Muffin-tin orbitals and the total energy of atomic clusters

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The Hohenberg-Kohn-Sham (HKS) density-functional equations are solved for clusters of atoms using the linear muffin-tin orbital method (LMTO) of Andersen. The approach is numerically efficient and the self-consistency condition applies to the full potential. Binding energies, equilibrium separations, vibration frequencies, and dipole moments calculated for a series of first-row diatomic molecules agree well with experiment, indicating that the HKS scheme gives a quantitative description of the energy and electron-density changes associated with chemical bonding. The ability of the LMTO method to treat non-muffin-tin potential terms and its energy-independent partial-wave basis make it ideally suited for application to larger systems.

I. INTRODUCTION

The calculation of total energies of atomic systems, whether arranged periodically in a lattice or in a cluster of finite size, has received considerably less attention from physicists than the determination of one-electron properties such as band structures and Fermi surfaces. One reason for this has been the absence of a systematic formalism for performing such calculations. Over the last few years, however, the density-functional formalism of Hohenberg, Kohn, and Sham¹ (HKS) has given remarkably good results for a wide variety of systems, in spite of the use of a simple local density functional for the exchangecorrelation energy. Detailed calculations of the surface energy and work function of simple metals,² and of the cohesive energies, atomic volumes, susceptibilities, and bulk moduli of transition metals³ show very good agreement with experiment. That this accuracy is not limited to extended systems has been demonstrated by Gunnarsson and Johansson,⁴ who obtained a very good binding-energy curve for the hydrogen molecule using the HKS formalism with a spin-density functional. In view of these successes, it is important to develop methods for solving the HKS equations in systems intermediate in size between H₂ (where discretization methods are accurate) and bulk close-packed metals (where a muffin-tin potential is adequate). The present paper describes such a method which is both efficient and accurate.

In the HKS scheme, the total energy E of a system of electrons in an external potential V^{ext} is regarded as a functional of the electron density $n(\vec{\mathbf{r}})$. The correct ground-state density minimizes the energy functional, and can be found by solving the one-particle problem

$$\left[-\frac{1}{2}\nabla^2 + V^{\text{eff}}(\mathbf{\ddot{r}}) - \epsilon_n\right]\psi_n(\mathbf{\ddot{r}}) = 0, \qquad (1.1)$$

with the self-consistency condition

$$V^{\text{eff}}(\mathbf{\ddot{r}}) = \phi(\mathbf{\ddot{r}}) + V^{\text{ext}}(\mathbf{\ddot{r}}) + V^{\text{xc}}(\mathbf{\ddot{r}}).$$
(1.2)

Here,

$$\begin{split} \phi(\mathbf{\tilde{r}}) &\equiv \int d\mathbf{\tilde{r}}' \frac{n(\mathbf{\tilde{r}})}{|\mathbf{\tilde{r}} - \mathbf{\tilde{r}}'|} ,\\ V^{xc}(\mathbf{\tilde{r}}) &\equiv \frac{\delta E^{xc}(n(\mathbf{\tilde{r}}))}{\delta n(\mathbf{\tilde{r}})} , \end{split}$$

and

$$n(\mathbf{\bar{r}}) \equiv \sum_{n} f_{n} |\psi_{n}(\mathbf{\bar{r}})|^{2}$$

The occupation number of the *n*th state is f_n , and $E^{xc}(n)$ is the exchange and correlation part of the energy functional. Once (1.1) and (1.2) have been solved, the energy of the system is given by

$$E = \sum_{n} f_{n} \epsilon_{n} - \int d\mathbf{\tilde{r}} n(\mathbf{\tilde{r}}) [\frac{1}{2} \phi(\mathbf{\tilde{r}}) + V^{xc}(\mathbf{\tilde{r}})] + E^{xc}[n(\mathbf{\tilde{r}})].$$
(1.3)

Following HKS, we use the local-density approximation for E^{xc} ,

$$E^{xc} = \int d\mathbf{\tilde{r}} n(\mathbf{\tilde{r}}) \epsilon^{x} (n(\mathbf{\tilde{r}})), \qquad (1.4)$$

where $\epsilon^{xc}(n)$ is the exchange and correlation energy per particle of a homogeneous-electron liquid of density $n.^5$ Since this is a well-studied function, Eqs. (1.1)-(1.4) constitute a parameter-free scheme for the calculation of energies and densities of systems with an arbitrary number of electrons.

The essential advantage of the HKS scheme is that all exchange and correlation effects are treated in a single functional which can be approximated simply and accurately.⁶ By contrast, quantum-chemical methods treat these effects by evaluating matrix elements of the form

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$$\langle \psi(\mathbf{\tilde{r}}_1,\ldots,\mathbf{\tilde{r}}_N) | \frac{1}{|\mathbf{\tilde{r}}_i-\mathbf{\tilde{r}}_j|} | \psi(\mathbf{\tilde{r}}_1,\ldots,\mathbf{\tilde{r}}_N) \rangle$$

where $\psi(\mathbf{\tilde{r}}_1, \ldots, \mathbf{\tilde{r}}_N)$ is the many-electron wave function and $\mathbf{\tilde{r}}_i$ is an electron coordinate. These are very sensitive to the detailed structure of the wave function, which cannot be approximated simply. The functions $\psi_n(\mathbf{\tilde{r}})$ in (1.1) can be viewed as molecular orbitals, but for a system of noninteracting electrons in the external potential V^{eff} . In this reference system, there is no correlation and an attempt to evaluate the total energy of the interacting system by forming a Slater determinant from the $\psi_n(\mathbf{\tilde{r}})$ and evaluating the expectation value of the many-electron Hamiltonian would yield poor results.

Experience in band-structure calculations has shown the advantage of methods for solving eigenvalue problems such as (1.1) which use a partialwave rather than a linear-combination-of-atomicorbitals basis. One of the most popular, the Korringa-Kohn-Rostoker (KKR) or scattered-wave method, has been used extensively in cluster calculations.⁷ Recently, a new band-structure method, the linear muffin-tin orbital method⁸ (LMTO) has been developed which also uses a partial-wave basis, but which has two pronounced advantages over KKR. Firstly, it has an energy-independent basis, constructed essentially by expanding the solution $\phi_{ii}(r_i, \epsilon)$ of the radial equation for each atomic sphere in a Taylor series about a reference



FIG. 1. Choice of cells for a diatomic molecule. R_i and R_i^{ext} denote muffin-tin and external radii, respectively, and $\tilde{\mathbf{r}}_i^0$ is the center point of the *i*th cell. Region II is that part of a cell outside the muffin-tin and is shown hatched for one cell. The cells have cylindrical symmetry about the molecular axis.

energy ϵ_{ii} . Secondly, the method gives a variational solution of the eigenvalue problem for a non-muffin-tin potential. This feature is essential for energy calculations, since the muffin-tin restriction leads to unphysical binding-energy curves in open systems.⁹

As an application of the HKS-LMTO method, we solve Eq. (1.1) and (1.2) for the ground state of some first-row diatomic molecules. Calculated values of binding energy, equilibrium separation, fundamental vibration frequency, and dipole moment are in good agreement with experiment and compare with the best available configurationinteraction calculations. The HKS-LMTO scheme, therefore, gives an accurate description of the energy associated with the formation of a chemical bond. This is significant in that the approach is not in principle limited to small systems. Since the LMTO secular matrix is linear in energy, matrix diagonalization will become time-limiting only when very large symmetry blocks are encountered. We anticipate that energy calculations can, therefore, be carried out for clusters large enough to be relevant to studies of defects in solids or chemisorption.

In Sec. II, we give an overview of the basic structure of the method and introduce the muffintin-orbital basis functions. These are discussed in detail in Sec. III and used to evaluate the LMTO secular matrix in Sec. IV. The discussion of these two sections follows closely that given by Andersen and Woolley¹⁰ and is included here for completeness. In Sec. V, we consider the evaluation of the charge density, potential and the energy and in Sec. VI we discuss partial-wave convergence. In Sec. VII, we present results for the binding-energy curves of some simple diatomic molecules, and conclude with remarks concerning prospects for further applications. To aid continuity of the main text, various details are discussed in the appendices. We use Hartree atomic units unless otherwise stated.

II. SOLUTION OF HKS PROBLEM USING MUFFIN-TIN ORBITALS

The basis functions we use will be discussed in detail in subsequent sections. They consist of muffin-tin orbitals $\chi_L^i(\kappa, \tilde{\mathbf{r}}_i); \tilde{\mathbf{r}}_i \equiv \tilde{\mathbf{r}} - \tilde{\mathbf{r}}_i^0$, associated with cells *i* (center $\tilde{\mathbf{r}}_i^0$) which fill all space. *L* is a combined (l,m) partial-wave index. An example of the subdivision of space into cells, which we have used for diatomic molecules, is shown in Fig. 1. Each nucleus is a cell center and there is a third "concave" cell, comprising all space outside the two atomic cells. The muffin-tin orbitals (MTO's) are constructed from the spherically sym-

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metrical part of V^{eff} in each cell and contain an arbitrary parameter, κ . If $\kappa^2 < 0$, the χ_L^i fall off exponentially in amplitude away from \vec{r}_i^0 , while if $\kappa^2 > 0$ they extend throughout the cluster.

For a given value of κ , the best solution of (1.1) of the form

$$\psi_n(\mathbf{\bar{r}}) = \sum_{Li} C_{Li}^n \chi_L^i(\kappa, \mathbf{\bar{r}}_i), \qquad (2.1)$$

and the appropriate eigenvalues $\epsilon_n(\kappa)$ are obtained by diagonalizing the LMTO secular matrix

$$M_{LL}^{ij} \equiv \langle \chi_L^i | -\frac{1}{2} \nabla^2 + V^{\text{eff}}(\mathbf{\tilde{r}}) - \epsilon | \chi_L^i \rangle.$$
 (2.2)

Although the spherical component of the potential is used to construct the basis MTO's, the matrix elements (2.2) are evaluated using the full threedimensional potential (see Sec. IV). The only approximation in solving (1.1) is then the lack of completeness of the basis set. The diagonalization of (2.2) is a linear eigenvalue problem and will require less computer time than the evaluation of the matrix elements in all but very large systems.

The best estimates of eigenfunctions and eigenvalues follow by varying κ and determining minima in $\epsilon_n(\kappa)$. In a previous paper,¹¹ we showed that this procedure generates essentially exact eigenvalues for a muffin-tin potential. In total energy calculations, however, it is computationally inconvenient that each eigenvalue ϵ_n have its own κ value. To simplify the calculation of the charge density, and to reduce storage requirements, we solve (1.1) for a single κ value, and use κ variation to minimize the total energy. Restricting the choice of κ in (2.1) limits the class of density variations we allow in the functional and leads necessarily to a higher energy than the minimum of the functional we would obtain if each eigenvalue had a different κ value. This in turn is higher than the exact minimum, since the LMTO basis set is not complete.

Once the eigenvalues and eigenvectors of (2.2) have been obtained, the new density and effective potential are calculated and the procedure iterated to self-consistency. Repetition for several κ values and interpolation gives the best estimate of the total energy that can be obtained using constant- κ MTO basis functions. This procedure can, of course, be carried out for any set of basis functions. The MTO's of Andersen have the particular advantage of combining accuracy with ease of computation as we now discuss.

III. MUFFIN-TIN ORBITALS FOR CLUSTERS

In Fig. 1, we define nonoverlapping muffin-tin spheres of radius R_i as the inscribed spheres

centered on \vec{r}_i^0 , for the convex cells, and for the concave cell as the region outside the sphere centered on the midpoint of the cluster. In each iteration, the potential $V^{eff}(\vec{r})$ is expanded in partial waves about each cell center

$$V^{eff}(\hat{\mathbf{r}}) = \sum_{Li} V_{Li}(r_i) Y_L(\hat{r}_i), \qquad (3.1)$$

where Y_L is a (real) spherical harmonic. The muffin-tin orbitals are then constructed from solutions $\phi_{ii}(\epsilon_{ii}, r_i)$ of the radial Schrödinger equation for the spherically symmetrical component $V_{0i}(r_i)$,

$$\frac{-\nabla^2}{2} + \frac{1}{(4\pi)^{1/2}} V_{0i}(r_i) + \frac{l(l+1)}{r_i^2} - \epsilon_{i} \\ \times \phi_{1i}(\epsilon_{1i}, r_i) = 0.$$
 (3.2)

Here, ϵ_{ii} is a site and partial-wave-dependent reference energy and ϕ_{ii} is normalized within the *i*th muffin tin

$$\langle \phi_{li}^2 \rangle \equiv \int_{r_i^{\min}}^{r_i^{\max}} dr \, r^2 \phi_{li}^2(\epsilon_{li}, r) = 1, \qquad (3.3)$$

where $r_i^{\min} = 0(R_i)$ and $r_i^{\max} = R_i(\infty)$ for *i* convex (concave). We define the derivative

$$\dot{\phi}_{Ii}(\epsilon_{Ii},r_i) \equiv \frac{\partial}{\partial \epsilon} \phi_{Ii}(\epsilon,r_i) \bigg|_{\epsilon=\epsilon_{Ii}}, \qquad (3.4)$$

and note that ϕ_{Ii} and $\dot{\phi}_{Ii}$ are orthogonal to each other and to all core states of the potential.⁸ Dimensionless radial logarithmic derivatives of ϕ_{Ii} , $\dot{\phi}_{Ii}$ are denoted by

$$D_{1i} \equiv \left(\frac{r_i}{\phi_{1i}(\epsilon_{1i}, r_i)} \frac{\partial}{\partial r_i} \phi_{1i}(\epsilon_{1i}, r_i)\right)_{r_i = R_i}, \qquad (3.5)$$

with an analogous expression for D_{ii} , the logarithmic derivative of $\dot{\phi}$. Finally, the definition

$$\omega_{Ii}(D) \equiv \frac{-\phi_{Ii}(\epsilon_{Ii}, R_i)}{\phi_{Ii}(\epsilon_{Ii}, R_i)} \frac{D - D_{Ii}}{D - D_{Ii}}$$
(3.6)

ensures that the linear combination

$$\Phi_{ii}(D,r_i) \equiv \phi_{ii}(\epsilon_{ii},r_i) + \omega_{ii}(D)\dot{\phi}_{ii}(\epsilon_{ii},r_i) \quad (3.7)$$

has logarithmic derivative D. This can be chosen to be equal to the logarithmic derivative of the spherical Bessel function

$$G_{i}^{i}(\kappa, r_{i}) \equiv \begin{cases} K_{i}(\kappa, r_{i}), & i \text{ convex}, \\ J_{i}(\kappa, r_{i}), & i \text{ concave}, \end{cases}$$
(3.8)

where

$$J_{I}(\kappa, r) \equiv \kappa^{-1} j_{I}(\kappa r), \qquad (3.9)$$
$$K_{I}(\kappa, r) \equiv \kappa^{I+1} \begin{cases} i h_{I}^{(1)}(\kappa r), & \kappa^{2} < 0, \\ -n_{I}(\kappa r), & \kappa^{2} > 0, \end{cases}$$

and κ is a given energy-independent parameter. The functions j_i , $h_i^{(1)}$, n_i are defined as in Abramowitz and Stegun.¹² The atomiclike function (3.7) has logarithmic derivative uniquely determined by κ and is independent of the energy ϵ which appears in the secular matrix. By contrast, its counterpart in the KKR method $\phi_{ii}(\epsilon, r_i)$ depends explicitly on ϵ and, for a given ϵ , has a fixed logarithmic derivative.

The basis functions of the LMTO method, the muffin-tin (MT) orbitals χ_L^i corresponding to a site *i* and partial wave *L*, are now defined as follows. Inside the *i*th cell,

$$\begin{split} \chi_{L}^{i}(\kappa,\tilde{\mathbf{r}}_{i}) &= \Phi_{L}^{i}(G,\tilde{\mathbf{r}}_{i}) \\ &\equiv Y_{L}(\hat{\boldsymbol{r}}_{i}) \begin{cases} \Phi_{Ii}(D(G_{i}^{i}),\boldsymbol{r}_{i}), & \boldsymbol{r}_{i} \text{ in } i \text{th } \text{MT}, \\ N_{I}^{i}(G)G_{i}^{i}(\kappa,\boldsymbol{r}_{i}), & \text{otherwise}, \end{cases} \end{split}$$

$$(3.10)$$

where the factor

$$N_{l}^{i}(G) \equiv \Phi_{li}(D(G_{l}^{i}), R_{i}) / G_{l}^{i}(\kappa, R_{i})$$
(3.11)

ensures the continuity of $\chi_L^i(\kappa, \vec{\mathbf{r}}_i)$ as well as its logarithmic derivative at R_i . In cell $j \neq i$, we expand the Bessel functions centered on $\vec{\mathbf{r}}_i^0$ about the origin of cell $j, \vec{\mathbf{r}}_j^0$, i.e.,

$$G_{L}^{i}(\tilde{\mathbf{r}}_{i}) = \sum_{L'} \overline{B}_{LL'}^{ij}(\kappa) F_{L'}^{j}(\tilde{\mathbf{r}}_{j}), \qquad (3.12)$$

where \overline{B}_{LL}^{ij} , (κ) are structure constants (see Appendix A)

$$F_{L}^{j}(\mathbf{\hat{r}}_{j}) = Y_{L}(\mathbf{\hat{r}}_{j}) \begin{cases} J_{l}(\kappa, r_{j}), & j \text{ convex}, \\ K_{l}(\kappa, r_{j}), & j \text{ concave}, \end{cases}$$
(3.13)

and we have used the notation

$$G_L^i(\mathbf{\tilde{r}}_i) \equiv G_l^i(\kappa, r_i) Y_L(\hat{r}_i).$$

In cell j, we define

$$\chi_{L}^{i}(\kappa, \mathbf{\bar{r}}_{i}) \equiv \sum_{L'} B_{LL'}^{ij}(\kappa) \Phi_{L}^{j}(F, \mathbf{\bar{r}}_{j}); \quad r \text{ in } j \text{th cell},$$
(3.14)

where

$$\Phi_{L}^{j}(F, \mathbf{\hat{r}}_{j}) \equiv Y_{L}(\mathbf{\hat{r}}_{j}) \begin{cases} \Phi_{ij}(D(F_{i}^{j}), r_{j}), & r_{j} \text{ in } j \text{th } MT, \\ N_{i}^{j}(F)F_{i}^{j}(\kappa, r_{j}), & \text{otherwise}, \end{cases}$$
(3.15)

and

$$\mathsf{B}_{LL}^{ij},(\kappa)\equiv\overline{B}_{LL}^{ij},(\kappa)N_{l}^{i}(G)/N_{l}^{j}(F).$$

The muffin-tin orbital defined by (3.10) and (3.14) is thus atomiclike in the muffin-tin spheres and is a spherical Bessel function between them. It is orthogonal to all core states of the cluster and is continuous and differentiable everywhere, subject to the convergence of the sum in (3.14). This

summation is an important feature of the LMTO method and allows partial-wave contributions which would be excluded in the corresponding KKR calculation.

We now show that the LMTO

$$\psi_n(\kappa, \mathbf{\bar{r}}) \equiv \sum_{L\,i} C_{L\,i}^n \chi_L^i(\kappa, \mathbf{\bar{r}}_i), \qquad (3.16)$$

where

$$\chi_{L}^{i}(\kappa, \mathbf{\bar{r}}_{i}) = \begin{cases} \Phi_{L}^{i}(G, \mathbf{\bar{r}}_{i}), & \mathbf{\bar{r}} \text{ in cell } i, \\ \sum_{L'} B_{LL'}^{ij}(\kappa) \Phi_{L'}^{i}(F, \mathbf{\bar{r}}_{j}), & \mathbf{\bar{r}} \text{ in cell } j \end{cases}$$

$$(3.17)$$

can be a good approximation to the eigenfunctions of the one-particle wave equation (1.1). For a given κ value and in a given muffin tin $i_{\bar{i}}$ (3.16) consists of contributions $\Phi_L^i(G, \bar{r}_i)$ from the MTO's belonging to cell *i* plus contributions $\Phi_L^i(F, \bar{r}_i)$ coming from the tails of MTO's centered on other sites. The net result is a combination of $\phi_{1i}(\epsilon_{1i}, r_i)$ and $\dot{\phi}_{1i}(\epsilon_{1i}, r_i)$ times a spherical harmonic. Provided that the coefficients C_{Li}^n can be chosen appropriately (for the values of the energy for which this is possible, see Appendix B), the radial function takes the form

$$\phi_{Ii}(\epsilon_{Ii}, r_i) + (\epsilon - \epsilon_{Ii}) \dot{\phi}_{Ii}(\epsilon_{Ii}, r_i), \qquad (3.18)$$

namely, the leading terms in a Taylor expansion of the correct solution $\phi_{ii}(\epsilon, r_i)$ of the radial equation of energy ϵ . For a muffin-tin potential, a value of κ exists for which (3.16) is an exact solution of (1.1) between the spheres. There exists, therefore, an LMTO which differs from the exact solution by quantities of order $(\epsilon - \epsilon_{ii})^2$, with eigenvalue which differs from the exact one by $O(\epsilon - \epsilon_{ii})^4$.¹³

As noted above (Sec. II), restricting the variation in κ rules out the possibility of obtaining the optimum LMTO solutions of (1.1). The stationary nature of the HKS functional means, however, that errors made in calculating eigenvalues and electron density largely cancel. Although systems with a large spread in eigenvalues might cause some difficulty with the constant κ approximation; the errors should not, in general, exceed those inherent in the LMTO method.

The definition of the basis function (3.7) requires a prescription for choosing the reference energies ϵ_{ii} . Since for a muffin-tin potential the error in the total energy due to linearization of the basis is of order $(\epsilon_n - \epsilon_{1i})^4$ we choose the ϵ_{1i} by minimizing

$$\sum_{n} f_{n} \sum_{m=-l}^{l} (C_{Li}^{n})^{2} (\epsilon_{n} - \epsilon_{li})^{4}.$$
(3.19)

For the systems we have considered the energy is

insensitive to the ϵ_{ii} and the above procedure gives results only marginally different from the more obvious one of setting $\epsilon_{ii} = \epsilon$, the center of gravity of the eigenvalue spectrum.

IV. CALCULATION OF SECULAR MATRIX ELEMENTS

If we define B_{LL}^{ii} , $\equiv 0$, the secular matrix elements

$$M_{LL'}^{ij} \equiv \langle \chi_L^i | -\frac{1}{2} \nabla^2 - V^{\text{eff}}(\mathbf{\hat{r}}) - \epsilon | \chi_{L'}^i \rangle$$
(4.1)

may be written as the sum of cellular integrals

$$\begin{split} M_{LL'}^{ij} &= \delta_{ij} \langle \Phi_{L}^{i}(G) \left| H - \epsilon \right| \Phi_{L'}^{i}(G) \rangle_{i} \\ &+ \sum_{L''} \left(B_{L'L''}^{ji} \langle \Phi_{L}^{i}(G) \right| H - \epsilon \left| \Phi_{L''}^{i}(F) \rangle_{i} \\ &+ \langle \Phi_{L''}^{j}(F) \right| H - \epsilon \left| \Phi_{L'}^{j}(G) \rangle_{j} B_{LL''}^{ij} \right) \\ &+ \sum_{kL'''L'''} B_{LL''}^{ik} \langle \Phi_{L''}^{k}(F) \right| H - \epsilon \left| \Phi_{L'''}^{k}(F) \rangle_{k} B_{L'L'''}^{jk}, \end{split}$$

$$(4.2)$$

where the subscript in $\langle \rangle_k$ denotes integration over the *k*th cell.

It is convenient to separate each cellular integral into three contributions.

a. Type I or muffin-tin contributions. These involve the spherical part of the potential and extend over the muffin tins, for example,

$$\begin{split} \left[M_{LL}^{i},(G,F)\right]_{\mathrm{I}} &= \left\langle \Phi_{L}^{i}(G) \right| - \frac{1}{2} \nabla^{2} \\ &+ \frac{1}{(4\pi)^{1/2}} V_{\mathrm{Of}}(r_{i}) - \epsilon \left| \Phi_{L}^{i},(F) \right\rangle_{r_{i} \in i \, \mathrm{th \ MT}}. \end{split}$$

$$\tag{4.3}$$

Using definition (3.7) and the properties of ϕ_{Ii} and $\dot{\phi}_{Ii}$, it is straightforward to show⁸ that

$$\begin{split} \left[M_{LL'}^i(G,F) \right]_{\mathbf{I}} &= \delta_{LL'} \left\{ \omega_{ii} \left(D(F_i^i) \right) + \left(\epsilon_{ii} - \epsilon \right) \right. \\ & \left. \times \left[1 + \omega_{ii} \left(D(F_i^i) \right) \omega_{ii} \left(D(G_i^i) \right) \left\langle \phi_{ii}^2 \right\rangle \right] \right\}, \end{split}$$

where

$$\langle \dot{\phi}_{li}^2 \rangle \equiv \int_{\frac{r_i^{\text{max}}}{r_i^{\text{min}}}}^{r_i^{\text{max}}} dr_i r_i^2 \dot{\phi}_{li}^2 (\epsilon_{li}, r_i).$$

The integrals $M_{LL'}^i(F,G)$, $M_{LL'}^i(G,G)$, $M_{LL'}^i(F,F)$ are obtained similarly.

b. Type II contributions. These involve the nonspherical part of the potential inside the muffin tins

$$\begin{bmatrix} M_{LL'}^{i}(G,F) \end{bmatrix}_{II}$$

$$= \langle \Phi_{L}^{i}(G) | \sum_{L''\neq 0} V_{L''i}(r_{i}) Y_{L}(\hat{r}_{i}) | \Phi_{L'}^{i}(F) \rangle_{r_{i} \text{ inside MT } i}.$$
(4.5)

Defining the Gaunt factors

$$C_{LL'L''} \equiv \int d\hat{\boldsymbol{r}} Y_L(\hat{\boldsymbol{r}}) Y_L(\hat{\boldsymbol{r}}) Y_{L''}(\hat{\boldsymbol{r}}), \qquad (4.6)$$

we reduce (4.5) to the sum of one-dimensional integrals

$$[M_{LL'}^{i}(G,F)]_{II} = \sum_{L''} C_{LL'L''} \int_{r_{i}^{\min}}^{r_{i}^{\max}} dr_{i} r_{i}^{2}$$

$$\times V_{L''i}(r_{i}) \Phi_{Ii}(D(G_{i}^{i}),r_{i}) \Phi_{Ii}(D(F_{i}^{i}),r_{i})$$
(4.7)

with the $\Phi_{ii}(D, r_i)$ defined by (3.7). The integrals in (4.7) are evaluated accurately by ten-point Gaussian integration.

c. Type III contributions. These are cellular integrals over the part of the cells outside the muffin tins

$$\begin{bmatrix} M_{LL}^{i}, (G, F) \end{bmatrix}_{III}$$

= $\langle \Phi_{L}^{i}(G) | \kappa^{2} + V^{\text{eff}}(\mathbf{\bar{F}}) - \epsilon | \Phi_{L}^{i}, (F) \rangle_{\text{cell } i};$
 $\mathbf{\bar{F}}_{i}$ outside *i*th MT. (4.8)

These integrals are evaluated using the projection operators of Andersen and Woolley¹⁰

$$\theta_{LL}^{i} \cdot (r_{i}) = \int d\hat{r}_{i} \, \theta^{i}(\tilde{r}_{i}) Y_{L}(\hat{r}_{i}) Y_{L}(\hat{r}_{i}), \qquad (4.9)$$

with $\theta^i(\mathbf{\tilde{r}}_i) = 1$ (0) for $\mathbf{\tilde{r}}_i$ inside (outside) cell *i*. If we define cellular potentials

$$\tilde{V}_{Li}(r_i) = \sum_{L'} \theta_{LL'}^i(r_i) V_{L'i}(r_i), \qquad (4.10)$$

then

(4.4)

$$\begin{split} [M_{LL'}^{i}(G,F)]_{III} &= \sum_{L''} C_{LL'L''} \int_{R'_{i}}^{R''_{i}} dr \, r^{2} N_{l}^{i}(G) \\ &\times N_{l'}^{i}(F) G_{i}^{i}(\kappa,r_{i}) F_{l}^{i}(\kappa,r_{i}) \\ &\times [\tilde{V}_{L''\,i}(r_{i}) + (\kappa^{2} - \epsilon)(4\pi)^{1/2} \theta_{L''\,0}^{i}(r_{i})], \end{split}$$

$$(4.11)$$

where $R'_i = R_i(R_i^{\text{ext}})$ and $R''_i = R_i^{\text{ext}}(R_i)$ for *i* convex (concave), with R_i^{ext} the distance from \overline{r}_i^0 to the farthest (nearest) point in cell *i*. The accuracy of this procedure is limited only by the accuracy to which projection operators (4.9) can be calculated. Since these operators depend solely on the shape of the cell they need be calculated once only. We used Monte-Carlo integration with 10⁵ points and checked that the cellular integrals (4.11) are accurate to a fraction of one percent, which is probably better than necessary.

V. CALCULATION OF CHARGE DENSITY, POTENTIAL, AND ENERGY

A. Partial-wave components of density and potential

With the HKS eigenfunctions given by LMTO's of the form (3.16), the charge density is

$$n(\vec{\mathbf{r}}) = \sum_{n} f_n \sum_{ijLL'} C_{Li}^n C_{L'j}^n \chi_L^i(\kappa, r_i) \chi_L^j(\kappa, r_j), \qquad (5.1)$$

where the LMTO normalization is given by

$$\sum_{ijLL'} C_{Li}^n C_{L'j}^n \langle \chi_L^i | \chi_{L'}^j \rangle = 1.$$
(5.2)

The matrix elements in (5.2) have already been calculated in evaluating the secular matrix elements. Expanding $n(\vec{r})$ in partial waves centered at \vec{r}_i^0 leads to partial densities

$$n_{L\,i}(r_{i}) = \sum_{n} f_{n} \sum_{L'L''} \left(C_{L'i}^{n} C_{L'i}^{n} C_{LL'L'''} \Phi_{i'}^{i} \left(D(G_{i'}^{i}), r_{i} \right) \Phi_{i''}^{i} \left(D(G_{i''}^{i}), r_{i} \right) \right. \\ \left. + 2 \sum_{j} C_{L'i}^{n} C_{L''i}^{n} \sum_{L_{1}} C_{LL'L_{1}} B_{L''L_{1}}^{ji} \Phi_{i'}^{i} \left(D(G_{i'}^{i}), r_{i} \right) \Phi_{i_{1}}^{i} \left(D(F_{i_{1}}^{i}), r_{i} \right) \right. \\ \left. + \sum_{j,k} C_{L',j}^{n} C_{L''k}^{n} \sum_{L_{1}L_{2}} B_{L'L_{1}}^{ji} B_{L''L_{2}}^{ki} C_{LL_{1}L_{2}} \Phi_{i_{1}}^{i} \left(D(F_{i_{1}}^{i}), r_{i} \right) \Phi_{i_{2}}^{i} \left(D(F_{i_{2}}^{i}), r_{i} \right) \right).$$

$$(5.3)$$

This expansion has nonzero contributions up to $2l_{int}$, where l_{int} is the maximum l value included in (3.17). From it we construct the cellular density

$$\tilde{n}_{Li}(r_i) \equiv \sum_{L'} \theta_{LL'}^i(r_i) n_{L'i}(r_i).$$
 (5.4)

From the partial densities (5.3) we calculate partial-wave components of the exchange-correlation potential $V^{xc}(\mathbf{\tilde{r}})$ and the exchange-correlation energy density, $\epsilon^{xc}(\mathbf{\tilde{r}})$. These quantities have nonlinear dependences on the density and each partial wave component must be calculated by two-dimensional (Gaussian) integration, for example

$$V_{Li}^{xc}(r_i) = \int d\hat{r}_i \, V^{x}(n(\hat{r}_i)) Y_L(\hat{r}_i), \qquad (5.5)$$

where

$$n(\vec{\mathbf{r}}_i) \equiv \sum_L n_{Li}(r_i) Y_L(\hat{r}_i).$$
 (5.6)

There is a corresponding expression for $\epsilon_{Li}^{xc}(r_i)$. In practice, 10–20 Gaussian points provide sufficient accuracy for such integrals.

The partial-wave components about each cell center of the Coulomb potential

$$\phi(\mathbf{\tilde{r}}) = \int dr' \frac{n(\mathbf{\tilde{r}}')}{|\mathbf{\tilde{r}} - \mathbf{\tilde{r}}'|}$$
(5.7)

are conveniently found by cellular integration. Defining the Coulomb potential arising from the charge density in cell i as

$$\phi_i(\mathbf{\vec{r}}) = \int_{\text{cell } i} d\mathbf{\vec{r}}' \ \frac{n(\mathbf{\vec{r}}')}{|\mathbf{\vec{r}} - \mathbf{\vec{r}}'|} .$$
(5.8)

so that

$$\phi(\mathbf{\bar{r}}) = \sum_{i} \phi_{i}(\mathbf{\bar{r}}), \qquad (5.9)$$

we obtain the partial-wave components of ϕ_i ,

$$\phi_{Li}(r_i) = \frac{4\pi}{2l+1} \int_{R_{i3}}^{R_{i4}} dr'_i r'_i^2 \frac{r'_{<}}{r_{>}^{l+1}} \tilde{n}_{Li}(r'_i).$$
(5.10)

The cellular density is given by (5.4), $r_{<}(r_{>})$ is the smaller (larger) of r_i, r'_i , and $R_{i3} = 0$ (R_i^{ext}), $R_{i4} = R_i^{ext}(\infty)$, for convex and concave cells respectively. The integral (5.10) is complicated by the discontinuity in the derivative of the integrand at r = r' and the Gaussian mesh used for the cellular density. We have used Gaussian integration to evaluate

$$\int_{R_{i3}}^{R_{i4}} dr'_{i} r'^{2}_{i} \frac{r'_{<}}{r^{1+1}_{>}} [\tilde{n}_{Li}(r'_{i}) - \tilde{n}_{Li}(r_{i})],$$

which has proved to be sufficiently accurate, in practice.

The partial-wave components of $\phi(\mathbf{\tilde{r}}_i)$ about cell center *i* are given in terms of the $\phi_{Li}(\mathbf{r}_i)$ by

$$\tilde{\phi}_{Li}(\hat{\mathbf{r}}_i) = \phi_{Li}(\mathbf{r}_i) + \sum_{j\neq 1} \sum_{L'} \int d\hat{\mathbf{r}}_i Y_L(\hat{\mathbf{r}}_i) Y_{L'}(\hat{\mathbf{r}}_j) \phi_{L'j}(\mathbf{r}_j)$$
(5.11)

and can be evaluated as a sum of one-dimensional integrals using the technique of Löwdin¹⁴ (see Appendix C). Once the ϕ_{Li} and the V_{Li}^{xc} are known, the HKS potential is in a form suitable for evaluating the cellular integrals required in Sec. IV.

Spherically symmetric terms (l=0) inside the muffin tin are used to construct the basis functions (3.6), as well as to perform cellular integrals, and are treated separately. The term $n_{0i}(r_i)$ is calculated on a linear mesh from $r_i = 0$ (R_i) to R_i (∞) for *i* convex (concave). This is interpolated onto the logarithmic mesh used for solving (3.2), and Poisson's equation is solved to

obtain the intrasite Coulomb potential, $V_{0i}^{intra}(r_i)$. The contribution due to the charge outside the muffin tin i, V_{0i}^{inter} , is evaluated using an expression similar to (5.11).

B. The total energy-"frozen-core" approximation

Once the self-consistent potential V^{eff} has been found, the energy is given by Eq. (1.3) and (1.4). Its evaluation is facilitated if we assume that the

 $E_{c} = \sum_{i}^{\text{nuclei}} \left(\sum_{n}^{\text{core}} \left\langle \psi_{n}^{i} \right| - \frac{1}{2} \nabla^{2} \left| \psi_{n}^{i} \right\rangle - 4\pi Z_{i} \int_{0}^{\infty} dr \, rn_{ci}(r) \right.$

core density does not depend on the internuclear separation. With this "frozen-core" approximation, the total energy can be decomposed into core (E_c) and valence contributions (E_v) . Let

$$n(\mathbf{\hat{r}}) = n_{v}(\mathbf{\hat{r}}) + n_{c}(\mathbf{\hat{r}}) = n_{v}(\mathbf{\hat{r}}) + \sum_{i}^{\text{address}} n_{ci}(r_{i}), \qquad (5.12)$$

where the core density is written as the sum of spherically symmetric terms which vanish for $r_i > R_i$. Then

$$+8\pi^{2}\int_{0}^{\infty}dr_{i}\int_{0}^{\infty}dr_{i}'\frac{r_{i}^{2}r_{i}'^{2}}{r_{>}}n_{ci}(r_{i})n_{ci}(r_{i}')+4\pi\int_{0}^{\infty}dr_{i}r_{i}^{2}n_{ci}(r_{i})\epsilon^{xc}(n_{ci}(r_{i})))\right)$$
(5.13)

and

$$E_{v} = \sum_{n}^{val} f_{n} \epsilon_{n} - \int d\vec{\mathbf{r}} n_{v}(\vec{\mathbf{r}}) [\frac{1}{2} \phi_{v}(\vec{\mathbf{r}}) + V^{xc}(\vec{\mathbf{r}}) - \epsilon^{xc}(n(\vec{\mathbf{r}}))] + \int d\vec{\mathbf{r}} n_{c}(\vec{\mathbf{r}}) [\epsilon^{xc}(n(\vec{\mathbf{r}})) - \epsilon^{xc}(n_{c}(\vec{\mathbf{r}}))] + \frac{1}{2} \sum_{i\neq j} \frac{Z_{vi} Z_{vj}}{\gamma_{ij}^{o}}, \quad (5.14)$$

where Z_{vi} is the net positive charge of core *i*. For the first-row diatomic molecules, E_v is always less than 50 a.u. and may be evaluated to sufficient accuracy using the cellular integration techniques and partial wave arrays described above.¹⁵ The core contribution E_c is independent of the nuclear positions and need be evaluated only if absolute energies are required. In the present work, we evaluate E_c using an atomic program and E_v using the HKS-LMTO program. For larger systems, a better procedure would be to evaluate E_v in the atomic program, in which case it would be unnecessary to calculate E_c .

There might be considerable advantage in separating from E_{n} a contribution arising from overlapping unrelaxed atomic densities. Apart from having calculational advantages, this would lead to a simple interpretation of the results and could suggest useful approximations. We note that the behavior of the HKS eigenvalues does not give a direct guide to the variation of the total energy. For example, a fixed-core density does not imply that the core eigenvalues remain constant with changing nuclear positions. The core eigenvalue shift is first order in the change of the self-consistent potential from atom to cluster in the regions surrounding the nuclei. Although this may be comparable with the binding energy, the changes in the core density and total energy are of lower order in the same quantities and should give a negligible contribution.

VI. PARTIAL-WAVE CONVERGENCE

All methods which employ a partial-wave basis can only be useful if large l components make no

essential contribution. In the KKR-cluster method,⁷ for example, there is one l_{max} to be chosen for each site, and these determine the size of the secular matrix. Eigenvalue convergence is obtained with small values of l_{max} , typically 1-3, while convergence of the density requires much larger values and is rarely attempted. This difficulty is related to the transfer of Bessel-function tails from site to site and the LMTO method has the advantage that the maximum l value associated with this transfer l_{int} does not determine the size of the secular matrix. The limit of the sums in (3.16), therefore, places no restriction on l_{int} , the limit of the internal summation (3.17).

The present calculations were performed with $l_{max} = 2$ for each site (including the concave cell). This gives a 27×27 secular matrix which is then symmetrized into blocks of size 9, 6, 6, 3, 3. Values of l_{int} up to 7 were used, although larger values could certainly be used for small molecules. For larger clusters, however, the rapid increase in computer time with l_{int} (~ l_{int}^4) would limit the calculation. Convergence of the method depends almost entirely on choosing cell boundaries such that the transfer sums (3.12) are used as far as possible from their radius of convergence. Details of our choice of cells for diatomic molecules are given in Appendix D. With these cells, the main effect of increasing l_{int} from 4 to 7 was a rigid shift in the binding-energy curves. For example, for the ground state of the N₂ molecule, this shift was 0.8 eV between $l_{int} = 4$ and 7 and 0.2 eV between $l_{int} = 6$ and 7. These shifts are to be compared with the calculated binding energy of 7.6 eV (and a total energy of ~2950 eV!). Equilibrium separations and vibration frequencies are

almost independent of l_{int} in the range 4-7.

In addition to l_{\max} and l_{int} , we must also choose the maximum l values for which potential and partial densities (5.3) are to be calculated. The density obtained from the LMTO's has components about each cell center up to $l_d = 2l_{int}$ and we have included all of these in the present calculations. We included potential components up to $l_v = l_{int}$ but many of these are negligible. In the case of N_2 , the binding-energy curve with $l_{int} = 7$ shifted rigidly by only 0.08 eV on changing l_v from 7 to 4.

Provided that the sums (3.12) are used inside their radius of convergence, the LMTO method is intrinsically convergent. To establish this convergence numerically is quite difficult (except in the case of H₂ where convergence to 0.01 eV occurred at $l_{int} = 4$), since Gaussian integration methods are less accurate for more rapidly varying functions. Thus the small energy differences we obtain between $l_{int} = 6$, 7 could equally be due to numerical inaccuracies. That these differences are small and that our results for a range of firstrow diatomic molecules are systematically accurate is evidence that values of $l_{int} \sim 6$ or 7 are sufficient, in practice.

VII. BINDING-ENERGY CURVES FOR FIRST-ROW DIATOMIC MOLECULES

Calculations for a series of first-row diatomic molecules have been carried out using the HKS-LMTO method. For reasons of space we do not give a detailed comparison of the results with the extensive literature on these systems.¹⁶ Our aim



FIG. 2. Calculations of the binding-energy curve for the H_2 molecule. The Hartree-Fock results are due to Kolos and Roothaan (Ref. 18) and K-W refers to the accurate variational calculation of Kolos and Wolniewicz (Ref. 19).

is to demonstrate the potential of the HKS density functional scheme and the accuracy of the LMTO method in connection with molecular bonding. In general, our results are better than those obtained by the Hartree-Fock method and compare with the best available configuration-interaction calculations. We emphasize that there are no adjustable parameters in the HKS scheme, the only input being the nuclear charges of the constituent atoms. We have used the Gunnarsson-Lundqvist⁶ approximation $\epsilon^{xc}(n,\zeta)$ for the exchange-correlation energy of a homogeneous electron gas of density nand spin density ζ . The spin density is zero in the ground state of all molecules we have considered, except for B_2 and O_2 where it has been estimated perturbatively using the spin-restricted eigenfunctions. Binding energies are determined by subtracting from the total energy of the molecule the energies of the constituent atoms. These are calculated using a spin-polarized program¹⁷ with the same approximation for $\epsilon^{xc}(n, \zeta)$.

The binding -energy curve we obtain for H₂ is shown in Fig. 2 together with the results of a spinrestricted Hartree-Fock calculation¹⁸ and an essentially exact variational calculation.¹⁹ Our vibration frequency of 4200 cm⁻¹ is somewhat smaller than the experimental value (4400 cm^{-1}), and the equilibrium internuclear separation of 1.44 a_0 , slightly larger (1.401 a_0). These trends are quite general for small molecules, although the comparison with experiment is less favorable when the bond is more complicated. The LMTO energy curve lies a constant 0.1 eV above that calculated by Gunnarsson and Johansson,⁴ who solved the HKS problem essentially exactly using a discretization method. This is in accordance with the variational principle for the energy and indicates that incompleteness of the LMTO basis is unimportant in the case of H_2 . Since there is only one eigenvalue and no core our other approximations introduce no error.

The binding-energy curve parameters of the first-row diatomic molecules B_2 , C_2 , N_2 , O_2 , F_2 , CO, and BF are shown in Fig. 3. The data plotted correspond to the experimental ground states,²⁰ which coincide with the HKS ground state except in the case of C_2 .²¹ Equilibrium separations r_e and vibration frequencies ω_e have been determined by fitting the points closest to the minimum (at least five in number) to a cubic equation

$$E(r) = E(r_e) + A(r - r_e)^2 + B(r - r_e)^3$$

where r is the internuclear separation. While not as remarkable as in the case of H₂, the level of accuracy is very satisfying. The trend across the series is given correctly and differences between theory and experimental are quite systematic.



FIG. 3. Binding energies (E_B) , equilibrium separations (r_e) , and vibrational frequencies for the ground states (experimental) of diatomic molecules. Experimental values are from Ref. 20.

Calculated equilibrium separations are too large by $\sim (0.1 - 0.2)a_{0}$, vibration frequencies and binding energies are too small by 100-200 cm⁻¹ and 1-2eV, respectively. It is not yet possible to say whether these discrepancies are due to the inaccuracy of the local density approximation for the exchange-correlation part of the energy functional or to the LMTO approximation used to determine its minimum. As we have stressed at several points above, however, we will always obtain a higher energy than the exact HKS energy, provided our calculation is converged in l_{int} . Since the atomic calculations are essentially exact solutions of the HKS equations, this means that the true HKS binding energies will be larger than those obtained here, and therefore in better agreement with experiment. Furthermore, the constant κ approximation will be most in error when the spread of the eigenvalues is greatest, that is, the smaller the internuclear separation. Therefore, the exact HKS binding -energy curve should deviate most from its LMTO approximation at smaller separations and give equilibrium separations in better agreement with experiment.

As a check on the electron density, we have calculated the dipole moment μ of CO and BF as a function of internuclear separation. In Fig. 4, the results are compared with Hartree-Fock calculations²² and with results derived from spectroscopic intensities.^{23,24} For CO, the dipolemoment function has been determined in the form of an expansion

$$\mu(r) = \mu_0 + \mu_1(r - r_e) + \mu_2(r - r_e)^2 + \mu_3(r - r_e)^3.$$
 (7.1)

For the nine points closest to r_e , we obtain μ_0 = -0.01 Debye (experiment: -0.112 D) and μ_1 = 1.70 (experiment: 1.64±0.03). The signs and order or magnitudes of μ_2 , μ_3 are also in good agreement with experiment.

On the basis of these results, we conclude that the HKS-LMTO method gives a quantitative description of the energy and electron density in a chemical bond. Discrepancies between theory and experiment are systematic and can be reduced by improving on the constant- κ approximation.

VIII. CONCLUDING REMARKS

We have described an approximate LMTO method for solving the HKS density functional equations for a cluster of atoms. Binding energy curves for seven first-row diatomic molecules confirm the



FIG. 4. Dependence of dipole moments of CO, BF on internuclear separation r. Experimental values of the equilibrium separation r_e are shown. Hartree-Fock results are taken from Huo (Ref. 22) and the values derived from spectroscopic intensities are from Lovas and Johnson (BF: Ref. 23) and Toth *et al.* (CO: Ref. 24), LD, for local density approximation, refers to the present work.

a. Larger systems. The partial-wave basis and a secular matrix linearly dependent on the energy make the LMTO method ideally suited to the study of larger clusters. Matrix diagonalization ($\sim N^3$, for N basis functions) will ultimately be timelimiting, but only for very large symmetry blocks. For the molecules considered here, our program requires only a few seconds per iteration on an IBM 370/168 computer. For larger systems, we expect the time requirement to increase roughly as N^2 and to be able to treat ten-atom clusters in less than 1 min per iteration. Applications currently under consideration are the simulation of chemisorption on transition-metal substrates using a 5-15 atom cluster, and the energy of defects in a solid. In both cases, an extension of the theory to include coupling of the cluster to an extended system would be very useful.

b. Small systems. It would be of interest to extend the present calculations in two ways. Firstly, to improve the solution of the HKS problem by (i) including core relaxation, (ii) giving up the constant- κ approximation, and (iii) improving the basis by allowing more than one MTO per site and partial wave. Secondly, to examine more general expressions for the exchange-correlation energy. For example, the nonlocal extension of the HKS functional proposed by Gunnarsson, Jonson and Lundqvist²⁵ leads to significant improvements in atoms, and we expect this to be true for molecules as well.

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APPENDIX A: STRUCTURE CONSTANTS

The Bessel functions $J_L(\kappa, \bar{\mathbf{r}}_i)$ and $K_L(\kappa, \bar{\mathbf{r}}_i)$ satisfy the following well-known expansion theorems²⁶

$$J_{L}(\kappa, \vec{\mathbf{r}} - \vec{\mathbf{r}}') = 4\pi \sum_{L'L''} i^{l'-l-l''} \kappa^{l'+l''-l} C_{LL'L''} J_{L'}(\kappa, \vec{\mathbf{r}}) J_{L''}(\kappa, \vec{\mathbf{r}}'),$$

$$K_{L}(\kappa, \vec{\mathbf{r}} - \vec{\mathbf{r}}') = \begin{cases} 4\pi \sum_{L'L''} i^{l'-l-l''} \kappa^{l+l'-l''} C_{LL'L''} J_{L'}(\kappa, \vec{\mathbf{r}}) K_{L''}(\kappa, \vec{\mathbf{r}}'); & \vec{\mathbf{r}}' \mid > \mid \vec{\mathbf{r}} \mid > \mid \vec{\mathbf{r}} \mid > \mid \vec{\mathbf{r}} \mid > \mid \vec{\mathbf{r}} \mid > |\vec{\mathbf{r}}' \mid . \end{cases}$$
(A1)

With the aid of (A1) the structure constants in Eq. (3.12) may be written

$$B_{LL'}^{ij}(\kappa) = \begin{cases} 4\pi \sum_{L''} i^{l'-l-l''} \kappa^{l+l'-l''} C_{LL'L''} K_{L''}(\kappa, \vec{\mathbf{r}}_{ij}^{0}), & i, j \text{ convex}, \\ 4\pi \sum_{L''} i^{l'-l-l''} \kappa^{l'+l''-l} C_{LL'L''} J_{L''}(\kappa, \vec{\mathbf{r}}_{ij}^{0}), & \begin{cases} i \text{ concave}, \\ j \text{ convex}, \end{cases} \\ 4\pi \sum_{L''} i^{l'-l-l'''} \kappa^{l+l''-l'} C_{LL'L'''} J_{L''}(\kappa, \vec{\mathbf{r}}_{ij}^{0}), & \begin{cases} i \text{ convex}, \\ j \text{ convex}, \end{cases} \end{cases} \end{cases}$$
(A2)

where $\vec{\mathbf{r}}_{ij}^0 = \vec{\mathbf{r}}_i^0 - \vec{\mathbf{r}}_j^0$.

APPENDIX B

If all L sums are carried to convergence, the wave function

$$\psi_n(\kappa, \vec{\mathbf{r}}) = \sum_{Li} C_{Li}^n \chi_L^i(\kappa, \vec{\mathbf{r}}_i)$$
(B1)

is continuously differentiable. For a muffin-tin potential it satisfies the Schrödinger equation in the interstitial region for the energy ϵ if

$$\kappa^2(\epsilon) = \epsilon - V_{II}, \qquad (B2)$$

where V_{II} is the constant potential in the interstitial region. For this value of κ , the function (B1) is therefore a solution if the *L*th component inside the muffin-tin sphere *i* is proportional to the exact solution of the radial Schrödinger equation

$$\phi_{li}(\epsilon, r_i) Y_L(\mathbf{\bar{r}}_i) . \tag{B3}$$

Using Eq. (3.17) to expand the MTO's in (B1), the condition (B3) is written

$$\begin{pmatrix} C_{Li}^{n} + \sum_{j \neq i} \sum_{L'} C_{L'j}^{n} B_{L'L}^{ji}(\kappa(\epsilon)) \end{pmatrix} \phi_{1i}(\epsilon_{1i}, r_{i}) \\ + \begin{pmatrix} C_{Li}^{n} \omega_{1i}(D(G_{i}^{i})) + \sum_{j \neq i} \sum_{L'} C_{L'j}^{n} \omega_{1i}(D(F_{i}^{i})) B_{L'L}^{ji}(\kappa(\epsilon)) \end{pmatrix} \\ \times \dot{\phi}_{1i}(\epsilon_{1i}, \mathbf{\bar{r}}_{i}) = A_{i}^{i} \phi_{1i}(\epsilon, r_{i}), \quad (B4)$$

where A_i^i is a constant. If a Taylor expansion in energy of $\phi_{1i}(\epsilon, r_i)$ is inserted in (B4), it immediately follows that (B4) is satisfied to first order in $(\epsilon - \epsilon_{1i})$ if

$$\begin{pmatrix} C_{Li}^{n} + \sum_{j \neq i} \sum_{L'} C_{L'j}^{n} B_{L'L}^{ji}(\kappa(\epsilon)) \end{pmatrix} (\epsilon - \epsilon_{li})$$

$$= C_{Li}^{n} \omega_{li}(D(G_{l}^{i})) + \sum_{j \neq i} \sum_{L'} C_{L'j}^{n} \omega_{li}(D(F_{l}^{i})) B_{L'L}^{ji}(\kappa(\epsilon)).$$
(B5)

At certain values of ϵ , the Eqs. (B5) have a solution and the corresponding function (B1) satisfies the Schrödinger equation to first order in ($\epsilon - \epsilon_{II}$). It follows that ϵ , whether determined from (B5) or by evaluating the expectation value of the oneelectron Hamiltonian using this function, differs from the exact eigenvalue by quantities of order $(\epsilon - \epsilon_{II})^4$. By regarding κ as a variational parameter instead of using (B2) we find the optimum LMTO without having to solve the nonlinear eigenvalue problem (B5).

APPENDIX C: EVALUATION OF COULOMB POTENTIAL

In evaluating the integrals in (5.11) required for the intrasite contribution to the Coulomb potential, we use the method suggested by Löwdin.¹⁴ Let the vector $\vec{\mathbf{r}}_{ij}^0$ linking two cell centers have direction cosines $\alpha\beta\gamma_{ij}$ with respect to the Z axis. Let $\hat{\gamma}'_i, \hat{\gamma}'_j$ be angular coordinates for cell i, j such that the Z' axis is along the direction $\vec{\mathbf{r}}_{ij}^0$. Then the spherical harmonics obey the relations

$$Y_L(\hat{\gamma}_i) = \sum_{m'=-i}^{m'=+i} Y_i^{m'}(\hat{\gamma}'_i) R_{m'm}^i(\alpha \beta \gamma_{ij}) , \qquad (C1)$$

where the $R_{m'm}^{i}(\Omega)$ are rotation matrices. The integrals appearing in (5.11) may now be written

$$\int d\hat{\boldsymbol{\gamma}}_{i} Y_{L}(\hat{\boldsymbol{\gamma}}_{i}) Y_{L'}(\hat{\boldsymbol{\gamma}}_{j}) V_{L'j}(\hat{\boldsymbol{\gamma}}_{j})$$

$$= \sum_{m''} \int d\hat{\boldsymbol{\gamma}}_{i}' Y_{l}^{m''}(\hat{\boldsymbol{\gamma}}_{i}') Y_{l'}^{m''}(\hat{\boldsymbol{\gamma}}_{j}') V_{L'j}(\boldsymbol{\gamma}_{j})$$

$$\times R^{l}_{m''m}(\alpha\beta\gamma_{ij}) R^{l'}_{m''m'}(\alpha\beta\gamma_{ij}), \quad (C2)$$

where we use the fact that \hat{r}'_i, \hat{r}'_j have a common ϕ coordinate. The integrals in (C2) are one dimensional

$$\int d\hat{r}'_{i} Y^{m}_{i}(\hat{r}'_{i}) Y^{m}_{i'}(\hat{r}'_{j}) V_{L'j}(r_{j})$$

$$= 2\pi N^{m}_{i} N^{m}_{i'} \int_{-1}^{1} d(\cos\theta_{i}) P^{m}_{i}(\cos\theta_{i}) P^{m}_{i'}(\cos\theta_{j}) V_{Lj}(r_{j}),$$
(C3)

where N_{1}^{m} is the normalization of Y_{1}^{m} and where

$$\cos\theta_{j} = \frac{r_{ij}^{0^{2}} - r_{i}r_{ij}^{0}}{r_{j}r_{ij}^{0}},$$

$$r_{j} = (r_{i}^{2} + r_{ij}^{0^{2}} - 2r_{i}r_{ij}^{0}\cos\theta_{i})^{1/2}.$$
(C4)

For a diatomic molecule the three cells can be chosen to have a common Z axis, $\vec{\mathbf{r}}_{ij}^0 = |\boldsymbol{r}_{ij}^0|\hat{Z}$, and the rotational matrices are Kronecker deltas.

APPENDIX D: CHOICE OF CELLS FOR DIATOMIC MOLECULES

The cells in Fig. 1 were chosen to optimize the convergence of the expansion theorem for the spherical Bessel functions (Appendix A). Expressing the tail of the *i*th MTO in terms of functions centered at \vec{r}_{i}^{o} requires that

$$C_{ij} \equiv r_j / r_{ij}^0 < 1 \quad \text{for all } \vec{r}_j \in \text{cell } j.$$
 (D1)

For the concave outer cell (j=0), we require

$$C_{i0} \equiv r_i^0 / r_0 < 1$$
 for all $\vec{r}_0 \in \text{outer cell}$. (D2)

To show that (D1) and (D2) place quite severe limits on the choice of cells, consider the case of a diatomic molecule with cubic atomic cells. The maximum value of C_{ij} is then 0.86 (for $\bar{\tau}_i$ at a cell corner), but some points in the bonding region yield C_{i0} equal to unity and expansion (3.12) does not converge. Optimum cells for this structure may be found by defining the outer cell boundary by

$$C_{i0} = C_{ij} . \tag{D3}$$

This yields cylindrically symmetric cells with a small interstitial region. The maximum values of C_{i0}, C_{ij} are 0.8 and rapid convergence of the l_{int} expansions results. For larger clusters with more complicated geometries, the maximum value of C_{i0} will be closer to unity and higher l_{int} values will be necessary. The optimum way to include them would be to introduce a site-dependent l_{int} and increase this only for those cases where C_{ij} or C_{i0} is large.

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