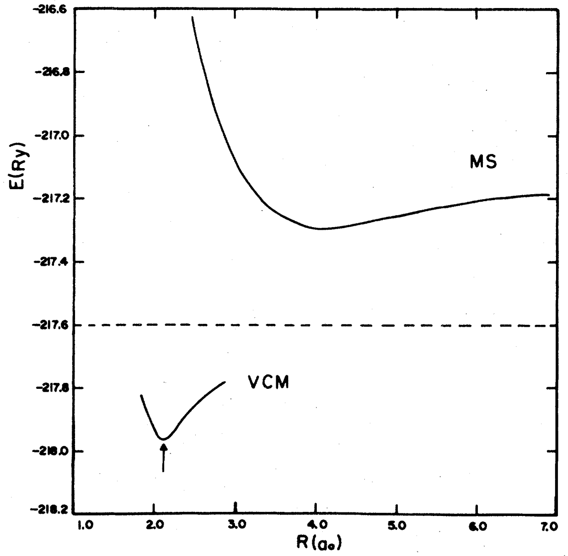

FIG. 4. Total energy of N_2 as a function of the interatomic distance. MS refers to the MS-$X\alpha$ results (Ref. 12). VCM refers to the variational cellular method calculation. The arrow indicates the minimum of the VCM curve. The dashed line denotes the atomic dissociation limit.

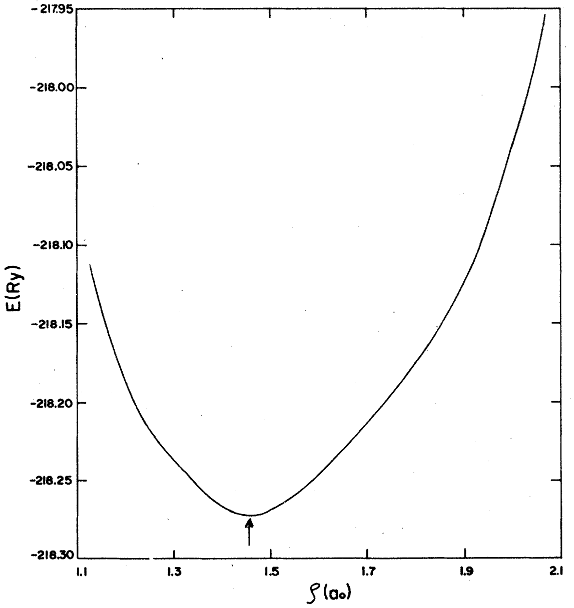

FIG. 5. Total energy of N_2 as a function of the cell parameter ρ, as calculated by the VCM Method. The arrow indicates the minimum total energy.

TABLE IV. Equilibrium separations R_e and dissociation energies D_e for the ground state N_2.

Data source	R_e (a_0)	D_e (eV)
EXP[a]	2.07	9.91
VCM[b]	2.10	9.13
MS-NMT[c]	2.20	7.71
RHF[d]	2.01	5.27

[a] See Ref. 13.
[b] This work.
[c] See Ref. 3.
[d] See Ref. 14.

TABLE V. Comparison of the theoretical and experimental ionization energies of the ground state of N_2; R is the interatomic distance and energies are in eV.

Orbital	EXP[a]	VCM[b] $R=2.1a_0$	MS[c] $R=2.068a_0$	RHF[d] $R=2.068a_0$
$1\sigma_{g,u}$	409.9	404.8	407.6	426.7
$2\sigma_g$	37.3	30.3	31.5	40.1
$3\sigma_g$	15.5	13.0	14.1	17.3
$2\sigma_u$	18.6	18.6	18.3	21.2
$1\pi_u$	16.8	16.7	18.2	16.8

[a] See Ref. 17.

[b] This work. Calculated according to transition-state concept.

[c] See Ref. 12. Calculated according to transition-state concept.

[d] See Ref. 14. Calculated according to Koopman's theorem from orbital energies listed in Table IV.

are dependent on the cell. Thus, in general, $\bar{n}_0$ is different from $\bar{n}_i$. From Fig. 5, where the results are shown, one observes that the functional total energy as a function of ρ has an extreme. It is a minimum at $\rho=1.452a_0$ and corresponds to a total energy equal to -218.271 Ry. Therefore VCM predicts a dissociation energy for N_2 very close to the experimental value of 9.91 eV.[13]

In Table IV we list the bond length and the dissociation energy for ground-state N_2, obtained from our calculations, along with the experimental results[13] and two other theoretical predictions for comparison. MS-NMT refers to the calculation carried out by Danese with the MS-$X\alpha$ method, including linear and second-order corrections in the non-muffin-tin (NMT) charge density.[3] RHF refers to the restricted Hartree-Fock results, obtained from an *ab initio* molecular-orbital–linear-combination-of-atomic-orbitals–self-consistent-field (MO-LCAO-SCF) calculation.[14] VCM results for R_e and D_e are in good agreement with the experimental ones. The VCM bond length for N_2 compares well with those calculated by MS-NMT and RHF methods. However, VCM predicts the best value for the molecular dissociation energy. Sambe and Felton reported the value $R_e=2.07a_0$ for N_2 obtained through an alternative approach to the NMT problem.[15] The so-called intersecting-sphere model developed recently by Antoci and co-workers was also applied to calculate the potential curve of this molecule.[16] It leads to the results $R_e=2.34a_0$ and $D_e=8.46$ eV, this last value taken in respect to the spin-restricted dissociation limit.

In Table V are the orbital binding energies for N_2. It includes the results obtained from the electron-spectroscopy-for-chemical-analysis experments[17] (EXP), followed by our calculations (VCM). The third column (MS) refers to a MS-$X\alpha$ calculation assuming the standard muffin-tin approximation to the molecular potential, and the fourth to the RHF results. The transition-state concept[7] was utilized to calculate the VCM and MS entries. The RHF values were obtained according to Koopman's theorem from orbital energies listed in Table IV of Ref. 14. Our calculations were carried out considering the atomic cells equal and $x=\rho=2a=2.10a_0$. The two other calculations used the value $2.068a_0$ for the bond length. The greatest discrepancy between the VCM and the experimental values is 7 eV and refers to the lower valence state $2\sigma_g$. The highest valence states $2\sigma_u$ and $1\pi_u$ are very well described. Both VCM and MS predict that the highest occupied molecular level should have σ_g symmetry, in agreement with experiment, whereas RHF predicts that should have π_u symmetry. However, we must bear in mind that electron relaxation effects were neglected in the LCAO calculation. We could improve the VCM description of the lower valence states further by assuming the value $1.452a_0$ for the cell parameter ρ. We point out that this corresponds to the minimum value for the molecular total energy.

The CO molecule in the ground state has paired spins in a molecular closed-shell configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(5\sigma)^2$. The free carbon and oxygen atoms in their lowest energy states are open-shell systems which have a ^3P configuration. The molecule will dissociate into two neutral atoms at infinite separation with Hartree-Fock total energy -224.996 Ry.[11]

Figure 6 shows the behavior of the cellular total-energy functional E given by Eq. (1) as a function of the interatomic distance R for CO. The curve is labeled VCM and refers to a non-spin-polarized calculation. The effects of the spin alignments are considered small near equilibrium. For comparison the MS-$X\alpha$ results, obtained from a spin-polarized calculation, are also shown.[3] The cell parameters used in our calculations were (see Fig. 1) $x_c=2a_c$, $x_0=2a_0$, and $\rho=(2a_ca_0)^{1/2}$. The parameters a_c and a_0 refer to carbon and

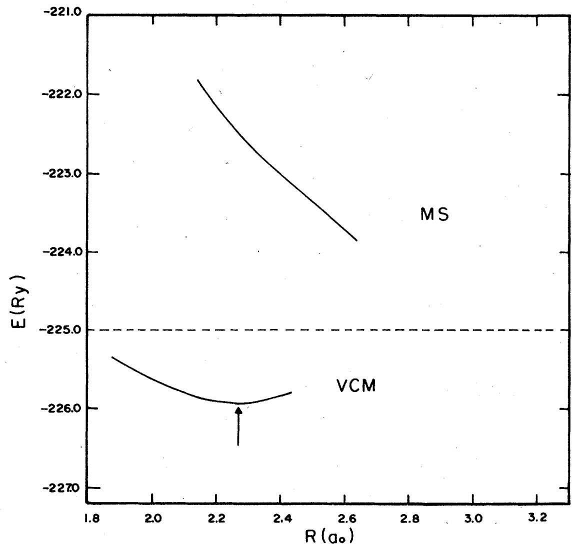

FIG. 6. Total energy of CO as a function of the interatomic distance. MS refers to the MS-$X\alpha$ results (Ref. 3). VCM refers to the variational cellular method calculation. The arrow indicates the minimum of the VCM curve. The dashed line denotes the atomic dissociation limit.

oxygen cells and are proportional to the covalent radii of carbon and oxygen[18]; $a_c + a_0$ is the interatomic distance R. The basis sets used had nine degrees of freedom, evenly distributed among the three cells. Only for the 4σ level we used the basis with eleven degrees of freedom listed in Table II. All the calculations were carried out assuming, for each interatomic distance, the same value for the average charge density outside the inscribed sphere of each cell (muffin-tin charge density).

The VCM curve in Fig. 6 displays a minimum at $R = 2.27a_0$, which corresponds to the molecular total energy −225.667 Ry. In Table VI the equilibrium separations and dissociation energies for ground-state CO as calculated by VCM and MS-NMT[3] are compared with the experimental values.[19] Agreement between VCM and experimental results similar to that for the N_2 molecule is found here. The MS-NMT method gives approximatively half of the molecular binding energy.

Table VII shows the one-electron energies for CO as calculated by VCM. The MS-$X\alpha$[20] and RHF[21] results are also included for comparison. Since the relaxation effects were neglected in these calculations, the experimental results for the ionization energies were not shown. The ordering of the levels is the same for the three calculations. The discrepancies between the VCM and MS results are small: approximately 6 eV for the core level 1σ and 1 eV for remaining levels. However, both methods lead to one-electron orbital energies quite different from RHF results.

TABLE VI. Equilibrium separations R_e and dissociation energies D_e for the ground state of CO.

Data source	R_e (a_0)	D_e (eV)
EXP[a]	2.13	11.1
VCM[b]	2.27	12.9
MS-NMT[c]	2.43	5.33

[a] See Ref. 19.
[b] This work.
[c] See Ref. 3.

CONCLUSIONS

The variational cellular method seems to be a very precise and fast method, at least for diatomic molecules. Its speed is comparable to that of the standard multiple-scattering method but it is much better in the calculation of the total molecular energy. From the theoretical point of view one can expect more precision from the VCM than from the MS, as one does not use a muffin-tin potential or an approximative expression for the total energy.

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TABLE VII. Orbital one-electron energies of CO; R is the interatomic distance and energies are in eV.

Orbital	VCM[a] $R = 2.132a_0$	MS[b] $R = 2.132a_0$	RHF[c] $R = 2.132a_0$
1σ	509.86	516.1	562.2
2σ	274.99	276.1	309.1
3σ	26.11	27.2	41.4
4σ	12.65	13.5	21.9
1π	11.69	12.8	17.4
5σ	7.21	8.1	15.1

[a] This work.
[b] See Ref. 20.
[c] See Ref. 21.

APPENDIX: CALCULATION OF COULOMB POTENTIAL AND TOTAL ENERGY

When c satisfies the Poisson equation, the functional U reduces to

$$U[n-p,c]=\tfrac{1}{2}\int(n-p)c-\frac{1}{16\pi}\sum_{\text{cells}}\int dS(C_j\partial_n C_i+C_i\partial_n C_j)+\frac{1}{16\pi}\sum_{\text{spheres}}\int dS(C_i'-C_i)\partial_n C_i'$$
$$+\frac{1}{16\pi}\sum_{\text{spheres}}\int dS\,C_i(\partial_n C_i'+\partial_n C_i)\,. \tag{A1}$$

We consider the equations

$$\frac{\partial U}{\partial A_{i,n}}=0\,, \tag{A2}$$

with $n=0$, 1 according to Eq. (13). Defining R_i as the radius of the inscribed sphere,

$$Q_i=Z_i-4\pi\int_0^{R_i}r^2 n_i(r)dr \tag{A3a}$$

$$=-4\pi\int_{R_0}^{\infty}r^2 n_0(r)dr\quad\text{(outer sphere)}, \tag{A3b}$$

$$S_i=1 \tag{A4a}$$

$$=-1\quad\text{(outer cell)}, \tag{A4b}$$

we obtain the following set of linear equations for $A_{i,n}$:

$$\sum_{j,m}\langle i,n|j,m\rangle A_{j,m}+\sum_j \alpha_{i,n,j}\bar{n}_j+\beta_{i,n}Q_i=0\,, \tag{A5}$$

where the coefficients of Q, $\bar{n}$, and A are

$$\beta_{i,0}=1\,, \tag{A6a}$$

$$\beta_{i,1}=-1/R_i\,, \tag{A6b}$$

$$\alpha_{i,0,i}=\tfrac{1}{6}\sum_j\int dS_{ij}r_i\partial_n r_i-\tfrac{4}{3}\pi R_i^3 s_i\,, \tag{A7a}$$

$$\alpha_{i,0,j}=\tfrac{1}{6}\int dS_{ij}r_j\partial_n r_j\quad(j\neq i)\,, \tag{A7b}$$

$$\alpha_{i,1,i}=\tfrac{1}{4}\sum_j\int dS_{ij}\,\partial_n r_i-\tfrac{4}{3}\pi R_i^2 s_i\,, \tag{A7c}$$

$$\alpha_{i,1,j}=\tfrac{1}{6}\int dS_{ij}\frac{r_j}{r_i}\partial_n r_j$$
$$-\tfrac{1}{12}\int dS_{ij}\frac{r_j^2}{r_i^2}\partial_n r_i\quad(j\neq i)\,, \tag{A7d}$$

$$\langle i,0|j,0\rangle=0\,, \tag{A8a}$$

$$\langle i,0|i,1\rangle=-\tfrac{1}{4}s_i\,, \tag{A8b}$$

$$\langle i,0|j,1\rangle=\frac{1}{16\pi}\int dS_{ij}\frac{\partial_n r_j}{r_j^2}\quad(j\neq i)\,, \tag{A8c}$$

$$\langle i,1|i,0\rangle=-\tfrac{1}{4}s_i\,, \tag{A8d}$$

$$\langle i,1|j,0\rangle=\frac{1}{16\pi}\int dS_{ij}\frac{\partial_n r_i}{r_i^2}\quad(j\neq i)\,, \tag{A8e}$$

$$\langle i,1|i,1\rangle=-\tfrac{1}{2}s_i R_i\,, \tag{A8f}$$

$$\langle i,1|j,1\rangle=\frac{1}{16\pi}\int dS_{ij}\left(\frac{\partial_n r_j}{r_i r_j^2}+\frac{\partial_n r_i}{r_j r_i^2}\right)\quad(j\neq i)\,. \tag{A8g}$$

Equations (A5) are not independent, owing to the possibility of shifting all the $A_{i,0}$ by the same amount. Equation (15) implies that, summing Eqs. (A5) for $n=0$ over all the cells i, one obtains an identity. This can be readily verified. From Eqs. (A8a), (A8b), and (A8c) one obtains

$$\sum_i\langle 1,0|j,0\rangle+\sum_i\langle i,0|j,1\rangle=0\,.$$

From Eqs. (A7a) and (A7b) one obtains

$$\sum_i\alpha_{i,0,j}=\tfrac{1}{3}\sum_i\int dS_{ij}r_j\partial_n r_j-\tfrac{4}{3}\pi R_j^3 s_j$$
$$=\tfrac{1}{6}\int\nabla^2(r_j^2)-\tfrac{4}{3}\pi R_j^3 s_j=\Omega_j\,,$$

where Ω_j is the volume of cell j outside the inscribed sphere. Then the sum of Eqs. (A5) for $n=0$ becomes

$$\sum_j\Omega_j\bar{n}_j-\sum Q_i=0\,,$$

which is satisfied owing to the charge neutrality of the molecule.

The above result implies that one can eliminate one of the equations for $n=0$ and choose at will one of the $A_{i,0}$. So we solve Eqs. (A5) in terms of one of the parameters. Later we fix the free parameter by imposing the continuity at the outer sphere; thus

$$A_{0,0}+A_{0,1}/R_0-\tfrac{4}{3}\pi\bar{n}_0R_0^2$$
$$=-\frac{8\pi}{R_0}\int_{R_0}^{\infty}r^2n_0(r)dr+8\pi\int_{R_0}^{\infty}rn_0(r)dr\,. \tag{A9}$$

Having determined the $A_{i,n}$, we impose the continuity at the other sphere to find A_i':

$$A_i'-\frac{2Z_i}{R_i}+\frac{8\pi}{R_i}\int_0^{R_i}r^2n_i(r)dr-8\pi\int_0^{R_i}rn_i(r)dr$$
$$=A_{i,0}+\frac{A_{i,1}}{R_i}-\tfrac{4}{3}\pi\bar{n}_iR_i^2\,. \tag{A10}$$

A short calculation gives the following expression for the electrostatic Coulomb energy:

$$U[n-p,c]-S[p]$$

$$=\tfrac{1}{2}\sum_{i,n,j} A_{i,n}\alpha_{i,n,j}\bar{n}_j+\tfrac{2}{3}\pi\sum_i \bar{n}_i R_i^2 Q_i-\tfrac{1}{2}\sum_i Z_i A'_i$$

$$+\tfrac{1}{2}\sum_i \int 4\pi r^2 n_i(r) C'_i(r)\,dr+\sum_{ij}\bar{n}_i\omega_{ij}\bar{n}_j\,, \qquad \text{(A11)}$$

where

$$\omega_{i,i}=\tfrac{64}{45}\pi^2 R_i^5 s_i-\tfrac{2}{15}\pi\sum_j\int dS_{ij}\,r_i^3\partial_n r_i\,, \qquad \text{(A12a)}$$

$$\omega_{i,j}=-\tfrac{2}{9}\pi\int dS_{ij}\,r_i^2 r_j \partial_n r_j \quad (i\neq j)\,. \qquad \text{(A12b)}$$

Finally, Eq. (1) for the total energy can be calculated by means of the one-electron energy eigenvalues ϵ_i,

$$E=\sum_i \epsilon_i+E_x[n]+U[n-p,c]-S[p]-\int vn\,. \qquad \text{(A13)}$$

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