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Localized-muffin-tin-orbital basis for atomic-cluster calculations within the local-density formalism

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A new approach for solving the Hohenberg-Kohn-Sham density-functional equations for atomic clusters of moderate size and arbitrary symmetry is described. A basis set is introduced in the spirit of the LCMTO (linear combination of muffin-tin orbitals) method of Andersen with a $(\phi,\dot{\phi})$ form inside each atomic sphere. However, advantageous features of the conventional linear-combination-of-atomic-orbitals method are brought in by introducing only atomiclike orbital tails in the region outside the spheres. The "common-κ" approximation and cellular partitioning of the LCMTO approach are abandoned; with this approach it becomes necessary to carry out some three-dimensional integrations. Techniques are introduced which allow all integrals contributing to the secular matrix and total energy to be evaluated either semianalytically or by the Gaussian integration of smooth functions. Preliminary results for H_2 and O_2 demonstrate the practicality of the scheme.

I. INTRODUCTION

A substantial body of work on atoms, small molecules, and crystalline solids has shown that the total energy as defined in the Hohenberg-Kohn-Sham (HKS) density-functional formalism[1] can be calculated with sufficient accuracy to warrant studies of solid-state and chemical systems where such information is currently lacking. Since the problem of total energy calculation is reduced to the self-consistent solution of a one-particle equation, it should be possible to treat systems whose size makes them unamenable to *ab initio* methods of quantum chemistry. Nevertheless, the minimization of the HKS functional is by no means an easy task. Both the LCMTO (linear combination of muffin-tin orbitals)[2] and LCAO (linear combination of atomic orbitals) techniques have proven successful in calculations for diatomics,[3,4] however, significant difficulties hinder their application in total energy calculations for larger clusters. Motivated by the observation that advantageous features of the LCMTO and LCAO methods could be made complementary, we have devised a technique incorporating elements of each which should make it feasible to treat atomic clusters of moderate size and arbitrary symmetry. This has been accomplished by using a $(\phi,\dot{\phi})$ basis combination inside the atomic spheres (see Sec. II for details) to achieve rapid basis convergence (a distinct advantage over conventional LCAO basis sets), while the basis outside the spheres is chosen to represent atomiclike tails. The latter choice for the basis allows us to avoid the cellular construct of the LCMTO method with the associated poor convergence of the single-site expansions and the need to recalculate projection operators every time the shape of the cell is changed. These features of the cellular partitioning negate the essential advantage of the LCMTO method, that only single-center integrals need be performed.[3] Since an outer bounding sphere is not needed with the atomiclike orbital form outside the spheres, no orbital expansion about the cluster center is necessary. On the other hand, as a consequence of abandoning the cellular construct of the LCMTO scheme, it becomes necessary to evaluate three-dimensional integrals, both in forming the secular matrix and in calculating the total energy, as in the LCAO approach. Also, though the charge density inside each atomic sphere is still given semianalytically as a single-site partial-wave expansion, as in the LCMTO method, this is no longer true outside the spheres. On giving up the outer sphere and cellular construct, the solution of Poisson's equation for the density outside the spheres must be carried out either by direct numerical means or by fitting the density to simple functions.

In this paper, we describe the construct of the method and the associated procedures used to treat specific problems. The essential elements of the method are (1) a basis of "localized" muffin-tin orbitals (MTO's) of $(\phi,\dot{\phi})$ form, determined by the dominant part of the cluster potential inside touching atomic spheres with atomiclike function form outside the spheres and (2) special procedures to deal with problems introduced by leaving the cellular construct: (a) density fitting over the volume outside the atomic spheres and (b) integrand smoothing which allows the use of Gaussian quadrature for all three-dimensional integrals. Further organization of the paper is as follows. In Sec. II, the new orbital basis set is defined and motivation for its selection is discussed. Details concerning evaluation of the secular matrix including special procedures for performing the three-dimensional integrals are given in Sec. III. Emphasis is placed on the important feature that all large contributions to $\hat{H}$ and $\hat{O}$ emanating from within the atomic spheres can be calculated semianalytically, as in the LCMTO method. Evaluation of the charge density and potential is considered in Sec. IV, and in Sec. V, the total energy calculation is outlined. Some preliminary results for H_2 and O_2 are presented in Sec. VI, and we conclude with a discussion of the adequacy of our orbital and density basis sets.

II. BASIS SET

In order to carry out total energy calculations for atomic clusters of moderate size (3–20 atoms), retaining the full form of the potential and charge density, we require a basis set that is small yet accurate. The LCMTO basis fulfulls these criteria, but the necessity of a "bounding" outer sphere is a disadvantage. With the basis functions we propose, the outer sphere is not needed.

A. Definition

The basis functions, χ_L^i, are $(\phi, \dot{\phi})$ combinations inside atomic spheres centered on the nuclear sites, while outside they are decaying functions of the form

$$G_L^i(\vec{r}_i) = \overline{G}_L^i [K_l(\kappa_l^i, r_i) + A_l^i K_l(\bar{\kappa}_l^i, r_i)] Y_L(\hat{r}_i) , \quad (2.1)$$

where L denotes (l, m) and $\overline{G}_L^i$ is a factor which matches $G_L^i(\vec{r}_i)$ to the corresponding intra-atomic basis function at the atom-sphere boundary. The function $K_l(\kappa, r)$ is simply related to the Hankel function[5] $h_l^{(1)}(\bar{\kappa} r)$,

$$K_l(\kappa, r) = i \bar{\kappa}^{l+1} h_l^{(1)}(\bar{\kappa} r) , \quad (2.2)$$

where $\bar{\kappa} = i\kappa$ with κ pure real [also see Appendix A 2, Eq. (A7)]. A consequence of relinquishing the outer sphere of the LCMTO method is that two Hankel functions having different κ's must be used to accurately represent atomiclike tails in the volume outside the atomic spheres ("interstitial" region). The second term in Eq. (2.1) has a larger exponential parameter and serves to counteract the tendency of the leading Hankel function to increase too rapidly at small r. Compared with the LCMTO interstitial basis function, the tail function $G_L^i(\kappa, r)$ is no longer a single Bessel function having either $\bar{\kappa}^2 > 0$ or $\bar{\kappa}^2 < 0$, but a sum of two Hankel functions, both characterized by $\bar{\kappa}^2 < 0$.

Within each atomic sphere, the basis set has a $(\phi, \dot{\phi})$ form as in the LCMTO method. A local spherical average of the potential function is formed in order to define the basis inside the spheres. Denoting a solution to the radial wave equation for the spherical part of the potential in site "*i*" at energy ϵ_ν by $\phi_l^i(\epsilon_\nu, r_i)$ and defining its energy derivative $\dot{\phi}_l^i \equiv d\phi_l^i(\epsilon, r_i)/d\epsilon \,|_{\epsilon=\epsilon_\nu}$, the basis function $\chi_L^i(r_i)$ is given by

$$\chi_L^i(r_i) = \phi_l^i(\epsilon_\nu, r_i) + \omega_l^i(D) \dot{\phi}_l^i(\epsilon_\nu, r_i) . \quad (2.3)$$

The reference energy ϵ_ν is site and l dependent, i.e., $\epsilon_\nu \equiv \epsilon_l^i$. The constant $\omega_l^i(D)$ is chosen (see Appendix A 1) so that $\chi_L^i(r_i) Y_L(\hat{r}_i)$ matches the tail function $G_L^i(\vec{r}_i)$ [Eq. (2.1)] with continuous logarithmic derivative at the ith sphere boundary. An important feature of the $(\phi, \dot{\phi})$ construct is that χ_L^i is orthogonal to all core states of site i (i.e., all states having negligible amplitude at the atomic-sphere boundary). Furthermore, this advantageous feature is true concerning *all* core states of the cluster if we choose χ_L^i to also have the $(\phi, \dot{\phi})$ construct within all the other spheres $j \neq i$. Although in principle any function could be chosen for the tail orbital $G_L^i(\vec{r}_i)$, the choice of Hankel functions simplifies matching the interstitial orbital to a $(\phi, \dot{\phi})$ basis form inside the other sites, $j \neq i$ (see also Appendix B). This is accomplished by using the Bessel function expansion theorems, e.g., $\chi_L^i(\vec{r}_i)$ is represented in sphere j by expanding each $K_L(\kappa, \vec{r}_i)$ in terms of the complementary functions, $J_L(\kappa, \vec{r}_j)$, about site j,

$$G_L^i(\kappa_l^i, \vec{r}_i) = \overline{G}_L^i \sum_{L'} [\overline{B}_{LL'}^{ij}(\kappa_l^i) J_{L'}(\kappa_l^i, \vec{r}_j) + A_l^i \overline{B}_{LL'}^{ij}(\bar{\kappa}_l^i) J_{L'}(\bar{\kappa}_l^i, \vec{r}_j)] , \quad (2.4)$$

where the $\overline{B}_{LL'}^{ij}(\kappa)$ are structure constants (Appendix A 2) and

$$J_L(\kappa, \vec{r}_j) \equiv \kappa^{-l} (\pi/2\kappa r_j)^{1/2} I_{l+1/2}(\kappa r_j) Y_L(\hat{r}_j) , \quad (2.5)$$

where the modified spherical Bessel functions $I_{l+1/2}$ are defined by Abramowitz and Stegun.[5] Then each $J_L(\kappa, r_j)$ is matched to a linear combination of $\phi_l^j(\epsilon_\nu, r_j)$ and $\dot{\phi}_l^j(\epsilon_\nu, r_j)$ at the jth sphere boundary $(r_j = R_{\mathrm{MT}}^j)$. The expression for the basis function defined over all space may then be written as

$$\chi_L^i(\kappa_l^i, \vec{r}_i) \equiv \begin{cases} [\phi_l^i(\epsilon_\nu, r_i) + \omega_l^i \dot{\phi}_l^i(\epsilon_\nu, r_i)] Y_L(\hat{r}_i) , & \vec{r} \text{ in sphere } i \\ G_L^i(\kappa_l^i, r_i) Y_L(\hat{r}_i) , & \vec{r} \text{ outside all spheres} \\ \sum_{L'} [S_{LL'}^{ij}(\kappa_l^i) \phi_{l'}^j(\epsilon_\nu, r_j) + T_{LL'}^{ij}(\kappa_l^i) \dot{\phi}_{l'}^j(\epsilon_\nu, r_j)] Y_{L'}(\hat{r}_j) , & \vec{r} \text{ in sphere } j \neq i . \end{cases} \quad (2.6)$$

The vector $\vec{r}$ is relative to some arbitrary origin, site "i" is at $\vec{R}_i$, and $\vec{r}_i = \vec{r} - \vec{R}_i$. Tail transfer matrices are defined by

$$S^{ij}_{LL'}(\kappa^i_l) \equiv \bar{G}^i_L[\bar{B}^{ij}_{LL'}(\kappa^i_l)\bar{J}^j_{l'}(\kappa^i_l) + A^i_l\bar{B}^{ij}_{LL'}(\tilde{\kappa}^i_l)\bar{J}^j_{l'}(\tilde{\kappa}^i_l)]\,, \tag{2.7}$$

$$T^{ij}_{LL'}(\kappa^i_l) \equiv \bar{G}^i_L\{\bar{B}^{ij}_{LL'}(\kappa^i_l)\bar{J}^j_{l'}(\kappa^i_l)\omega^i_{l'}[J^j_{l'}(\kappa^i_l)] + A^i_l\bar{B}^{ij}_{LL'}(\tilde{\kappa}^i_l)\bar{J}^j_{l'}(\tilde{\kappa}^i_l)\omega^j_{l'}[J^j_{l'}(\tilde{\kappa}^i_l)]\}\,,$$

with

$$\bar{J}^j_l(\kappa) \equiv \frac{J_l(\kappa, R^j_{\mathrm{MT}})}{\{\phi^j_l(\epsilon_\nu, R^j_{\mathrm{MT}}) + \omega^j_l[J^j_l(\kappa)]\dot{\phi}^i_l(\epsilon_\nu, R^j_{\mathrm{MT}})\}}\,, \tag{2.8}$$

where $\omega^j[J^j(\kappa)]$ is that constant assuring smooth matching of the (ϕ, ϕ) combination in sphere j onto the Bessel function $J_L(\kappa, \vec{r}_j)$. For each site and each partial wave of allowed symmetry, we define the localized orbital $\chi^i_L(\kappa^i_l, \vec{r}_i)$, and solutions to the HKS single-particle equations are expanded in the linear form of an LCAO-like representation

$$\psi_n(\vec{r}) = \sum_{i,L} C^n_{iL}\chi^i_L(\kappa^i_l, \vec{r}_i)\,, \tag{2.9}$$

with expansion coefficients C^n_{iL}. However, the appearance of the κ^i_l denotes a nonlinear variational flexibility, and these parameters are in practice varied to minimize the total energy.

B. Completeness

It is evident from Eq. (2.6) that χ^i_L differs from an MTO only in the definition of $G^i_L(\kappa^i_l, r_i)$ and consequently the expansions of these functions in other sites, $j \neq i$. To understand the connection between the new basis and the MTO's, suppose the new basis is used to treat a cluster with a muffin-tin form of the potential. Then for levels below the "muffin-tin zero," the choice $A^i_l = 0$ in Eq. (2.1) reduces all χ^i_L to single MTO's. The resulting eigenvalue will then be correct to order $(\epsilon - \epsilon_\nu)^4$, as discussed elsewhere.[3] The role of the second Hankel function is immediately apparent on considering eigenvalues above the muffin-tin zero. In the LCMTO method, the cluster boundary condition forces the introduction of an outer bounding sphere in which case the single Bessel function describing an orbital in the interstitial region need not be a decaying one. In particular, the curvature of G^i_L at the atomic-sphere boundary might be positive. This effect can be simulated by expansion [Eq. (2.1)], however, if the second Hankel function $K(\tilde{\kappa}^i_l, r_i)$ has a larger exponential parameter than the first, $\tilde{\kappa}^i_l > \kappa^i_l$, and a negative coefficient, $A^i_l < 0$. The region designated as a "concave muffin-tin" in the LCMTO method[2] is described in this modified approach as a multicenter expansion of decaying Hankel functions centered on the nuclear positions. The wave function in the interstitial region is represented by linear combinations of two decaying Hankel functions from each site, and each Hankel function is characterized by a free parameter κ^i_l, allowing considerable flexibility. For a muffin-tin potential, the LCMTO basis is clearly superior in that an essentially exact solution is attained in the variational equations. An actual three-dimensional potential, however, may vary greatly, especially in the interstitial region, as for example, in open clusters simulating chemisorption. Here, the fact that the LCMTO basis is nearly complete for the muffin-tin part of the potential is of no apparent advantage, and it is quite possible for the modified basis to be superior, in spite of the smaller number of basis functions involved.

III. SECULAR MATRIX

It may be questioned why a wave equation is introduced at all in the total energy problem since the potential function merely defines the radial part of the basis set. In principle, all that is necessary is a minimization of the functional in the multiparameter space of $\{\kappa, C,$ and $\phi_l\}$. In practice, however, minimization in a multiparameter space is far from straightforward, and the true role of the one-electron equation in the HKS scheme is to guide the variation parameters rapidly into the region of the minimum.

With a given set of nonlinear parameters, the solution of the linear secular equations for the Cs is carried out by evaluation and diagonalization of the secular matrix with elements

$$H_{ij} = \langle\chi^i_L|(\hat{H} - E)|\chi^j_{L'}\rangle\,. \tag{3.1}$$

Evaluation of these elements is carried out by separating each into three components. Letting H_0 denote the muffin-tin part of the Hamiltonian, we have

$$H = H_0 + V(\vec{r}) - V_0(r_i)\,,\quad \vec{r} \text{ in } \Omega_i \tag{3.2}$$

where $V_0(r_i)$ is the spherical average of $V(\vec{r})$ within Ω_i (the ith sphere). Then the three constituents of the matrix element are given by

$$\langle\chi^i_L|(H - E)|\chi^j_{L'}\rangle_\infty = \langle\chi^i_L|(H_0 - E)|\chi^j_{L'}\rangle_{\Omega\,\mathrm{MT}} + \langle\chi^i_L|[V(\vec{r}) - V_0(r)]|\chi^j_{L'}\rangle_{\Omega\,\mathrm{MT}} + \langle G^i_L(\kappa^i_l, \vec{r}_i)|[-\nabla^2 + V(\vec{r}) - E]|G^j_{L'}(\kappa^j_{l'}, \vec{r}_j)\rangle_{\Omega_\mathrm{I}}\,, \tag{3.3}$$

where $\langle\;\rangle_{\Omega_{\mathrm{MT}}}$ $(\langle\;\rangle_{\Omega_\mathrm{I}})$ denotes integration over the region inside (outside) the muffin-tin spheres.

A. Type I: Muffin-tin matrix elements

The first component in Eq. (3.3) is an all-muffin-tin-type integral which, from the definition and properties of ϕ and $\dot{\phi}$ (Appendix A1), is expressed analytically in terms of ϵ_l^i and $\langle\dot{\phi}_l^i|\dot{\phi}_l^i\rangle_{\Omega_i}=\langle\dot{\phi}_l^{i^2}\rangle_{\Omega_i}$. Writing $\langle\chi_L^i|(H_0-E)|\chi_{L'}^j\rangle=H_{0LL'}^{ij}+EO_{LL'}^{ij}$, it is straightforward to show

$$\begin{aligned}H_{0\,LL'}^{ij}=&\{\epsilon_l^i[1+\omega^2(G_l^i)\langle\dot{\phi}_l^{i2}\rangle_{\Omega_i}]+\omega(G_l^i)\}\delta_{ij}\delta_{LL'}\\&+S_{L'L}^{ji}(\kappa_{l'}^j)\epsilon_l^i+T_{L'L}^{ji}(\kappa_{l'}^j)[1+\epsilon_l^i\omega(G_l^i)\langle\dot{\phi}_l^{i2}\rangle_{\Omega_i}]+S_{LL'}^{ij}(\kappa_l^i)[\epsilon_{l'}^j+\omega(G_{l'}^j)]+T_{LL'}^{ij}(\kappa_l^i)\omega(G_{l'}^j)\epsilon_{l'}^j\langle\dot{\phi}_{l'}^{j2}\rangle_{\Omega_j}\\&+\sum_{k=1}^{N}\sum_{L''}\{S_{LL''}^{ik}(\kappa_l^i)[S_{L'L''}^{jk}(\kappa_{l'}^j)\epsilon_{l''}^k+T_{L'L''}^{jk}(\kappa_{l'}^j)]+T_{LL''}^{ik}(\kappa_l^i)T_{L'L''}^{jk}\epsilon_{l''}^k\langle\dot{\phi}_{l''}^{k^2}\rangle_{\Omega_k}\},\end{aligned}\tag{3.4}$$

and

$$\begin{aligned}O_{LL'}^{ij}=&[1+\omega^2(G_l^i)\langle\dot{\phi}_l^{i2}\rangle_{\Omega_i}]\delta_{ij}\delta_{LL'}+S_{L'L}^{ji}(\kappa_{l'}^j)+T_{L'L}^{ji}(\kappa_{l'}^j)\omega(G_l^i)\langle\dot{\phi}_l^{i2}\rangle_{\Omega_i}+S_{LL'}^{ij}(\kappa_l^i)+T_{LL'}^{ij}(\kappa_l^i)\omega(G_{l'}^j)\langle\dot{\phi}_{l'}^{j2}\rangle_{\Omega_j}\\&+\sum_{k=1}^{N}\sum_{L''}[S_{LL''}^{ik}(\kappa_l^i)S_{L'L''}^{jk}(\kappa_{l'}^j)+T_{LL''}^{ik}(\kappa_l^i)T_{L'L''}^{jk}\langle\dot{\phi}_{l''}^{k2}\rangle_{\Omega_k}],\end{aligned}\tag{3.5}$$

where N is the number of atoms in the cluster. Equations (3.4) and (3.5) then define type-I matrix elements as semianalytic terms involving the potential parameters and structure constants of the system and the integrals $\langle\dot{\phi}_l^i|\dot{\phi}_l^i\rangle_{\Omega_k}$.

B. Type II: Intra-atom nonspherical components

The second term in Eq. (3.3) arises from the nonspherical components of $V(\vec{r})$ inside each atomic sphere, i.e., the contributions $\Delta V(\vec{r})=V(\vec{r})-V_0(r_i)$. These integrals may be evaluated in terms of the structure constants and non-muffin-tin-potential integrals $V_{LL'}^k$ defined by

$$V_{LL'}^k=\int_{\Omega_k}d\vec{r}_k\,g_l^k(r_k)f_{l'}^k(r_k)Y_L(\hat{r}_k)Y_{L'}(\hat{r}_k)\Delta V(\vec{r}_k),\tag{3.6}$$

where each function g_l^k and f_l^k may denote ϕ_l^k or $\dot{\phi}_l^k$.

The integrals $V_{LL'}^k$ in turn can be evaluated either by three-dimensional (Gaussian) quadrature or by forming a single-site partial-wave expansion of $\Delta V(\vec{r})$ in each sphere k,

$$\Delta V(\vec{r}_k)=\sum_L V_L^k(r_k)Y_L(\hat{r}_k),\tag{3.7}$$

and summing a series of one-dimensional integrals multiplied by Gaunt factors. The latter approach is adopted here. Detailed expressions for type-II matrix elements are given in Appendix D1.

C. Type III: Interstitial matrix elements

The last term in Eq. (3.3) arises from matrix elements in the basis components G_L^i and involves integration over Ω_{I}, the volume outside all atomic spheres. Using the derivative properties of the Hankel functions, the interstitial matrix element may be written

$$\langle G_L^i(\kappa_l^i,\vec{r}_i)|\{\bar{G}_{L'}^j[\kappa_{l'}^{j2}|K_{L'}(\kappa_{l'}^j,r_j)\rangle+A_{l'}^j\tilde{\kappa}_{l'}^{j2}|K_{L'}(\tilde{\kappa}_{l'}^j,\vec{r}_j)\rangle_{\Omega_{\text{I}}}]+[V(\vec{r})-E]|G_{L'}^j(\kappa_l^j,\vec{r}_j)\rangle_{\Omega_{\text{I}}}\}.\tag{3.8}$$

Each integral in Eq. (3.8) is complicated to evaluate because of the awkward region of integration. In the following, we describe procedures used to treat this difficulty.

D. Integrand smoothing

The atomic spheres are excluded from the integration region appearing in Eq. (3.8). However, we can include the spherical regions in the integration (then defined over all space) if separately we subtract out the overcounted atomic-sphere contributions. In order to achieve consistent accuracy, the integrand is smoothly extended into the spheres by defining a "pseudized" form $\tilde{f}(\vec{r})$ to each functional part $f(\vec{r})$ of the integrand. In the case of the interstitial matrix elements, we augment the tail functions G_L^i by an analytic fit to a simple function inside the spheres, e.g., we define

$$\tilde{G}_L^i(\kappa_l^i,\vec{r})=\begin{cases}(a_l^i+b_l^ir_i^2)Y_L(\hat{r}_i)\,, & \vec{r}\text{ in }\Omega_i\\ G_L^i(\kappa_l^i,r_i)Y_L(\hat{r}_i)\,, & \vec{r}\text{ outside }\Omega_i\end{cases}\tag{3.9}$$

where $\vec{r}_i=\vec{r}-\vec{R}_i$. Similarly, the potential is pseudized within each sphere by defining $\tilde{V}(\vec{r})$,

$$\tilde{V}(\vec{r})=\begin{cases}V(\vec{r})\,, & \vec{r}\text{ outside all spheres}\\ V(\vec{r})+[\tilde{V}_0(r_i)-V_0(r_i)]\,, & r_i\text{ in }\Omega_i\,.\end{cases}\tag{3.10}$$

Here $V_0(r_i)$ denotes the spherical average of $V(\vec{r})$ inside sphere i and $\tilde{V}_0(r_i)$ is a polynomial which matches $V_0(r_i)$ smoothly at the sphere boundary but is regular at $r_i=0$. Again, a quadratic form is generally suitable. The integral over the interstitial volume is then extended to run over all space and is efficiently evaluated by Gaussian quadrature (in elliptic coordinates). Subtraction of the overcounted contributions from within the spherical regions then yields the proper interstitial matrix element. In particular, the Bessel-function expansion theorems are used to reduce each three-dimensional integral to a sum of one-dimensional integrals of radial functions (see Appendix D 2).

In addition to the above use, integrand smoothing permits the efficient evaluation of integrals wherein the integrand $f(\vec{r})$ is nonsingular, but large (and/or rapidly varying) near each nucleus. Evaluation of the total energy (Sec. V) is a case encountered. Defining pseudized integrand components according to Eq. (3.10), the integral over all space separates into a series of one-dimensional integrals which can be evaluated to any desired accuracy, plus a single integral over all space of a smooth integrand $\tilde{f}(r)$ for which Gaussian quadrature on a suitable mesh is appropriate.

IV. DENSITY AND POTENTIAL EVALUATION

The electron density, given by

$$n(\vec{r}) = \sum_{L,i;L',j} Q^{ij}_{LL'} \chi^{i}_{L}(\kappa^{i}_{l}, \vec{r}_i) \chi^{j}_{L'}(\kappa^{j}_{l'}, \vec{r}_i) , \tag{4.1}$$

where

$$Q^{ij}_{LL'} = \sum_{n} a_n C^{n}_{iL} C^{n}_{jL'}$$

and the a_n are the occupation numbers for the state under consideration, can be expressed in each atomic sphere as a single-site partial-wave expansion. For $\vec{r}$ in the kth sphere, we have

$$n(\vec{r}) = \sum_{L} n^{k}_{L}(r_k) Y_L(\hat{r}_k) , \tag{4.2}$$

where

$$\begin{aligned} n^{k}_{L}(r_k) = {} & \sum_{L'} \sum_{L''} C_{LL'L''} Q^{kk}_{L'L''} \Phi^{k}_{l'}(r_k) \Phi^{k}_{l''}(r_k) + 2 \sum_{L'L'',i} \sum_{L_1} C_{LL'L_1} Q^{ik}_{L''L'} \Phi^{k}_{l'}(r_k) [S^{ik}_{L''L_1} \Phi^{k}_{l'}(r_k) + T^{ik}_{L''L_1} \dot{\phi}^{k}_{l_1}(r_k)] \\ & + \sum_{L',i} \sum_{L'',j} Q^{ij}_{L'L''} \sum_{L_1} \sum_{L_2} C_{LL_1L_2} [S^{ik}_{L'L_1} \phi^{k}_{l_1}(r_k) + T^{ik}_{L'L_1} \dot{\phi}^{k}_{l_1}(r_k)][S^{jk}_{L''L_2} \phi^{k}_{l_2}(r_k) + T^{jk}_{L''L_2} \dot{\phi}^{k}_{l_2}(r_k)] . \end{aligned} \tag{4.3}$$

Using expansions given by Eq. (4.2), the electrostatic potential due to the charge inside the spheres is calculated as a multicenter expansion

$$\phi(\vec{r}) = \sum_{L,i} \phi^{i}_{L}(r_i) Y_L(\hat{r}_i) , \tag{4.4}$$

with

$$\phi^{i}_{L}(r_i) \equiv \frac{8\pi}{2l+1} \int_0^{R^{i}_{\mathrm{MT}}} dr_i r_i^2 \frac{r^{l}_{<}}{r^{l+1}_{>}} n^{i}_{L}(r_i) . \tag{4.5}$$

For $\vec{r}$ outside all spheres, the partial-wave components of the Coulomb potential can be expressed in the form

$$\phi^{i}_{L}(r_i) = Q^{i}_{L} / r_i^{l+1} . \tag{4.6}$$

Since the exchange-correlation potential is nonlinear, its partial-wave components must be evaluated by numerical integration. We employ standard Gaussian methods for the sphere. As usual, the spherical components of density and potential are treated separately and evaluated explicitly on a logarithmic radial mesh. Other components are evaluated on a Gaussian radial mesh with, typically, ten points.

Outside the atomic sphere, no simple representation of the density is available. Since the exchange-correlation potential and energy density are local, we can use Eq. (4.1) directly for each point of the integration mesh. For the Coulomb potential, the solution of Poisson's equation for this density must be achieved by direct numerical methods, by an analytic approach, or by using the density represented as a sum of simple functions. In the absence of an analytic procedure, we have chosen to fit the density to simple basis functions for which Poisson's equation can be solved. Specific to this approach, the orbital tail (Hankel) functions, G^{i}_{L}, are appropriate. This fit basis offers the advantage that the Coulomb potential has an analytic multicenter expansion, and the overcounted density inside the spheres can be projected out using expansion theorems. The interstitial density is approximated by the multicenter expansion

$$n_I(\vec{r}) = \sum_{i,L} n^{L}_{i} D^{i}_{L}(\kappa^{i}_{l}, \vec{r}_i), \quad \vec{r}_i \text{ in } \Omega_{\mathrm{I}} . \tag{4.7}$$

Each D^{i}_{L} denotes a series of Hankel functions with corresponding weights and exponents which, together with the n^{L}_{i}, form a set of fit parameters. In this work, we include only two functions in each D^{i}_{L}, in direct analogy with the orbital basis, and perform a constrained nonlinear least-squares fit. Alternatively, all exponential parameters could be predetermined and a linear fit carried out as in LCAO methods.[4,6] Note that the fit is required only over the region outside the atomic spheres, where the density is relatively smooth, in contrast to conventional schemes requiring the fit over all space. The fit parameters are used only in the calculation of the Coulomb potential so that, for example, the error in the electrostatic energy attributable to an imperfect fit is linear in $n(\vec{r}) - n_I(\vec{r})$. The contribution to the Coulomb potential from the density inside the spheres is treated exactly, so we expect relatively less sensitivity to the density fit than encountered in conventional schemes.

Once the interstitial density fit is achieved, the corresponding electrostatic potential has the multicenter representation

$$\phi_I(\vec{r}) = \sum_i \sum_L \phi^I_{L,i}(r_i) Y_L(\hat{r}_i)\,, \tag{4.8}$$

with

$$\phi^I_{L,i}(r_i) \equiv \frac{8\pi}{(2l+1)} \left(n_i^L \int_{R_i}^{\infty} dr'_i r'^2_i \frac{r^l_<}{r^{l+1}_>} D^i_l(r'_i) - \int_0^{R_i} dr'_i r'^2_i \frac{r^l_<}{r^{l+1}_>} \Lambda^i_L(r'_i) \right), \tag{4.9}$$

where

$$\Lambda^i_L(r_i) = \sum_{j\neq i} \sum_{L'} n_j^{L'} F^{ji}_{L'L}(r_i)\,. \tag{4.10}$$

The function $F^{ji}_{LL'}(r_i)$ is defined such that

$$D^i_L(\kappa^i_l, \vec{r}_i) = \sum_{L'} F^{ij}_{LL'}(r_j) Y_{L'}(\hat{r}_j) \quad \text{for } \vec{r} \text{ in sphere } j\,. \tag{4.11}$$

Since D^i_L is a sum of Bessel functions, the $F^{ij}_{LL'}$ are simple products of structure constants and complementary Bessel functions given by the expansion theorem. The first term in Eq. (4.9) describes the potential contribution from density component D^i_L. The second term arises from a fictitious density $\Lambda^i_L(\vec{r}_i)$ to cancel the unwanted density inside sphere i contributed from fit components on the other sites $j \neq i$. Since D^i_L and Λ^i_L are both linear combinations of Bessel functions, the one-dimensional integrations in Eq. (4.9) can be carried out analytically. Thus, within the accuracy of the fit, the Coulomb potential of the entire density can be written as a multicenter expansion, valid over all space. In the interstitial region, this is the form used; inside the spheres the potential is converted to a single-site partial-wave expansion by numerical integration. The entire potential is thus expressed in a form suitable for matrix-element evaluation.

V. ENERGY CALCULATION

For a given set of one-electron solutions $\psi_n(\vec{r})$, the independent electron wave function describing the state under study can be constructed as a determinantal sum, and the density is given by

$$n(\vec{r}) = \sum_n a_n \,|\psi_n(\vec{r})\,|^2\,. \tag{5.1}$$

The corresponding value of the density functional $E[n(\vec{r})]$ is (in rydbergs)

$$E[n(\vec{r})] = T_0(n) + \int d\vec{r}\, n(\vec{r}) \{\tfrac{1}{2}\phi(\vec{r}) + \epsilon_{\text{xc}}[n(\vec{r})] + V_N(\vec{r})\} + \sum_{i\neq j} \frac{Z_i Z_j}{R_{ij}}\,. \tag{5.2}$$

Here $\phi(\vec{r})$ is the electrostatic potential due to the electron density $n(\vec{r})$, $V_N(\vec{r})$ that of all nuclei, Z_i is the nuclear charge, $\epsilon_{\text{xc}}(n)$ is the exchange-correlation energy of a homogeneous electron gas of density n, and

$$T_0(n) \equiv -\sum_n a_n \int d\vec{r}\, \psi^*_n(\vec{r}) \nabla^2 \psi_n(\vec{r})\,. \tag{5.3}$$

The occupation numbers a_n are determined by the symmetry of the state in question.[7] Invoking the frozen-core approximation, Eq. (5.2) can be written as a term independent of the nuclear positions plus the term

$$E_V[n(\vec{r})] = T^v_0[n] + \int d\vec{r}\, n_v(\vec{r}) \{\tfrac{1}{2}\phi_v(\vec{r}) + \epsilon_{\text{xc}}[n(\vec{r})] + \phi_c(\vec{r})\} + \int d\vec{r}\, n_c(\vec{r}) \{\epsilon_{\text{xc}}[n(\vec{r})] - \epsilon_{\text{xc}}[n_c(\vec{r})]\} + \sum_{i\neq j} \frac{Z^c_i Z^c_j}{R_{ij}}\,, \tag{5.4}$$

where $n_v(\vec{r})$ is the valence density given by Eq. (5.1) with the sum extending over (N) valence states only. The fixed core density is $n_c(\vec{r})$ and Z^c_i the net charge of the ith core. The electrostatic potential of the nuclei and core electrons is represented by $\phi_c(\vec{r})$ and $T^v_0[n]$ denotes the kinetic energy of the valence electrons. Using the wave equation to express T^v_0 in terms of the valence eigenvalues,

$$E_V[n(\vec{r})] = \sum_n^N a_n \epsilon_n + \int d\vec{r}\, n_v(\vec{r}) \{\tfrac{1}{2}\phi_v(\vec{r}) + \epsilon_{\text{xc}}[n(\vec{r})] + \phi_c(\vec{r}) - \overline{V}(\vec{r})\} + \int d\vec{r}\, n_c(\vec{r}) \{\epsilon_{\text{xc}}[n(\vec{r})] - \epsilon_{\text{xc}}[n_c(\vec{r})]\} + \sum_{i\neq j} \frac{Z^c_i Z^c_j}{R_{ij}}\,. \tag{5.5}$$

In Eq. (5.5), $\overline{V}(\vec{r})$ is the potential for which $\psi_n(\vec{x})$ are the eigenfunctions. Note that $\overline{V}(\vec{r})$ is the effective potential defined by the density obtained in the previous iteration ($\overline{V}(\vec{r})$ is given by its "self-consistent" form, $\phi_v(\vec{r}) + \mu_{\text{xc}}[n(\vec{r})] + \phi_c(\vec{r})$ only at full self-consistency). The only nontrivial quantity to evaluate in Eq. (5.5) is the second term which may be written

$$\int d\vec{r}\, n_v(\vec{r})\{\tfrac{1}{2}\phi_v(\vec{r})+\epsilon_{xc}[n(\vec{r})]-\overline{V}_v(\vec{r})\}\,, \qquad (5.6)$$

where $\overline{V}_v(\vec{r})$ replaces $\overline{V}(\vec{r})-\phi_c(\vec{r})$. Inside the spheres, partial-wave expansions are available for all components of this integral, thus simplifying its evaluation. There is no simple representation for the integrand in the interstitial region, and it is evaluated directly over the mesh specified by the numerical quadrature (see below).

Note that the magnitude of the integral [Eq. (5.6)] is E^V_{es}, the electrostatic energy of the valence electrons. This can be a large quantity and Eq. (5.6) must then be evaluated to high accuracy. To accomplish this, the integrand smoothing procedure described in Sec. III D is used. Letting

$$\mathcal{E}(\vec{r})\equiv\tfrac{1}{2}\phi_v(\vec{r})+\epsilon_{xc}[n(\vec{r})]-\overline{V}_v(\vec{r})\,, \qquad (5.7)$$

both $n_v(\vec{r})$ and $\mathcal{E}(\vec{r})$ are pseudized in each atomic sphere. Then Eq. (5.6) can be written as a sum of integrals over each sphere of the form

$$I_i=\int_{\Omega_i} d\vec{r}_i[n_v(\vec{r})\mathcal{E}(\vec{r})-\tilde{n}_v(\vec{r})\tilde{\mathcal{E}}(\vec{r})]\,, \qquad (5.8)$$

plus one global integral of the smoothed integrand,

$$I_t=\int d\vec{r}\,\tilde{n}_v(\vec{r})\tilde{\mathcal{E}}(\vec{r})\,. \qquad (5.9)$$

The integrals I_i reduce to one-dimensional integrals over each atomic sphere, and I_t is evaluated by Gaussian quadrature over a suitable mesh. For a diatomic geometry, elliptic coordinates are an obvious choice, and for H_2 and O_2 this procedure gave an accuracy of ~0.007 Ry with 50 and 200 points, respectively, for the half-space.[8] For atomic clusters that are roughly spherical, I_t can be evaluated by Gaussian integration over a bounding sphere using a suitable mapping of the radial variable onto the interval (0, 1). Tests with a Fermi function mapping onto the Gaussian variable y,

$$y=\frac{1+e^{-\beta r_0}}{1+e^{\beta(r-r_0)}}\,, \qquad (5.10)$$

showed that sufficient accuracy can be achieved with an acceptable number of points even for quite aspherical clusters.

VI. RESULTS AND DISCUSSION

As a preliminary check of the accuracy of this approach, we have applied the method to a study of diatomic molecules. Our initial aim is to compare with existing studies for these systems and to assess the adequacy of the orbital and density fit basis sets.

Each basis function, χ^i_L, depends on the three parameters, $\tilde{\kappa}^i_l$, κ^i_l, and A^i_l, which specify the tail function G^i_L. The additional parameter $\epsilon_\nu=\epsilon^i_l$, the reference energy, is prescribed a value roughly at the center of gravity of the relevant part of the eigenvalue spectrum. The initially chosen set of ϵ_ν is kept fixed during the calculation consistent with the basic concept of the $(\phi,\dot{\phi})$ construct that results depend weakly on ϵ_ν. In contrast, the tail parameters are varied to establish a minimum in the total energy. It is not feasible to perform a complete search of the three-parameter space, nor is it necessary, since the space is extremely flat. In practice, it is adequate to link two of the parameters in each orbital, $\tilde{\kappa}^i_l$ and A^i_l, to the leading exponent κ^i_l. The linkages are obtained by analysis of the radial solutions for atoms with a screened potential. Variations in the three parameters as systematic changes are made in the single-site potential (for example, fractional nuclear-charge shifts) generate a family of atomic-like solutions. Fitting the orbitals to the form G^i_L, Eq. (2.1), outside some radius defining the smallest atomic sphere needed in the cluster calculation then provides a sequence of $\tilde{\kappa}^i_l$, A^i_l, and κ^i_l values. A linkage of $\tilde{\kappa}^i_l$ and A^i_l to κ^i_l is established (approximately linear seems to be the rule), and with one free (nonlinear) parameter per inequivalent orbital, the variational problem for a general cluster is manageable. Extension to include "polarization" basis functions (partial waves not bound in the atom) can be carried out by the following procedure. The radial wave equation with an atomic potential is integrand outwards to the atomic-sphere radius R at some chosen energy and the logarithmic derivative determined. Integration from infinity inwards to $R'>R$ is performed and the leading κ^i_l determined by fitting a single Hankel function to the outside radial solution. The remaining parameters defining G^i_L are then obtained by requiring a match to the inside logarithmic derivative at R.

Once linkages are established, minimization of E_v is achieved by varying each orbital in sequence, according to its importance in the bonding. For O_2, for example, the $2p$ orbitals are first varied with the $2s$ held fixed. Subsequent variation of the $2s$ orbitals lowers the total energy only slightly and these two steps are sufficient to give a good estimate of the minimum in the two-parameter space. This straightforward procedure works reasonably well since in a given application either it is obvious which tail functions are most sensitive to the environment, or such information can be readily gained by performing limited trial calculations. In fact, our experience suggests that the behavior of the energy after the first iteration with a given set of κ's is sufficient to establish the minimum region. More sophisticated exponent optimization procedures in a multidimensional space also can be adopted. Finally, we note that the problem of determining the minimum arises only because it is possible to vary the orbitals independently of one another, i.e., there is considerable variational freedom inherent in this basis. Thus, we overcome a major limitation of the LCMTO method,[3] where a minimal basis calculation is tractable only within the common-κ approximation.

The basis functions used to fit the interstitial density have the same form as the orbital tail functions, and calculations in the atomic limit were again carried out to link the parameters $\tilde{\kappa}_l^i$ and A_l^i to κ_l^i. A nonlinear least-squares fit of the density over the interstitial volume established the linear parameters and the set of κ_l^i for the density representation $n_I(r)$, Eq. (4.7), which was then used solely for calculating the corresponding Coulomb potential.

One of our initial aims was to study the sensitivity of the total energy to the quality of the fit, in particular, to the number of partial waves that must be included in the density basis, Eq. (4.7). Figure 1 shows the results obtained for the hydrogen molecule.[9] The p orbitals were held fixed (a single trial run showed very little sensitivity of the energy to even marked changes in κ_p), and the energy was minimized with respect to variations in κ_s alone. Although gross errors in the density fit were apparent with only s waves[9] in the density basis, Fig. 1 shows that the calculated energy curve (dashed) is quite close to the essentially exact results (open circles) of Gunnarsson and Johansson[10] (GJ) using the same functional. Adding p waves[9] to the density basis improved the fit greatly (maximum errors were a few percent) but had little influence on the energy (full curve in Fig. 1). Except at separations inside the minimum where almost all the electrons are outside the atomic spheres, the only effect was an upward shift ~0.1 eV. That the full curve lies above the GJ result is due, presumably, to incompleteness of the orbital basis. The triangles in Fig. 1 were obtained using the LCMTO method and a basis which included d waves for both convex and concave muffin tins.[3] This basis is closer to completeness for H_2, as the results show. However, for practical purposes, the differences between any of the calculated energy curves shown in Fig. 1 are unimportant and would give virtually the same spectroscopic parameters.

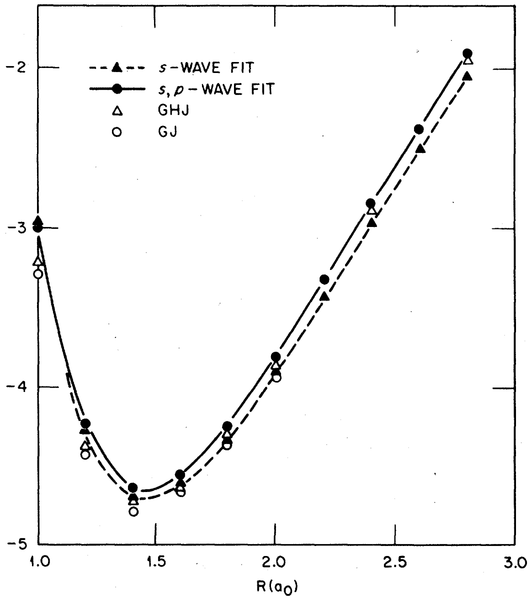

FIG. 1. Calculations of binding-energy curves for the H_2 molecule in the local density approximation. Curves shown are obtained from present scheme using s-wave density fit (dashed) and s, p-wave fit (solid). The open triangles are results from the LCMTO calculations of GHJ (Ref. 3); the open circles are results of GJ (Ref. 10).

That the result for H_2 is so insensitive to the density fit is encouraging, if somewhat surprising. In general, one expects the long range of the Coulomb potential to smooth out local inaccuracies in the fit density, that is, $\phi(\vec{r})$ is less sensitive to the fit parameters than the density itself, provided the latter is correctly normalized. The extent of this effect is difficult to assess, but we speculate that an s-wave fit will be adequate for systems where σ bonding is predominant; where π bonding is substantial, the s-wave approximation will be suspect. Preliminary results for O_2 show that p waves are essential in the density basis. For example, the s-wave fit yields spectroscopic parameters $E_B = 8.7$ eV, $R_e = 2.35a_0$ while inclusion of p waves gives $E_B = 7.6$ eV and $R_e = 2.27a_0$. These results, achieved with an orbital s-p basis, are preliminary and a full set of data for first-row molecules will be presented elsewhere. We note, however, that even the simplest calculation using the present basis accounts for almost all of the basis error in the binding energy of O_2 inherent in the common-κ approximation of the LCMTO method.[3]

In conclusion, we have introduced a new basis set and presented a practical method for the minimization of the HKS density functional for a general cluster of atoms. The basis is predominantly defined by the potential parameters of the system, and the method may be viewed as a refinement of the LCMTO approach. However, advantageous features of the LCAO method are introduced to form a more general and sophisticated scheme. We have discussed how all quantities relating to secular matrix and energy evaluation can be calculated and demonstrated the feasibility of the scheme for diatomic molecules. The approach appears practical for studies of larger clusters, for example our present program, in no sense optimized, requires only ~3 s per iteration (IBM 370/168) for a diatomic geometry. Typically, stationarity of the energy for a given set of κ's (i.e., on varying the potential towards self-consistency) requires 4–8 iterations. The weak points in the method are (1) the need for a fitting of the density over the region outside the atomic spheres and (2) the appearance of three-dimensional integrals in the evaluation of the energy. At this point, it is difficult to see how these features are to be avoided, but there is no inherent reason why either should prove limiting in applications to larger clusters.

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APPENDIX A: BASIC DEFINITIONS

1. The $\phi,\dot{\phi}$ construct

Inside the atomic spheres, the basis function is defined in terms of solutions $\phi_l^i(\epsilon_l^i, r_i)$ to the radial wave equation for the spherical part of the potential in the ith site at energy ϵ_l^i, and $\dot{\phi}_l^i(\epsilon_l^i, r_i)$ is the corresponding energy derivative, $d\phi_l^i(\epsilon, r_i)/d\epsilon|_{\epsilon=\epsilon_l^i}$.

The linear combination

$$\chi_l^i(r_i, D) = \phi_l^i(\epsilon_l^i, r_i) + \omega_l^i(D)\dot{\phi}_l^i(\epsilon_l^i, r_i) \tag{A1}$$

has logarithmic derivative D at $r_i = R_{\mathrm{MT}}^i$, provided that

$$\omega_l^i(D) = -\frac{\phi_l^i(\epsilon_l^i, R_{\mathrm{MT}}^i)}{\dot{\phi}_l^i(\epsilon_l^i, R_{\mathrm{MT}}^i)}\frac{(D - D_l^i)}{(D - \dot{D}_l^i)}, \tag{A2}$$

where D_l^i and $\dot{D}_l^i$ are the logarithmic derivatives at $r_i = R_{\mathrm{MT}}^i$ of ϕ_l^i and $\dot{\phi}_l^i$, respectively. It can be easily shown that from the definitions of ϕ and $\dot{\phi}$, the following relationships hold true:

$$\begin{aligned} H_0|\phi_l\rangle &= \epsilon_l|\phi_l\rangle, \\ H_0|\dot{\phi}_l\rangle &= |\phi_l\rangle + \epsilon_l|\dot{\phi}_l\rangle. \end{aligned} \tag{A3}$$

From these it follows

$$\begin{aligned} &\langle\phi_l|H_0|\phi_{l'}\rangle = \epsilon_l\delta_{ll'}, \quad \langle\phi_l|\phi_{l'}\rangle = \delta_{ll'}, \\ &\langle\phi_l|H_0|\dot{\phi}_{l'}\rangle = \delta_{ll'}, \quad \langle\phi_l|\dot{\phi}_{l'}\rangle = 0, \\ &\langle\dot{\phi}_l|H_0|\phi_{l'}\rangle = 0, \quad \langle\dot{\phi}_l|\phi_{l'}\rangle = 0, \\ &\langle\dot{\phi}_l|H_0|\dot{\phi}_{l'}\rangle = \epsilon_l\langle\dot{\phi}_l^2\rangle\delta_{ll'}, \quad \langle\dot{\phi}_l|\dot{\phi}_{l'}\rangle = \langle\dot{\phi}_l^2\rangle\delta_{ll'}. \end{aligned} \tag{A4}$$

2. Structure constants

The structure constants used in this work are the same as those given in Appendix I.A of Ref. 3. They are repeated here for reference purposes along with expansion theorems for the Bessel functions:

$$\overline{B}_{LL'}^{ij}(\kappa) = 4\pi\sum_{L''} i^{l'-l-l''}\kappa^{l+l'-l''}C_{LL'L''}K_{L''}(\kappa, \vec{\mathrm{R}}_{ij}^0), \tag{A5}$$

where

$$C_{LL'L''} \equiv \int d\hat{r}\, Y_L(\hat{r})Y_{L'}(\hat{r})Y_{L''}(\hat{r}), \tag{A6}$$

and $Y_L(\hat{r})$ is a real spherical harmonic. The functions $K_L(\kappa, \vec{\mathrm{r}})$ are related to the modified spherical Bessel functions of the third kind[5] $\mathcal{K}_{l+1/2}$ by

$$K_L(\kappa, \vec{\mathrm{r}}) = \kappa^{l+1}(2/\pi\kappa r)^{1/2}\mathcal{K}_{l+1/2}(\kappa r)Y_L(\hat{r}). \tag{A7}$$

The complementary function

$$J_L(\kappa, r) = \kappa^{-l}(\pi/2\kappa r)^{1/2}I_{l+1/2}(\kappa r)Y_L(\hat{r}), \tag{A8}$$

defines the expansion of $K_L(\kappa_l, \vec{\mathrm{r}}_i)$, defined at site $\vec{\mathrm{R}}_i$, about another site at $\vec{\mathrm{R}}_j$:

$$K_L(\kappa_l, \vec{\mathrm{r}}_i) = \sum_{L'}\overline{B}_{LL'}^{ij}(\kappa_l)J_{L'}(\kappa_l, \vec{\mathrm{r}}_j). \tag{A9}$$

APPENDIX B: ORBITAL TAIL FUNCTIONS

The choice of two Hankel functions for the tail part of the basis was motivated primarily by the existence of simple expansion theorems for these functions. To investigate how many tail orbitals are required, the following atomic calculations were carried out. Firstly, the total energy of the atom in a given configuration was calculated using a frozen-core atomic program. Next a calculation using valence orbitals of the type proposed here was performed. For each orbital,

$$\chi_L(\vec{\mathrm{r}}) \equiv Y_L(\hat{r}) \times \begin{cases} \phi_l(\epsilon_\nu^l, r) + \omega_l(\epsilon_\nu^l)\dot{\phi}(\epsilon_\nu^l, r), & r \leqslant R_c \\ G_l(\kappa, r), & r > R_c \end{cases} \tag{B1}$$

where R_c is chosen greater than some smallest radius encountered in a cluster calculation (minimum R_c approximately half the equilibrium separation for the relevant dimer). In the present case, it is feasible to adjust the set of reference energies ϵ_ν^l in each iteration to equal the eigenvalues from the preceding one. Then the minimum of the total energy with respect to the variation parameters defining the set of functions $G_l(\kappa, r)$ generates an energy which approaches the exact result from self-consistency equations E_0 as $R_c \to \infty$ [the ϵ_ν^l then approach the exact eigenvalues and $\omega_l(\epsilon_\nu^l) \to 0$]. For finite R_c, the energy $E(R_c)$ departs from E_0, since the tail functions do not form a complete set [$\Delta E(R_c) = E(R_c) - E_0$ provides a measure of basis incompleteness]. Obviously, this is a decreasing function of R_c since the region of space spanned by the orbital tails increases rapidly as R_c decreases. Tests were carried out with the following selections for $G_L(\kappa, r)$: (1) one Hankel function, (2) two Hankel functions, (3) one Slater-type orbital (STO), (4) two STO's and (5) two Gaussians. For minimum R_c, the results for single functions were all poor. The STO was better than the Hankel function because the latter increases too rapidly as r decreases. For the oxygen atom, the single Hankel function gave $\Delta E(1.24a_0) \sim 4$ eV compared with 1 eV for the single STO. Addition of a second Hankel function (three variation parameters) decreased this error to essentially zero (<0.001 eV). Similar results were obtained with two STO's, while two Gaussians gave an error ~0.1 eV. Our conclusion, therefore, is that *two* tail functions are necessary and sufficient to represent our cluster basis orbital outside the spheres, and that no advantage accrues from choosing STO's rather than Hankel functions. It must be borne in mind, of course, that the basis error in a cluster calculation will be much greater than for a free atom due to the more complicated potential. Whereas a minimal basis LCAO can be made exact by a suitable choice of basis functions in the atomic case, it is not feasible to achieve this for a general cluster potential.

APPENDIX C: BASIS ACCURACY

From Eq. (2.6) it is seen that the localized orbital $\chi_L^i(\kappa_l^i, \vec{r}_i)$ depends on all three parameters contained in $G_L^i(\kappa_l^i, r_i)$, so that, with fixed reference energy ϵ_l^i, these parameters determine the basis function uniquely over all space (within a normalization factor). To illustrate further the kinds of basis error expected from approximating a cluster wave function by Eq. (2.9), assume the free parameters κ_l^i, $\tilde{\kappa}_l^i$, and A_l^i chosen so that each G_L^i is as close as possible to a solution of the wave equation for energy ϵ at all points outside the spheres. Then the linear combination

$$\sum_{L,i} C_L^i \chi_L^i(\kappa_l^i(\epsilon), \vec{r}_i), \tag{C1}$$

where the nonlinear variational parameters are now fixed by the energy, is close to a solution in the interstitial region. Inside sphere j, Eq. (C1) takes the form

$$\sum_L C_L^i [\phi_l^j + \omega_l^i(\epsilon)\dot{\phi}_l^j] Y_L(\hat{r}_j) + \sum_{L',\, i\neq j} C_{L'}^i [S_{L'L}^{ij}(\epsilon)\phi_l^j + T_{L'L}^{ij}(\epsilon)\dot{\phi}_l^j] Y_{L'}(\hat{r}_j), \tag{C2}$$

which can be written

$$\sum_L A_L^i [\phi_l^i + (\epsilon - \epsilon_\nu)\dot{\phi}_l^i] Y_L(\hat{r}_i), \tag{C3}$$

provided the coefficients C_L^j satisfy the linear equations:

$$C_L^i [\omega_l^i(\epsilon) + (\epsilon_\nu - \epsilon)] Y_L(\hat{r}_j) + \sum_{L',\, i\neq j} C_{L'}^i [T_{L'L}^{ij}(\epsilon) + (\epsilon_\nu - \epsilon) S_{L'L}^{ij}(\epsilon)] Y_{L'}(\hat{r}_j) = 0 . \tag{C4}$$

These homogeneous equations can have a solution only for certain energies, at which Eq. (C2), by construction, satisfies the wave equation for the spherical part of the potential to order $(\epsilon - \epsilon_\nu)^2$. This is the crucial advantage of the $(\phi, \dot{\phi})$ construction. If it were the case that Eq. (C1) gave an exact solution outside the spheres, and to the extent that the nonspherical part of the potential inside the spheres is negligible, the entire wave function would deviate from an exact solution only by quantities of order $(\epsilon - \epsilon_\nu)^2$ and the eigenvalues would be correct to order $(\epsilon - \epsilon_\nu)^4$.

In practice, of course, this can never be the case and errors will arise both outside and inside the spheres. By performing a variational calculation with respect to the basis function parameters and the linear coefficients, one minimizes such errors, though there is never a guarantee that they will be sufficiently small. Viewed within the framework of density functional theory, one in fact performs variation at three levels. According to Hohenberg, Kohn, and Sham,[1] the density functional is minimized on solving exactly a one-electron problem together with a self-consistency condition. If one evaluates the density functional using one-electron wave functions obtained by solving the problem of N noninteracting electrons in a given potential $V(\vec{r})$, different from the self-consistent value, the result is necessarily higher than the model ground-state energy. (By which we mean, the exact minimum of the functional in use, which will depend, of course, on the approximation one makes for the exchange-correlation part, and may be larger or smaller than the *exact* ground-state energy of the physical system under study.)

In practice, one achieves only an approximate solution for potential $V(\vec{r})$ and it might be thought that the minimum principle is violated. This is, however, not the case, for an approximate set of eigenvalues and eigenfunctions corresponding to potential $V(\vec{r})$ is, presumably, an exact set for some other potential[11] $V'(\vec{r})$. While the value of the functional for this set may give a lower energy than would the exact solution for potential $V(\vec{r})$ [that is, by accident $V'(\vec{r})$ may be closer to the self-consistent potential than $V(\vec{r})$], it can never give a value lower than the model ground-state energy (in the sense indicated above). In this way, one sees that the potential employed in the calculation, the linear parameters C_L^i and the nonlinear Hankel-function parameters, κ_l^i can all be regarded as variational parameters for the density functional, and it is the stationarity of this, and not of the eigenvalues of a given potential, that is crucial. In essence, one is arguing that the error in the total energy due to basis inadequacies, can be substantially less than the errors in the eigenvalues for any given potential.[12]

APPENDIX D: MATRIX ELEMENT EXPANSIONS

1. Type-II matrix elements

$$\begin{aligned}
\langle\chi_L^i|V(\vec{r})-V_0(r)|\chi_{L'}^j\rangle_{\Omega_{\mathrm{MT}}} &= \langle\chi_L^i|\Delta V|\chi_{L'}^j\rangle_{\Omega_{\mathrm{MT}}}\\
&=[\langle\phi_L^i|\Delta V|\phi_{L'}^i\rangle_{\Omega_i}+\omega(G_l^i)\langle\dot{\phi}_L^i|\Delta V|\phi_{L'}^i\rangle_{\Omega_i}+\omega(G_{l'}^i)\langle\phi_L^i|\Delta V|\dot{\phi}_{L'}^i\rangle_{\Omega_i}\\
&\quad+\omega(G_l^i)\omega(G_{l'}^i)\langle\dot{\phi}_L^i|\Delta V|\dot{\phi}_{L'}^i\rangle_{\Omega_i}]\delta_{ij}\\
&\quad+\sum_{L''}\{S_{L'L''}^{ji}(\kappa_{l'}^j)[\langle\phi_L^i|\Delta V|\phi_{L''}^i\rangle_{\Omega_i}+\omega(G_l^i)\langle\dot{\phi}_L^i|\Delta V|\phi_{L''}^i\rangle_{\Omega_i}]\\
&\qquad+T_{L'L''}^{ji}(\kappa_{l'}^j)[\langle\phi_L^i|\Delta V|\dot{\phi}_{L''}^i\rangle_{\Omega_i}+\omega(G_l^i)\langle\dot{\phi}_L^i|\Delta V|\dot{\phi}_{L''}^i\rangle_{\Omega_i}]\\
&\qquad+S_{LL''}^{ij}(\kappa_l^i)[\langle\phi_{L''}^j|\Delta V|\phi_{L'}^j\rangle_{\Omega_j}+\omega(G_{l'}^j)\langle\phi_{L''}^j|\Delta V|\dot{\phi}_{L'}^j\rangle_{\Omega_j}]\\
&\qquad+T_{LL''}^{ij}(\kappa_l^i)[\langle\dot{\phi}_{L''}^j|\Delta V|\phi_{L'}^j\rangle_{\Omega_j}+\omega(G_{l'}^j)\langle\dot{\phi}_{L''}^j|\Delta V|\dot{\phi}_{L'}^j\rangle_{\Omega_j}]\}\\
&\quad+\sum_{k=1}^{N}\sum_{L''}\sum_{L'''}\{S_{LL''}^{ik}(\kappa_l^i)[S_{L'L'''}^{jk}(\kappa_{l'}^j)\langle\phi_{L''}^k|\Delta V|\phi_{L'''}^k\rangle_{\Omega_k}+T_{L'L'''}^{jk}(\kappa_{l'}^j)\langle\phi_{L''}^k|\Delta V|\dot{\phi}_{L'''}^k\rangle_{\Omega_k}]\\
&\qquad+T_{LL''}^{ik}(\kappa_l^i)[S_{L'L'''}^{jk}(\kappa_{l'}^j)\langle\dot{\phi}_{L''}^k|\Delta V|\phi_{L'''}^k\rangle_{\Omega_k}+T_{L'L'''}^{jk}(\kappa_{l'}^j)\langle\dot{\phi}_{L''}^k|\Delta V|\dot{\phi}_{L'''}^k\rangle_{\Omega_k}]\}\,. \qquad \text{(D1)}
\end{aligned}$$

The type-II matrix elements are thus expressed in terms of the potential integrals

$$V_{LL'}^k=\int_{\Omega_k}d\vec{r}_k g_l^k(r_k)f_{l'}^k(r_k)Y_L(\hat{r}_k)Y_{L'}(\hat{r}_k)\Delta V(\vec{r}_k)\,,$$

which are evaluated by first expanding $\Delta V(\vec{r}_k)$ in spherical harmonics. The $V_{LL'}^k$ then are given as a sum of one-dimensional integrals multiplied by Gaunt factors.

2. Type-III interstitial matrix elements

The secular matrix element contribution from the region outside the atomic spheres has the form

$$M_{\mathrm{III}_{LL'}}^{ij}=\overline{G}_{l'}^j\langle G_L^i(\kappa_l^i,\vec{r}_i)|\{[V(\vec{r})-\kappa_{l'}^{j2}-E]|K_{L'}^j(\kappa_{l'}^j)\rangle_{\Omega_{\mathrm{I}}}+A_{l'}^j[V(\vec{r})-\tilde{\kappa}_{l'}^{j2}-E]|K_{L'}^j(\tilde{\kappa}_{l'}^j)\rangle_{\Omega_{\mathrm{I}}}\}\,. \qquad \text{(D2)}$$

Introducing the smoothing procedure described in Sec. II, we define

$$\tilde{K}_l^i(\kappa_l^i,r_i)\equiv\begin{cases}K_l^i\,, & r_i\geqslant R_{\mathrm{MT}}^i\\ a_l^i+b_l^ir_i^2\,, & r_i<R_{\mathrm{MT}}^i\end{cases} \qquad \text{(D3)}$$

and

$$V_{ps}(\vec{r})=\tilde{V}(\vec{r})=\begin{cases}V(\vec{r})\,, & \vec{r}\text{ outside all atom spheres}\\ V(\vec{r})+[\tilde{V}_0(r_i)-V_0(r_i)]\,, & \vec{r}\text{ in sphere }i\,.\end{cases} \qquad \text{(D4)}$$

Here $V_0(r_i)$ is the local $l=0$ potential in sphere i and $\tilde{V}_0(r_i)=c_i+d_ir_i^2$ is the local pseudized potential. We then write

$$M^{ij}_{\mathrm{III}_{LL'}} = \tilde{M}^{ij}_{\mathrm{III}_{LL'}} - (KE^{ij}_{LL'} + \tilde{V}^{ij}_{LL'} - E\tilde{O}^{ij}_{LL'}) \,, \tag{D5}$$

where $\tilde{M}^{ij}_{\mathrm{III}_{LL'}}$ is evaluated directly by three-dimensional Gaussian integration extending over all space:

$$M^{ij}_{\mathrm{III}_{LL'}} = \bar{G}^j_{l'} \langle \tilde{G}^i_L(\kappa^i_l, \vec{\mathrm{r}}_i) | \{ [V_{ps}(\vec{\mathrm{r}}) - \kappa^{j\,2}_{l'} - E] | \tilde{K}^j_{L'}(\kappa^j_{l'}) \rangle_\infty + A^j_{l'} [V_{ps}(\vec{\mathrm{r}}) - \tilde{\kappa}^{j\,2}_{l'} - E] | \tilde{K}^j_{L'}(\tilde{\kappa}^j_{l'}) \rangle_\infty \} \,. \tag{D6}$$

The remaining terms in Eq. (D5) are corrective terms to subtract off the overcounted contributions in Eq. (D6) arising from the regions inside the atomic spheres. Using the expansion theorems for the K^i_L's,

$$\begin{aligned}
\tilde{V}^{ij}_{LL'} = \bar{G}^i_l \bar{G}^j_{l'} \Bigg(& \sum_{L''} \{ \bar{B}^{ji}_{L'L''}(\kappa^j_{l'}) [\langle \tilde{K}^i_L(\kappa^i_l) | V_{ps} | J^i_{L''}(\kappa^j_{l'}) \rangle_{\Omega_i} + A^i_l \langle \tilde{K}^i_l(\tilde{\kappa}^i_l) | V_{ps} | J^i_{L''}(\kappa^j_{l'}) \rangle_{\Omega_i}] \\
& + A^j_{l'} \bar{B}^{ji}_{L'L''}(\tilde{\kappa}^j_{l'}) [\langle \tilde{K}^i_L(\kappa^i_l) | V_{ps} | J^i_{L''}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_i} + A^i_l \langle \tilde{K}^i_L(\tilde{\kappa}^i_l) | V_{ps} | J^i_{L''}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_i}] \\
& + \bar{B}^{ij}_{LL''}(\kappa^i_l) [\langle J^j_{L''}(\kappa^i_l) | V_{ps} | K^j_{l'}(\kappa^j_{l'}) \rangle_{\Omega_j} + A^j_{l'} \langle J^j_{L''}(\kappa^i_l) | V_{ps} | \tilde{K}^j_{L'}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_j}] \\
& + A^i_l \bar{B}^{ij}_{LL''}(\tilde{\kappa}^i_l) [\langle J^j_{L''}(\tilde{\kappa}^i_l) | V_{ps} | K^j_{L'}(\kappa^j_{l'}) \rangle_{\Omega_j} + A^j_{l'} \langle J^j_{L''}(\tilde{\kappa}^i_l) | V_{ps} | \tilde{K}^j_{L'}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_j}] \} \\
& + \sum_{k=1}^{N} \sum_{L''} \sum_{L'''} \{ \bar{B}^{ik}_{LL''}(\kappa^i_l) [\bar{B}^{jk}_{L'L'''}(\kappa^j_{l'}) \langle J^k_{L''}(\kappa^i_l) | V_{ps} | J^k_{L'''}(\kappa^j_{l'}) \rangle_{\Omega_k} + A^j_{l'} \bar{B}^{jk}_{L'L'''}(\tilde{\kappa}^j_{l'}) \langle J^k_{L''}(\kappa^i_l) | V_{ps} | J^k_{L'''}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_k}] \\
& + A^i_l \bar{B}^{ik}_{LL''}(\tilde{\kappa}^i_l) [\bar{B}^{jk}_{L'L'''}(\kappa^j_{l'}) \langle J^k_{L''}(\tilde{\kappa}^i_l) | V_{ps} | J^k_{L'''}(\kappa^j_{l'}) \rangle_{\Omega_k} \\
& + A^j_{l'} \bar{B}^{jk}_{L'L'''}(\tilde{\kappa}^j_{l'}) \langle J^k_{L''}(\tilde{\kappa}^i_l) | V_{ps} | J^k_{L'''}(\tilde{\kappa}^j_{l'}) \rangle_{\Omega_k}] \} \Bigg) \,.
\end{aligned} \tag{D7}$$

The terms in $KE^{ij}_{LL'}$ follow from those of $\tilde{V}^{ij}_{LL'}$ by simply replacing the potential V_{ps} by the constant, $-\kappa^{j\,2}_{l'}$, in Eq. (D7). Similarly, the overlap matrix $\tilde{O}^{ij}_{LL'}$ is obtained on replacing V_{ps} in Eq. (D7) by unity. The case $j=i$ is handled in a straightforward manner.

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[7] The influence of unpaired spins is taken into account as in Ref. 3, i.e., by replacing $\epsilon_{\mathrm{xc}}(n)$ by $\epsilon_{\mathrm{xc}}[n(r), m(r)]$, the exchange-correlation (xc) energy of a homogeneous electron gas of density n and spin polarization m.

[8] Using a quadratic pseudizing, $I_t(0_2)$ is of the order 65 Ry so the percentage accuracy of this technique is extremely high. As a check on accuracy, we employ an identical procedure to evaluate the amount of valence charge, which depends not only on the accuracy of the final integral, but also on the overlap integrals that are used in normalizing the eigenfunctions.

[9] We used an s,p-wave orbital basis with the following parameter linkages: $\tilde{\kappa}_s = 1.11\kappa_s + 0.45$; $A_s = -0.982$; $\kappa_p = 0.7$; $\tilde{\kappa}_p = 1.1$; $A_p = -1.05$. Linkages for the s- and p-wave density basis sets were $\tilde{\kappa}^D_s = 1.05\kappa^D_s$; $A^D_s = -1.0$ and $\tilde{\kappa}^D_p = \kappa^D_p + 0.11$; $A^D_p = -1.0$, respectively.

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[11] The assumption here is only slightly stronger than that needed to justify the HKS approach in the first place.

[12] Note that the eigenvalues of a nonlinear eigenvalue problem do not obey a variational principle. If $\epsilon_i \equiv \langle \psi_i | H(\psi_i) | \psi_i \rangle$ is the exact eigenvalue of the self-consistent potential, then

$$\begin{aligned}
\epsilon^{\phi i}_i &\equiv \langle \phi_i | H(\phi_i) | \phi_i \rangle \\
&= \langle \phi_i | H(\psi_i) | \phi_i \rangle + \langle \phi_i | [H(\phi_i) - H(\psi_i)] | \phi_i \rangle \,,
\end{aligned}$$

i.e.,

$$\epsilon^{\phi i}_i \geqslant \epsilon_i + \langle \phi_i | [H(\phi_i) - H(\psi_i)] | \phi_i \rangle \,.$$