Nonsingular Hankel functions as a new basis for electronic structure calculations

E. Bott, M. Methfessel, W. Krabs, and P. C. Schmidt

Citation: Journal of Mathematical Physics **39**, 3393 (1998); doi: 10.1063/1.532437
View online: http://dx.doi.org/10.1063/1.532437
View Table of Contents: http://scitation.aip.org/content/aip/journal/jmp/39/6?ver=pdfcov
Published by the AIP Publishing

Nonsingular Hankel functions as a new basis for electronic structure calculations

E. Bott
Institut für Physikalische Chemie der Technischen Universität Darmstadt, D-64287 Darmstadt, Germany

M. Methfessel
Institute for Semiconductor Physics, Walter-Korsing Str. 2, D-15230 Frankfurt (Oder), Germany

W. Krabs
Fachbereich Mathematik der Technischen Universität Darmstadt, D-64289 Darmstadt, Germany

P. C. Schmidt
Institut für Physikalische Chemie der Technischen Universität Darmstadt, D-64287 Darmstadt, Germany

(Received 23 December 1997; accepted for publication 12 February 1998)

As a basis for electronic structure calculations, Gaussians are inconvenient because they show unsuitable behavior at larger distances, while Hankel functions are singular at the origin. This paper discusses a new set of special functions which combine many of the advantageous features of both families. At large distances from the origin, these ''smoothed Hankel functions'' resemble the standard Hankel functions and therefore show behavior similar to that of an electronic wave function. Near the origin, the functions are smooth and analytical. Analytical expressions are derived for two-center integrals for the overlap, the kinetic energy, and the electrostatic energy between two such functions. We also show how to expand such a function around some point in space and discuss how to evaluate the potential matrix elements efficiently by numerical integration. This supplies the elements needed for a practical application in an electronic structure calculation. © *1998 American Institute of Physics.* [S0022-2488(98)02206-3]

I. INTRODUCTION

The calculation of the electronic structure of molecules and crystals is becoming increasingly important as a means to understand phenomena on a microscopic level and to supply data which are inaccessible to experiment.[1] The approaches range from Hartree–Fock and configuration-interaction methods to density-functional calculations and the Car–Parrinello method for quantum-mechanical molecular dynamics. In all these approaches, the wave functions must be represented in an accurate but easily handled manner and several central quantities, such as the expectation values for a potential of general shape, must be evaluated. The choice of the basis set used in the representation has a large influence on the calculational efficiency, the numerical stability, and the effort of implementation. In this paper, we present a new set of analytical functions which were designed to optimize these aims.

In general, most applications use one of the following three approaches: (1) an expansion in plane waves, equivalent to a numerical representation on a real-space mesh, (2) an expansion in some kind of analytical basis set centered on the atoms, or (3) an expansion in numerical atomic functions such as the orbitals of a free atom. The expansion in plane waves is extremely popular, thanks to the simple formulation, general flexibility, and numerical robustness. This approach is often used for norm-conserving[2] or ultrasoft[3] pseudopotentials as well as in the linear augmented plane-wave (LAPW) method.[4] These successful methods rely heavily on fast-Fourier-transform algorithms for efficient execution. Unfortunately, plane waves treat all parts of space in the same way, even though more detail is needed close to the atoms. Depending on the system, a large

number of basis functions are needed, leading to slow program execution and large storage requirements.

In contrast, representations using some kind of atom-centered local functions generally involve considerably fewer basis functions, with the potential of large savings in computer time and storage. Whether these gains are realized depends on the type of function used. For example, a basis of Gaussian functions leads to simple algorithms since most operations can be done analytically. Unfortunately, the behavior of the true wave functions is closer to exponential than Gaussian. Consequently several basis functions must be contracted to form chemical basis sets and numerical stability becomes an issue. These problems are avoided by Hankel or Slater functions, for example, in the linear-muffin-tin orbital (LMTO) method[4] which uses a basis of augmented Hankel functions centered on the atoms. The cost for this type of approach is that the mathematical operations are more complicated, making it difficult to implement essential features such as the forces on the atoms. Furthermore, due to the inherent simplicity of the plane-wave methods, their execution speeds are quite difficult to match in practice despite the smaller function set. Finally, Hankel functions are singular near the nucleus. This restricts their use to augmentation methods which replace each function by a numerical representation near the atom.

The new functions presented here are intended to combine as far as possible the positive features of Hankel functions and Gaussians. In essence, they are Hankel functions from which the singularities have been removed, leading to smooth functions which are analytical in all of space. They have the following advantages. Since their behavior at larger radii is that of Hankel functions, they are similar to the true wave functions and avoid the need for basis contractions and stability problems. The degree of smoothing can be tuned, making it possible to optimize the basis so that fewer functions are needed for an accurate representation. Because these functions are analytical, numerical operations on a real-space mesh can be done reasonably efficiently. In addition, many important operations (for example, all relevant two-center integrals) can be done analytically. Finally, since the functions are nonsingular and smooth over all of space they seem predestined for an implementation of pseudopotential methods using local orbitals.

An implementation of density-functional program, based on these functions and using augmentation to supply local atomic detail, has recently been completed.[5] In this paper, we present the mathematical properties of these new ''smoothed Hankel functions.'' Our aim is to supply those properties and equations which are needed for an electronic structure calculation. Ultimately, for any selected basis set $\{\varphi_i(\mathbf{r})\}$ the tasks are to evaluate the overlap matrix

$$S_{i,j}=\int \varphi_i(\mathbf{r})^*\varphi_j(\mathbf{r})d^3r, \tag{1.1}$$

the matrix of the kinetic energy

$$T_{i,j}=\int \varphi_i(\mathbf{r})^*(-\Delta)\varphi_j(\mathbf{r})d^3r, \tag{1.2}$$

and the matrix of the potential energy

$$V_{i,j}=\int \varphi_i(\mathbf{r})^*V(\mathbf{r})\varphi_j(\mathbf{r})d^3r \tag{1.3}$$

to high accuracy and reasonably efficiently, and to assemble the charge density out of the products

$$\rho_{ij}(\mathbf{r})=\varphi_i(\mathbf{r})^*\varphi_j(\mathbf{r}) \tag{1.4}$$

in a form which can be used in the further steps of the calculation. More specifically, we would like to evaluate the simpler terms such as S_{ij} and T_{ij} analytically. If the potential matrix element is to be calculated numerically, the functions must be easy to generate on a mesh. For realistic descriptions involving either augmentation or nonlocal pseudopotentials, it is necessary to expand each function locally in the vicinity of an atom. Finally, for the application to crystals, all these steps must be done for Bloch sums of the original functions. These points are addressed in the following.

The rest of this paper is organized as follows. In the following Secs. II and III we define some useful differential operators and collect some results concerning Fourier transforms which are needed in the following sections. In Sec. IV, we present a family of functions $F_L(\mathbf{r})$ of which the smoothed Hankel functions $H_L(\mathbf{r})$ and the related generalized Gaussians $G_{pL}(\mathbf{r})$ are special cases. Following this we introduce the functions $G_{pL}(\mathbf{r})$ and $H_L(\mathbf{r})$ in Secs. V and VI.

One pleasant feature of the smoothed Hankels is that the matrix elements Eqs. (1.1), (1.2) can be expressed analytically, using the functions $H_L(\mathbf{r})$ themselves, their energy derivatives $\dot{H}_L(\mathbf{r})$, and related functions $W_{pL}(\mathbf{r})$. These are discussed in Sec. VII. Sections VIII–X give expressions for the matrix elements in the nonperiodic case, show how to evaluate the Bloch sums of the $H_L(\mathbf{r})$, and how to obtain the matrix elements for the Bloch-periodic case.

In Secs. XI and XII we show how to evaluate Coulomb integrals involving the $H_L(\mathbf{r})$ (Sec. XI) and how to expand the functions around an arbitrary site, using a convenient technique which can be used for any type of smooth function (Sec. XII). Finally, in the Appendix, we give an integral representation of the $H_L(\mathbf{r})$ and elucidate the connection to the well-known Ewald summation method for lattice sums.

II. SPHERICAL HARMONICS $Y_L(\hat{\mathbf{r}})$ AND $\mathscr{Y}_L(\mathbf{r})$

In the following sections we shall be working with real valued spherical harmonics, labeled with the compound index $L=(\ell,m_\ell)$:

$$Y_L(\hat{\mathbf{r}}) := Y^{m}_{\ell}(\hat{\mathbf{r}}) \tag{2.1}$$

as given in (59:14:8) of Ref. 6 and with the spherical harmonic polynomials

$$\mathscr{Y}_L(\mathbf{r}) := r^{\ell} Y_L(\hat{\mathbf{r}}). \tag{2.2}$$

The $\mathscr{Y}_L(\mathbf{r})$ are real polynomials in the Cartesian coordinates x,y,z of $\mathbf{r}$. Therefore we can use expressions such as

$$\mathscr{Y}_L(i\mathbf{r}) \quad \text{or} \quad \mathscr{Y}_L(-\nabla) \tag{2.3}$$

obtained by substituting ix, iy, and iz and $-\partial/\partial x$, $-\partial/\partial y$, and $-\partial/\partial z$, respectively, for x, y, and z in the polynomial $\mathscr{Y}_L(\mathbf{r})$. Furthermore each additive term of the polynomial $\mathscr{Y}_L$ is a product of a real valued coefficient and exactly ℓ variables. Hence we obtain in particular

$$\mathscr{Y}_L(a\mathbf{g}) = a^{\ell}\mathscr{Y}_L(\mathbf{g}), \tag{2.4}$$

where a is any complex number and $\mathbf{g}$ is any possible argument for $\mathscr{Y}_L$ with three components which commute with the complex numbers.

Let S denote the unit sphere surface. The $Y_L(\hat{\mathbf{r}})$ form a complete orthonormal basis of $\mathscr{L}_2(S)$, i.e., of the set of all complex valued functions $f(\hat{\mathbf{r}})$ with

$$\int_0^{2\pi}\int_0^{\pi} |f(\hat{\mathbf{r}})|^2 \sin\theta d\theta d\varphi < \infty. \tag{2.5}$$

Since the $Y_L(\hat{\mathbf{r}})$ are bounded on the unit sphere surface, we can consequently write

$$Y_K(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}}) = \sum_M a_M Y_M(\hat{\mathbf{r}}) \tag{2.6}$$

and using the orthonormality of the $Y_L(\hat{\mathbf{r}})$ we see

$$a_M = C_{KLM}, \tag{2.7}$$

where the C_{KLM} denote the real Gaunt integrals (or Clebsch–Gordan coefficients)

$$C_{KLM}=\int_0^{2\pi}\int_0^{\pi} Y_K(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}})Y_M(\hat{\mathbf{r}})\sin\,\theta d\theta d\varphi. \tag{2.8}$$

By multiplying both sides of (2.6) with $r^{k+\ell}$ and using (2.2) we obtain the corresponding expression for the spherical harmonic polynomials:

$$\mathscr{Y}_K(\mathbf{r})\mathscr{Y}_L(\mathbf{r})=\sum_M C_{KLM}(x^2+y^2+z^2)^{(k+\ell-m)/2}\mathscr{Y}_M(\mathbf{r}), \tag{2.9}$$

where $K=(k,m_k)$, $L=(\ell,m_\ell)$, and $M=(m,m_m)$. According to the selection rules for the Gaunt integrals, $k+l-m$ is a non-negative even integer when C_{KLM} is nonzero.

III. FOURIER TRANSFORMS

Here we list some results from the theory of Fourier transformation and Fourier series expansion which we require later on. We shall apply Fourier transformation to elements of the class $\mathscr{S}(\mathscr{R}^3)$ of *rapidly decreasing functions* on $\mathscr{R}^3$ only, where $\mathscr{S}(\mathscr{R}^3)$ is defined by

$$\mathscr{S}(\mathscr{R}^3):=\left\{\sigma:\mathscr{R}^3\to\mathscr{C}\,\middle|\,\begin{array}{c}\sigma\in C^\infty(\mathscr{R}^3)\ \text{ and }\ \sup_{\mathbf{r}}|\mathbf{r}^\alpha D^\beta\sigma(\mathbf{r})|<\infty\ \text{ for all multi-indices}\\ \alpha=(\alpha_1,\alpha_2,\alpha_3),\beta=(\beta_1,\beta_2,\beta_3)\in\mathscr{N}_0^3\end{array}\right\}, \tag{3.1}$$

$$\mathbf{r}^\alpha:=x^{\alpha_1}y^{\alpha_2}z^{\alpha_3}, \tag{3.2}$$

$$D^\beta\sigma(\mathbf{r}):=\frac{\partial^{|\beta|}}{\partial x^{\beta_1}\partial y^{\beta_2}\partial z^{\beta_3}}\sigma(\mathbf{r}), \tag{3.3}$$

$$|\beta|:=\beta_1+\beta_2+\beta_3 \tag{3.4}$$

(see Definition 17.1 in Ref. 7), i.e., $\mathscr{S}(\mathscr{R}^3)$ is the class of all functions $\sigma:\mathscr{R}^3\to\mathscr{C}$ with the properties that σ is arbitrarily often differentiable, is continuous together with all its derivatives, and that σ and all its derivatives go to zero faster than the inverse of any polynomial as $|\mathbf{r}|\to\infty$. Obviously $\mathscr{S}(\mathscr{R}^3)$ is a linear space over the complex numbers $\mathscr{C}$.

We denote the Fourier transform of a rapidly decreasing function $\sigma(\mathbf{r})\in\mathscr{S}(\mathscr{R}^3)$ by $\hat{\sigma}(\mathbf{q})$ and define it by

$$\hat{\sigma}(\mathbf{q}):=\int_{\mathscr{R}^3} e^{-i\mathbf{q}\cdot\mathbf{r}}\sigma(\mathbf{r})d^3r. \tag{3.5}$$

In the following we shall simply write $\int$ for $\int_{\mathscr{R}^3}$.

A central theorem ensures that $\hat{\sigma}$ belongs to $\mathscr{S}(\mathscr{R}^3)$ for all $\sigma\in\mathscr{S}(\mathscr{R}^3)$ and that the Fourier transformation $\sigma\mapsto\hat{\sigma}$ is an isomorphism from $\mathscr{S}(\mathscr{R}^3)$ onto $\mathscr{S}(\mathscr{R}^3)$ (cf. Theorem 17.3 in Ref. 7). One can reconstruct $\sigma(\mathbf{r})$ from $\hat{\sigma}(\mathbf{q})$ by

$$\sigma(\mathbf{r})=\frac{1}{(2\pi)^3}\int e^{i\mathbf{q}\cdot\mathbf{r}}\hat{\sigma}(\mathbf{q})d^3q \tag{3.6}$$

(cf. Theorem 17.2 in Ref. 7).

Concerning the interrelationship between Fourier transformation and derivation, one has the following general results for $\sigma(\mathbf{r})\in\mathscr{S}(\mathscr{R}^3)$:

$$D_{\mathbf{q}}^\beta\hat{\sigma}(\mathbf{q})=\widehat{((-i\mathbf{r})^\beta\sigma(\mathbf{r}))}(\mathbf{q}), \tag{3.7}$$

$$\widehat{(D_{\mathbf{r}}^\beta\sigma)}(\mathbf{q})=(i\mathbf{q})^\beta\hat{\sigma}(\mathbf{q}) \tag{3.8}$$

(cf. pp. 146, 142 of Ref. 7) whereby $D_{\mathbf{q}}$ and $D_{\mathbf{r}}$ denote the differentiation with respect to $\mathbf{q}$ and $\mathbf{r}$, respectively.

If we consider a function $\sigma(\mathbf{r}) \in \mathscr{S}(\mathscr{R}^3)$ which can be separated into a radial and an angular part according to

$$\sigma(\mathbf{r}) = \frac{u(r)}{r} Y_L(\hat{\mathbf{r}}), \tag{3.9}$$

then the corresponding Fourier transform $\hat{\sigma}(\mathbf{q})$ is given by

$$\hat{\sigma}(\mathbf{q}) = \frac{v(q)}{q} Y_L(\hat{\mathbf{q}}), \tag{3.10}$$

where

$$v(q) = 4\pi(-i)^{\ell} \int_0^{\infty} u(r) j_{\ell}(qr) qr dr, \tag{3.11}$$

$$u(r) = \frac{4\pi i^{\ell}}{(2\pi)^3} \int_0^{\infty} v(q) j_{\ell}(qr) qr dq \tag{3.12}$$

(cf. pp. 35/36 of Ref. 8), whereby the j_{ℓ} denote the spherical Bessel functions (see 10.1.1 in Ref. 9).

Further useful relationships are (cf. Eq. (17.11) in Ref. 7)

$$\widehat{(e^{-a^2 r^2})}(\mathbf{q}) = \left(\frac{\pi}{a^2}\right)^{3/2} e^{-q^2/4a^2} \tag{3.13}$$

and for any $\sigma, \rho \in \mathscr{S}(\mathscr{R}^3)$:

$$\widehat{(\sigma(\mathbf{r}-\mathbf{R}))}(\mathbf{q}) = \hat{\sigma}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}} \tag{3.14}$$

(obvious from (3.5)), and

$$\int \sigma(\mathbf{r})^* \rho(\mathbf{r}) d^3 r = \frac{1}{(2\pi)^3} \int \hat{\sigma}(\mathbf{q})^* \hat{\rho}(\mathbf{q}) d^3 q \tag{3.15}$$

(cf. Exercise 1 on p. 153 in Ref. 7).

Next, consider a Bloch sum

$$K^b(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} K(\mathbf{r}-\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} K(\mathbf{r}-\mathbf{R}) \tag{3.16}$$

for some rapidly decreasing function $K(\mathbf{r}) \in \mathscr{S}(\mathscr{R}^3)$ where $\mathbf{R}$ runs over the Bravais vectors of some lattice. Since the function $\mathbf{r} \mapsto \Sigma_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} K(\mathbf{r}-\mathbf{R})$ is periodic in direct space and has the translational symmetry of the Bravais lattice, it can be expanded as a Fourier series in terms of the plane waves $e^{i\mathbf{G}\cdot\mathbf{r}}$ associated with the reciprocal lattice vectors $\mathbf{G}$:

$$\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} K(\mathbf{r}-\mathbf{R}) = \frac{1}{\Omega} \sum_{\mathbf{G}} \hat{K}(\mathbf{k}+\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{3.17}$$

(cf. Appendix D in Ref. 10) where Ω is the volume of a direct lattice unit cell. From (3.16) we therefore obtain

$$K^b(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} \hat{K}(\mathbf{k}+\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \tag{3.18}$$

Starting from a second Bloch sum for some function $L(\mathbf{r}) \in \mathscr{S}(\mathscr{R}^3)$ with the same vector $\mathbf{k}$ as in the case of $K^b(\mathbf{r})$,

$$L^b(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} L(\mathbf{r}-\mathbf{R}) \tag{3.19}$$

we obtain from (3.18) and

$$\int_{\mathrm{UC}} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} d^3r = \Omega\, \delta_{\mathbf{G}\mathbf{G}'} \tag{3.20}$$

(cf. Appendix D (D3)–(D5) in Ref. 10) the expression

$$\int_{\mathrm{UC}} K^b(\mathbf{r})^* L^b(\mathbf{r}) d^3r = \frac{1}{\Omega} \sum_{\mathbf{G}} \hat{K}(\mathbf{k}+\mathbf{G})^* \hat{L}(\mathbf{k}+\mathbf{G}). \tag{3.21}$$

In these equations, $\int_{\mathrm{UC}}$ denotes the integration over a unit cell.

IV. PROPERTIES OF THE FUNCTIONS $F_L(\mathbf{r}) := \mathscr{Y}_L(-\nabla) f(r)$

In this section we introduce a general method for creating families of functions (cf. Ref. 11) and present some properties which all these families have in common. Among others, the families G_L of generalized Gaussians and H_L of smoothed Hankels to be introduced in the Secs. V and VI are specific instances of such families.

Let $f(r) = f(|\mathbf{r}|)$ be a function defined in three-dimensional space which depends only on $r = |\mathbf{r}|$ and is an element of the linear space $\mathscr{S}(\mathscr{R}^3)$ of Eq. (3.1). In particular $f(r)$ is arbitrarily often differentiable and we can define a family of functions $F_L(\mathbf{r}) \in \mathscr{S}(\mathscr{R}^3)$ by

$$F_L(\mathbf{r}) := \mathscr{Y}_L(-\nabla) f(r). \tag{4.1}$$

Applying (3.8), (2.4), and (2.2) we see that the Fourier transform of F_L is given by

$$\widehat{F_L}(\mathbf{q}) = \mathscr{Y}_L(-i\mathbf{q})\widehat{f(r)}(\mathbf{q}) = (-i)^\ell q^\ell \widehat{f(r)}(\mathbf{q}) Y_L(\hat{\mathbf{q}}). \tag{4.2}$$

Since $f(r)$ depends on $\mathbf{r}$ only through $|\mathbf{r}| = r$, we obtain from Corollary 20.6 in Ref. 7 that $\widehat{f(r)}(\mathbf{q})$ depends on $\mathbf{q}$ only through $|\mathbf{q}| = q$. Therefore, $\widehat{F_L}(\mathbf{q})$ is of the form (3.10) and from (3.9)–(3.12) we can conclude that

$$F_L(\mathbf{r}) = f_\ell(r) Y_L(\hat{\mathbf{r}}), \tag{4.3}$$

where

$$f_\ell(r) = \frac{4\pi}{(2\pi)^3} \int_0^\infty q^{\ell+2} \widehat{f(r)}(\mathbf{q}) j_\ell(qr) dq. \tag{4.4}$$

By noting that $\mathscr{Y}_0(\mathbf{r}) = Y_0(\hat{\mathbf{r}}) = 1/\sqrt{4\pi}$ and comparing (4.3) with (4.1) we obtain

$$f_0(r) = f(r). \tag{4.5}$$

From (4.4) we see that $f_\ell(r)$ depends on r only through the spherical Bessel function j_ℓ. From the recurrence relation

$$j_\ell(qr) = \frac{1}{q}\left[-\frac{\partial}{\partial r} + \frac{\ell-1}{r}\right] j_{\ell-1}(qr) \quad \text{for } \ell \geqslant 1 \tag{4.6}$$

for the j_ℓ (cf. 10.1.22 in Ref. 9) we consequently get a recurrence relation for the f_ℓ:

$$f_\ell(r)=\left[-\frac{\partial}{\partial r}+\frac{\ell-1}{r}\right]f_{\ell-1}(r) \quad \text{for } \ell\geqslant 1. \tag{4.7}$$

Using (4.7) and (4.5) one can prove by induction over ℓ

$$f_\ell(r)=r^\ell\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell f(r) \quad \text{for all } \ell\in\mathcal{N}_0 \tag{4.8}$$

(see p. 39 in Ref. 8). We see from (4.8) that we can write $f_\ell(r)$ in the form

$$f_\ell(r)=r^\ell\chi_\ell(r), \tag{4.9}$$

where $\chi_\ell(r)$ is given by

$$\chi_0(r)=f_0(r)=f(r), \tag{4.10}$$

$$\chi_\ell(r)=\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell f(r) \quad \text{for all } \ell\in\mathcal{N}_0, \tag{4.11}$$

$$\chi_\ell(r)=-\frac{1}{r}\frac{\partial}{\partial r}\chi_{\ell-1}(r) \quad \text{for } \ell\geqslant 1. \tag{4.12}$$

To conclude this section, we derive a recurrence relation for the radial functions $\chi_\ell(r)$ for the special case that $f(r)$ fulfills

$$\Delta f(r)=p(\mathbf{r}) \tag{4.13}$$

for some known function $p(\mathbf{r})$.

For any $f(r)\in\mathcal{S}(\mathbb{R}^3)$ we have $\Delta f(r)=p(\mathbf{r})\in\mathcal{S}(\mathbb{R}^3)$. By writing the Laplacian operator Δ in polar coordinates (see, e.g., p. 32 in Ref. 12) we see that the function $\Delta f(r)$ also depends only on $r=|\mathbf{r}|$, i.e.,

$$p(\mathbf{r})=p(r). \tag{4.14}$$

By applying the operator $\mathcal{Y}_L(-\nabla)$ to both sides of (4.13) we obtain

$$\Delta F_L(\mathbf{r})=P_L(\mathbf{r}), \tag{4.15}$$

where

$$P_L(\mathbf{r})=\mathcal{Y}_L(-\nabla)p(r)=p_\ell(r)Y_L(\hat{\mathbf{r}}). \tag{4.16}$$

Next, we write the Laplacian in polar coordinates in the form

$$\Delta=\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\cdot)-\frac{\widehat{\ell^2}}{r^2\hbar^2}, \tag{4.17}$$

where

$$\widehat{\ell^2}Y_L(\hat{\mathbf{r}})=\ell(\ell+1)\hbar^2Y_L(\hat{\mathbf{r}}) \tag{4.18}$$

(cf. pp. 32, 150, 151 in Ref. 12). This lets us derive from (4.15) the following relationship between $f_\ell(r)$ and $p_\ell(r)$:

$$\frac{\partial^2}{\partial r^2}f_\ell(r)+\frac{2}{r}\frac{\partial}{\partial r}f_\ell(r)-\frac{\ell(\ell+1)}{r^2}f_\ell(r)=p_\ell(r). \tag{4.19}$$

Applying (4.8) we can obtain from this equation

$$-p_{\ell-1}(r)=\left[\frac{\partial}{\partial r}+\frac{\ell+1}{r}\right]f_\ell(r) \quad \text{for } \ell\geqslant 1. \tag{4.20}$$

Together with (4.7) this leads to

$$f_{\ell+1}(r)=\frac{2\ell+1}{r}f_\ell(r)+p_{\ell-1}(r) \quad \text{for } \ell\geqslant 1, \tag{4.21}$$

which by virtue of (4.9) is equivalent to

$$r^2\chi_{\ell+1}(r)=(2\ell+1)\chi_\ell(r)+r^{-(\ell-1)}p_{\ell-1}(r) \quad \text{for } \ell\geqslant 1. \tag{4.22}$$

Since $\chi_0(r)$ equals $f(r)$, relationship (4.22) can be used to calculate the $\chi_\ell(r)$ for higher angular momenta by recursion, assuming that the $p_\ell(r)$ are known and that $\chi_1(r)$ has already been obtained. For example, $\chi_1(r)=-(1/r)(\partial/\partial r)\chi_0(r)$ can be used to do this (cf. (4.12)). The functions $f_\ell(r)=r^\ell\chi_\ell(r)$ are then also supplied, giving a method to calculate the functions of the family F_L in practical applications. Note, however, that a power series expansion is more stable numerically for small values of r.

V. THE GENERALIZED GAUSSIANS

In this section, we introduce functions G_L and G_{pL} which will be needed in the succeeding sections as part of recurrence relations, for the evaluation of the Hamiltonian and overlap matrix elements between smoothed Hankel functions, for the evaluation of Coulomb integrals, and in the expansion of smoothed Hankel functions around a chosen site.

The functions G_L are generalized Gaussians used in standard quantum mechanical molecular orbital approaches[13] defined for some energy parameter $\varepsilon=-\kappa^2\leqslant 0$ $(\kappa\geqslant 0)$ and an additional parameter $a>0$ by

$$G_L(\mathbf{r}):=\mathscr{Y}_L(-\nabla)g(r), \tag{5.1}$$

where

$$g(r):=\left(\frac{a^2}{\pi}\right)^{3/2}e^{\varepsilon/4a^2}e^{-a^2r^2}=\left(\frac{a^2}{\pi}\right)^{3/2}e^{\gamma\varepsilon}e^{-a^2r^2}, \tag{5.2}$$

$$\gamma:=\frac{1}{4a^2}. \tag{5.3}$$

The root function $g(r)$ is a normalized Gaussian of width $1/a$, multiplied by the factor $e^{\gamma\epsilon}$ for convenience in later expressions. Obviously $g(r)$ is an element of $\mathscr{S}(\mathscr{R}^3)$ and hence

$$G_L(\mathbf{r})\in\mathscr{S}(\mathscr{R}^3) \quad \text{for all } L. \tag{5.4}$$

From our general results of the last section it follows that

$$G_L(\mathbf{r})=g_\ell(r)Y_L(\hat{\mathbf{r}})=r^\ell\mu_\ell(r)Y_L(\hat{\mathbf{r}}) \tag{5.5}$$

with

$$\mu_\ell(r)=\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell g(r)=(2a^2)^\ell g(r)=\left(\frac{a^2}{\pi}\right)^{3/2}e^{\gamma\varepsilon}(2a^2)^\ell e^{-a^2r^2}. \tag{5.6}$$

Consequently we can write in closed form

$$G_L(\mathbf{r})=\left(\frac{a^2}{\pi}\right)^{3/2}e^{\gamma\varepsilon}(2a^2)^\ell e^{-a^2r^2}r^\ell Y_L(\hat{\mathbf{r}}). \tag{5.7}$$

The following sections also require the Fourier transform $\widehat{G_L}$ of G_L which by (5.1), (3.8), (5.2), (5.3) and (3.13) can easily be determined to be

$$\widehat{G_L}(\mathbf{q}) = \mathscr{Y}_L(-i\mathbf{q}) e^{\gamma(\varepsilon - q^2)}. \tag{5.8}$$

The second set of functions to be introduced in this section are the functions G_{pL}, obtained by repeatedly applying the Laplace operator to the G_L defined above:

$$G_{pL}(\mathbf{r}) := \Delta^p G_L(\mathbf{r}) = \Delta^p(\mathscr{Y}_L(-\nabla) g(r)) = \mathscr{Y}_L(-\nabla)(\Delta^p g(r)). \tag{5.9}$$

To evaluate these functions in practice, a recurrence relation (in p) for the G_{pL} can be derived as follows. Due to

$$g(r) \in \mathscr{S}(\mathscr{R}^3) \Rightarrow \Delta^p g(r) \in \mathscr{S}(\mathscr{R}^3) \tag{5.10}$$

we can apply our general results of Sec. IV [cf. (4.3)] and introduce radial functions $g_{p\ell}(r)$, $\mu_{p\ell}(r)$, and $\varphi_{p\ell}(r)$ such that

$$G_{pL}(\mathbf{r}) = g_{p\ell}(r) Y_L(\hat{\mathbf{r}}) = \mu_{p\ell}(r) r^\ell Y_L(\hat{\mathbf{r}}) = \varphi_{p\ell}(r) \left(\frac{a^2}{\pi}\right)^{3/2} e^{\gamma\varepsilon} e^{-a^2 r^2} r^\ell Y_L(\hat{\mathbf{r}}). \tag{5.11}$$

We proceed by deriving a recurrence relation in p for the $\varphi_{p\ell}(r)$. Due to $G_{p+1,L}(\mathbf{r}) = \Delta G_{pL}(\mathbf{r})$ and the definition (5.11) of the $\varphi_{p\ell}(r)$ we have

$$\varphi_{p+1,\ell}(r) \left(\frac{a^2}{\pi}\right)^{3/2} e^{\gamma\varepsilon} e^{-a^2 r^2} r^\ell Y_L(\hat{\mathbf{r}}) = \Delta\left[\varphi_{p\ell}(r) \left(\frac{a^2}{\pi}\right)^{3/2} e^{\gamma\varepsilon} e^{-a^2 r^2} r^\ell Y_L(\hat{\mathbf{r}})\right]. \tag{5.12}$$

Using the Laplacian Δ in polar coordinates (4.17)/(4.18), this leads to

$$\varphi_{p+1,\ell}(r) = \frac{\partial^2}{\partial r^2}\varphi_{p\ell}(r) + \left[\frac{2(\ell+1)}{r} - 4a^2 r\right]\frac{\partial}{\partial r}\varphi_{p\ell}(r) + [4a^4 r^2 - 2a^2(2\ell+3)]\varphi_{p\ell}(r). \tag{5.13}$$

A comparison of the definition (5.11) of $\varphi_{p\ell}(r)$ with the explicit expression (5.7) for $G_L(\mathbf{r}) = G_{0L}(\mathbf{r})$ shows that

$$\varphi_{0\ell}(r) = (2a^2)^\ell \quad \text{for all } \ell \in \mathscr{N}_0. \tag{5.14}$$

From (5.13) we then obtain

$$\varphi_{1\ell}(r) = (2a^2)^{\ell+1}(2a^2 r^2 - (2\ell+3)) \quad \text{for all } \ell \in \mathscr{N}_0 \tag{5.15}$$

and that the $\varphi_{p\ell}(r)$ are of the form

$$\varphi_{p\ell}(r) = a_0 + a_2 r^2 + \ldots + a_{2p} r^{2p}. \tag{5.16}$$

Following (5.9), (5.8), and (3.8), the Fourier transform of $G_{pL}(\mathbf{r})$ is given by

$$\widehat{G_{pL}}(\mathbf{q}) = (-q^2)^p \mathscr{Y}_L(-i\mathbf{q}) e^{\gamma(\varepsilon - q^2)}. \tag{5.17}$$

Using this and relation (3.7), one can prove the following recurrence relation for the $G_{pL}(\mathbf{r})$ (by showing the equality of the Fourier transforms of the right- and left-hand sides):

$$G_{pL}(\mathbf{r}) = 4a^4 r^2 G_{p-1,L}(\mathbf{r}) - 2a^2(4p + 2\ell - 1) G_{p-1,L}(\mathbf{r}) - 8a^4(p-1)(2p+2\ell-1) G_{p-2,L}(\mathbf{r}) \tag{5.18}$$

for $p \geqslant 2$. Finally, from (5.18) and the definition (5.11) of $\varphi_{p\ell}(r)$ we immediately obtain the desired recurrence relation, which enables us to calculate the $\varphi_{p\ell}(r)$ for $p \geqslant 2$:

$$\varphi_{p\ell}(r)=4a^4r^2\varphi_{p-1,\ell}(r)-2a^2(4p+2\ell-1)\varphi_{p-1,\ell}(r)-8a^4(p-1)(2p+2\ell-1)\varphi_{p-2,\ell}(r). \tag{5.19}$$

Together with the explicit expressions for $\varphi_{0\ell}(r)$ and $\varphi_{1\ell}(r)$ given above, all required functions $\varphi_{p\ell}(r)$ can now be evaluated.

VI. UNSMOOTHED AND SMOOTHED HANKEL FUNCTIONS

In this section we present our convention for the (ordinary) Hankel functions $\check{H}_L$, define the smoothed Hankel functions H_L, derive a recurrence relation that allows the evaluation of the $H_L(\mathbf{r})$, and compare the smoothed Hankels H_L with the unsmoothed Hankels $\check{H}_L$. Next, we introduce the functions $H_{pL}(\mathbf{r}):=\Delta^p H_L(\mathbf{r})$ which are needed in recurrence relations, in the evaluation of the Hamiltonian and overlap matrix elements, and for the calculation of Coulomb integrals. Finally we give a recurrence relation for the calculation of the $H_{pL}(\mathbf{r})$ and obtain their Fourier transform $\widehat{H_{pL}}(\mathbf{q})$.

We start with the definition of the unsmoothed Hankels $\check{H}_L$ for the energy parameter $\varepsilon=-\kappa^2<0$ $(\kappa>0)$. They are singular at $\mathbf{r}=\mathbf{0}$ and are generated from a root function as discussed above:

$$\check{H}_L(\mathbf{r}):=\mathscr{Y}_L(-\nabla)\check{h}(r), \tag{6.1}$$

where

$$\check{h}(r):=\frac{e^{-\kappa r}}{r}. \tag{6.2}$$

The usual spherical Hankel functions of the first kind, $h^{(1)}_\ell(r)$, (see 10.1.1 in Ref. 9) and the $\check{H}_L$ are related by

$$\check{H}_L(\mathbf{r})=-i^\ell\kappa^{\ell+1}h^{(1)}_\ell(i\kappa r)Y_L(\hat{\mathbf{r}}). \tag{6.3}$$

The smoothed Hankel functions $H_L(\mathbf{r})$ with energy parameter $\varepsilon=-\kappa^2<0$ $(\kappa>0)$ and an additional ''smoothing'' parameter $a>0$ are defined in a similar way, starting from a modified root function $h(r)$:

$$H_L(\mathbf{r}):=\mathscr{Y}_L(-\nabla)h(r), \tag{6.4}$$

where

$$h(r):=\frac{1}{2r}(u_+(r)-u_-(r)), \tag{6.5}$$

$$u_\pm(r):=e^{\mp\kappa r}\left[1-\mathrm{erf}\left(\frac{\kappa}{2a}\mp ar\right)\right], \tag{6.6}$$

where erf(z) is the error function (cf. 7.1.1 in Ref. 9). It will be seen below that $h(r)$ is similar to $\check{h}(r)=\exp(-\kappa r)/r$ but is nonsingular. The function $h(r)$ is arbitrarily often continuously differentiable at every point in $\mathscr{R}^3$ including zero, i.e.,

$$h(r)\in C^\infty(\mathscr{R}^3), \tag{6.7}$$

and can be represented by a power series

$$\sum_{j=0}^{\infty}a_jr^{2j} \tag{6.8}$$

containing only even powers of r (cf. pp. 48/49 in Ref. 8). Using Eqs. (6.5)/(6.6) together with the property

$$\lim_{x\to\infty} \operatorname{erf}(\pm x) = \pm 1 \tag{6.9}$$

and the rule of de l'Hospital to determine $\lim_{r\to\infty} u_-(r)$ one can see:

$$h(r) \text{ behaves like } \frac{e^{-\kappa r}}{r} \text{ for large } r. \tag{6.10}$$

This fact together with (6.7) allows the conclusion

$$h(r) \in \mathscr{S}(\mathscr{R}^3) \tag{6.11}$$

[see (3.1) for the definition of $\mathscr{S}(\mathscr{R}^3)$].

Using the Laplacian Δ written in polar coordinates [Eq. (4.17)], one can prove by explicit calculation that $h(r)$ satisfies the following differential equation:

$$(\Delta+\varepsilon)h(a,\varepsilon;r) = -4\pi g(a,\varepsilon;r), \tag{6.12}$$

where we have noted the parameters a and ε of $h(r)$ [Eq. (6.5)] and of $g(r)$ [Eq. (5.2)] explicitly. Applying the operator $\mathscr{Y}_L(-\nabla)$ to both sides of (6.12) we obtain by means of (6.7), (6.4), and (5.1) the relation

$$(\Delta+\varepsilon)H_L(a,\varepsilon;\mathbf{r}) = -4\pi G_L(a,\varepsilon;\mathbf{r}). \tag{6.13}$$

To understand the relation between the smoothed and unsmoothed Hankel functions, it is useful to digress briefly into a formulation which involves distributions (avoided in the rest of this paper). It can be shown[11] that the corresponding differential equation for the unsmoothed Hankel functions is

$$(\Delta+\varepsilon)\check{H}_L(\varepsilon;\mathbf{r}) = -4\pi D_L(\mathbf{r}), \tag{6.14}$$

where

$$D_L(\mathbf{r}) = \mathscr{Y}_L(-\nabla)\,\delta(\mathbf{r}). \tag{6.15}$$

Comparing this with (6.13), we interpret the result as follows. The distribution $D_L(\mathbf{r})$ is a point multipole centered at the origin. The standard Hankel function $\check{H}_L(r)$ is the response of the Helmholtz operator $\Delta+\varepsilon$ to this singular source term. Our smoothed Hankel function $H_L(\mathbf{r})$ is the response of the same operator to a smeared-out version of the point multipole. This smooth multipole is the Gaussian $G_L(a,\varepsilon;\mathbf{r})$ which converges to $D_L(\mathbf{r})$ as $a\to\infty$. Since the source term is now smooth and analytical, the same is true for the function H_L itself. At large distances, the smooth Gaussians and the point multipoles are indistinguishable and the two types of functions coincide, by virtue of our definition of G_L involving an energy-dependent factor $e^{\gamma\varepsilon}$.

Still using distributions for now, the equations above are especially clear in Fourier space. Differential equation (6.13) translates to

$$(-q^2+\varepsilon)\widehat{H_L}(\mathbf{q}) = -4\pi\mathscr{Y}_L(-i\mathbf{q})e^{\gamma(\varepsilon-q^2)} \tag{6.16}$$

from which we deduce that the Fourier transform of the smoothed Hankel function is

$$\widehat{H_L}(\mathbf{q}) = \frac{-4\pi}{\varepsilon-q^2}\,\mathscr{Y}_L(-i\mathbf{q})e^{\gamma(\varepsilon-q^2)}. \tag{6.17}$$

These two equations apply to the standard Hankel function $\check{H}_L$ if γ is set to zero. The right-hand side of (6.16) then is $-4\pi\mathscr{Y}_L(-i\mathbf{q})$, which is the Fourier transform of the distribution $D_L(\mathbf{r})$ giving the point multipole.

Next, we derive a recurrence relation for the smoothed Hankel functions to permit their evaluation in practice. Due to (6.11) and $\Delta h(r) = -\varepsilon h(r) - 4\pi g(r)$ we can apply the results (4.3), (4.9), (4.10), (4.12), and (4.13)–(4.22) from Sec. IV. Using in addition the explicit formulas (6.5)/(6.6) for $h(r)$ and (5.6) for $\mu_\ell(r)$ we obtain

$$H_L(\mathbf{r}) = h_\ell(r) Y_L(\hat{\mathbf{r}}) = \chi_\ell(r) r^\ell Y_L(\hat{\mathbf{r}}), \tag{6.18}$$

$$\chi_0(r) = \frac{1}{2r}(u_+(r) - u_-(r)), \tag{6.19}$$

$$\chi_1(r) = \frac{1}{2r^3}(u_+(r) - u_-(r)) + \frac{\kappa}{2r^2}(u_+(r) + u_-(r)) - \frac{2a}{\sqrt{\pi} r^2} e^{\varepsilon/4a^2} e^{-a^2 r^2}, \tag{6.20}$$

$$\chi_{\ell+1}(r) = \frac{2\ell+1}{r^2}\chi_\ell(r) - \frac{\varepsilon}{r^2}\chi_{\ell-1}(r) - \frac{4\pi}{r^2}\left(\frac{a^2}{\pi}\right)^{3/2} e^{\varepsilon/4a^2}(2a^2)^{\ell-1} e^{-a^2 r^2} \quad \text{for } \ell \geqslant 1. \tag{6.21}$$

Equations (6.19)–(6.21) cannot directly be applied for $\mathbf{r} = \mathbf{0}$. For this point, using the rule of de l'Hospital we obtain

$$\chi_0(0) = -\kappa\left[1 - \operatorname{erf}\left(\frac{\kappa}{2a}\right)\right] + \frac{2a}{\sqrt{\pi}} e^{\varepsilon/4a^2} \tag{6.22}$$

and hence from (6.18) and $Y_0(\hat{\mathbf{r}}) = 1/\sqrt{4\pi}$,

$$H_0(\mathbf{0}) = -\frac{\kappa}{\sqrt{4\pi}}\left[1 - \operatorname{erf}\left(\frac{\kappa}{2a}\right)\right] + \frac{a}{\pi} e^{\varepsilon/4a^2}. \tag{6.23}$$

As we shall see below, the χ_ℓ are nonsingular for $r \to 0$ and therefore we have from (6.18)

$$H_L(\mathbf{0}) = 0 \quad \text{for all } \ell \neq 0. \tag{6.24}$$

In the following, we compare the behavior of the smoothed Hankel functions H_L with that of the unsmoothed Hankel functions $\check{H}_L$ in more detail. Considering first the radial parts of the functions near $r = 0$, note that we can represent $h(r)$ by a power series in r containing only even powers of r [see (6.8)]. Therefore we conclude from (4.10) and (4.12) that this is also true for all the $\chi_\ell(r)$. Furthermore, since $h_\ell(r)$ equals $\chi_\ell(r) r^\ell$ we can represent $h_\ell(r)$ by a power series in r which starts with a term proportional to r^ℓ. Hence the radial part $h_\ell(r)$ of $H_L(\mathbf{r})$ behaves as r^ℓ for small r, whereas the radial part of $\check{H}_L(\mathbf{r})$ behaves as $1/r^{\ell+1}$ (see p. 7127 in Ref. 14). In summary, $h_\ell(r)$ bends over near the origin and approaches 0 as r^ℓ whereas the radial part of $\check{H}_L(\mathbf{r})$ diverges when 0 is approached.

In Fig. 1 this behavior can be seen. For large values of r, the radial parts of H_L and $\check{H}_L$ become identical since from (6.10), (6.2), (6.4), and (6.1) we have

$$\lim_{|\mathbf{r}| \to \infty} H_L(a, \varepsilon; \mathbf{r}) = \check{H}_L(\varepsilon; \mathbf{r}). \tag{6.25}$$

Furthermore, from the definition (6.5)/(6.6) of $h(r)$ one can conclude

$$\lim_{a \to \infty} h(r) = \frac{e^{-\kappa r}}{r}. \tag{6.26}$$

Therefore we obtain from (6.2), (6.4), and (6.1) the relationship

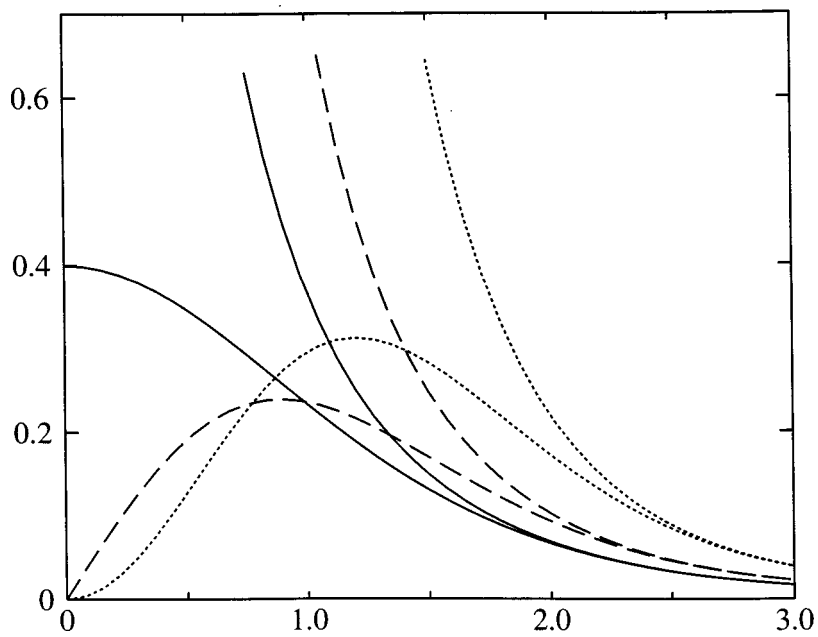

FIG. 1. Comparison of the radial parts of smoothed and unsmoothed Hankel functions for $\ell=0$ (continuous lines), $\ell=1$ (dashed lines) and $\ell=2$ (dotted lines). The energy parameter ε equals -1 in all cases and the smoothing parameter a for the smoothed Hankels equals 1.

$$\lim_{a\to\infty} H_L(a,\varepsilon;\mathbf{r})=\check{H}_L(\varepsilon;\mathbf{r}). \tag{6.27}$$

Consequently, as the parameter a is increased, the function $H_L(a,\varepsilon;\mathbf{r})$ becomes less and less ''smooth'' near the origin and begins to resemble the unsmoothed Hankel function. This motivates the name ''smoothing'' parameter for a. For large radii, the Gaussian source term in (6.13) is negligible and the differential equations (6.13) and (6.14) for the two types of functions H_L and $\check{H}_L$, respectively, are essentially the same.

Let us point out one important motivation of using the smoothed Hankel functions as basis functions in place of the normal unsmoothed functions. In the interstitial region close to muffin-tin spheres, the smoothed Hankel functions H_L show more resemblance to true wave functions than do the $\check{H}_L$. It follows that one can restrict oneself to substantially smaller basis sets with a corresponding gain in efficiency. To understand this, note that a true wave function ψ is a solution of Schrödinger's equation (here presented in atomic units):

$$\Delta\psi(\mathbf{r})=(-E+V(\mathbf{r}))\psi(\mathbf{r}). \tag{6.28}$$

The unsmoothed Hankel function $\check{H}_L(\varepsilon)$ with energy parameter $\varepsilon<0$ satisfies for $\mathbf{r}\neq\mathbf{0}$ the differential equation

$$\Delta\check{H}_L(\varepsilon;\mathbf{r})=-\varepsilon\check{H}_L(\varepsilon;\mathbf{r}) \tag{6.29}$$

(cf. p. 7130 in Ref. 14), i.e., it is a solution of Schrödinger's equation for energy $\varepsilon<0$ and $V(\mathbf{r})\equiv 0$. In comparison, according to (6.13) the smoothed Hankel function $H_L(a,\varepsilon)$ satisfies the differential equation

$$\Delta H_L(a,\varepsilon;\mathbf{r})=\left(-\varepsilon-4\pi\frac{G_L(a,\varepsilon;\mathbf{r})}{H_L(a,\varepsilon;\mathbf{r})}\right)H_L(a,\varepsilon;\mathbf{r}), \tag{6.30}$$

which is Schrödinger's equation for energy $\varepsilon<0$ and the potential

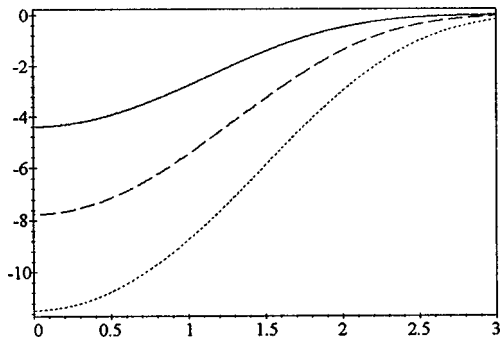

FIG. 2. The function $-4\pi G_L(a,\varepsilon;\mathbf{r})/H_L(a,\varepsilon;\mathbf{r})$ which plays the role of the potential when the differential equation (6.30) is interpreted as the Schrödinger equation, plotted along an arbitrary straight line starting from the origin for the case $\varepsilon=-1$, $a=1$ for $\ell=0$ (continuous line), $\ell=1$ (dashed) and $\ell=2$ (dotted). At intermediate distances outside the muffin-tin sphere, the functions can be adjusted to mimic the shape of the true potential which decreases as the Coulomb attraction of the screened nucleus becomes noticeable. This leads to a substantial reduction in the required basis size.

$$V(\mathbf{r})=-4\pi\frac{G_L(a,\varepsilon;\mathbf{r})}{H_L(a,\varepsilon;\mathbf{r})}. \tag{6.31}$$

This quantity is similar to a realistic potential at intermediate distances since it mimics the decrease of the screened Coulomb potential as the nucleus is approached (Fig. 2). In other words, a true wave function ''bends over'' as r becomes smaller and the potential drops below the absolute value of the energy because then the curvature (i.e., the second derivative) becomes negative. Such behavior is built into the smoothed Hankel functions but is not displayed by the normal Hankel functions. In practice, the shape of a wave function can be reasonably accurately represented by a single smoothed Hankel function outside the muffin-tin sphere or the core region if the two parameters ε and a are chosen appropriately, while a single standard Hankel function is generally inadequate.

To conclude this section, later on we will require the functions

$$H_{pL}(\mathbf{r}):=\Delta^p H_L(\mathbf{r}) \tag{6.32}$$

for which one can prove [by induction over p and using (6.13)] the following recurrence relation:

$$H_{0L}(a,\varepsilon;\mathbf{r})=H_L(a,\varepsilon;\mathbf{r}), \tag{6.33}$$

$$H_{p+1,L}(a,\varepsilon;\mathbf{r})=-\varepsilon H_{pL}(a,\varepsilon;\mathbf{r})-4\pi G_{pL}(a,\varepsilon;\mathbf{r}) \quad \text{for all } p\geqslant 0. \tag{6.34}$$

These equations enable one to calculate the $H_{pL}(\mathbf{r})$ in practice, whereby the $H_L(a,\varepsilon;\mathbf{r})$ are obtained from (6.18) to (6.24) and the $G_{pL}(a,\varepsilon;\mathbf{r})$ are obtained from (5.11), (5.14), (5.15), and (5.19). The Fourier transforms $\widehat{H_{pL}}$ follow from (6.32), (3.8), (6.13), and (5.8) and are given by

$$\widehat{H_{pL}}(\mathbf{q})=-\frac{4\pi}{\varepsilon-q^2}\,\mathscr{Y}_L(-i\mathbf{q})(-q^2)^p e^{\gamma(\varepsilon-q^2)}. \tag{6.35}$$

When p is set to zero, this expression gives the Fourier transform for the smoothed Hankel function $H_L(\mathbf{r})$. Since a product in reciprocal space corresponds to a convolution of the original functions, the following interesting interpretation arises. The smoothed Hankel function $H_L(\mathbf{r})$ can be seen as the convolution of the standard singular Hankel function $\check{H}_L$ [with Fourier transform $-4\pi\mathscr{Y}_L(-i\mathbf{q})/(\varepsilon-q^2)$] and a Gaussian (with Fourier transform $e^{-\gamma q^2}$), multiplied by our chosen normalization factor $e^{\gamma\varepsilon}$. Alternatively, it can up to a constant factor $1/\sqrt{4\pi}$ be considered the convolution of the generalized Gaussian G_L with the standard Hankel function of angular momentum zero. The two relevant length scales are the ''smoothing radius'' $R_{\mathrm{sm}}=1/a$ and the decay length $D=1/\kappa=1/\sqrt{-\varepsilon}$. These specify the width of the Gaussian and the Hankel functions,

respectively. If $R_{\mathrm{sm}} \ll D$, the smoothed Hankel function approaches the standard Hankel function, while a Gaussian is reproduced if $R_{\mathrm{sm}} \gg D$. Thus the smoothed Hankel functions interpolate between the two families and combine the features of both.

VII. THE FUNCTIONS $\dot{H}_L(\mathbf{r})$ AND $W_{pL}(\mathbf{r})$

To evaluate the elements of the kinetic energy and the overlap matrix we will need a further type of related functions, namely, the W_{pL} defined below. To calculate these explicitly we require the energy derivatives of the H_L, $\dot{H}_L$, which we consider first.

We denote the energy derivative of an arbitrary function f which depends on the energy parameter ε by $\dot{f}$ and we are interested here in the specific case

$$\dot{H}_L(\mathbf{r}) := \frac{\partial H_L(\mathbf{r})}{\partial \varepsilon}. \tag{7.1}$$

From (6.18) we have

$$\dot{H}_L(\mathbf{r}) = \dot{h}_\ell(r) Y_L(\hat{\mathbf{r}}) = \dot{\chi}_\ell(r) r^\ell Y_L(\hat{\mathbf{r}}). \tag{7.2}$$

To calculate $\dot{\chi}_\ell(r)$ we can derive a simple expression. Due to $\varepsilon = -\kappa^2$ we have

$$\frac{\partial}{\partial \varepsilon} = -\frac{1}{2\kappa}\frac{\partial}{\partial \kappa} \tag{7.3}$$

and from this we can obtain using (6.19)–(6.21) and (6.6)

$$\dot{\chi}_0(r) = \frac{1}{4\kappa}(u_+(r) + u_-(r)). \tag{7.4}$$

By induction over $\ell \in \dot{\mathcal{N}}_0$ it can be shown that

$$\dot{\chi}_{\ell+1}(r) = \tfrac{1}{2}\chi_\ell(r) \quad \text{for all } \ell \in \dot{\mathcal{N}}_0 \tag{7.5}$$

(cf. pp. 56/57 in Ref. 8). Therefore, we can calculate $\dot{H}_L(\mathbf{r})$ in the form (7.2) by calculating $\dot{\chi}_0(r)$ directly from (7.4) and obtaining the $\dot{\chi}_{\ell+1}(r)$ for $\ell \geqslant 0$ from (7.5). Hereby the $\chi_\ell(r)$ are obtained recursively from (6.19) to (6.21). For the special case $\mathbf{r} = \mathbf{0}$ we use

$$\dot{H}_0(\mathbf{0}) = \dot{\chi}_0(0)\frac{1}{\sqrt{4\pi}}, \tag{7.6}$$

$$\dot{H}_L(\mathbf{0}) = \lim_{\mathbf{r}\to\mathbf{0}} \dot{\chi}_\ell(r) r^\ell Y_L(\hat{\mathbf{r}}) = 0 \quad \text{for } \ell > 0. \tag{7.7}$$

Next, we turn to the $W_{pL}(\mathbf{r})$ mentioned above. As usual, they are generated from a root function $w(r)$ as

$$W_{pL}(\mathbf{r}) = \Delta^p \mathcal{Y}_L(-\nabla) w(r). \tag{7.8}$$

Here $w(r) \in \mathcal{S}(\mathcal{R}^3)$ with parameters $\varepsilon = -\kappa^2 < 0$ $(\kappa > 0)$ and $a > 0$ is defined by its Fourier transform $\widehat{w(r)}(\mathbf{q})$:

$$\widehat{w(r)}(\mathbf{q}) := \frac{4\pi e^{\gamma(\varepsilon - q^2)}}{(\varepsilon - q^2)^2}, \tag{7.9}$$

where γ equals $1/4a^2$ as before. According to (3.8) the Fourier transform of $W_{pL}(\mathbf{r})$ is

$$\widehat{W_{pL}}(\mathbf{q}) = \frac{4\pi}{(\varepsilon - q^2)^2}\, \mathscr{Y}_L(-i\mathbf{q})(-q^2)^p e^{\gamma(\varepsilon - q^2)}. \tag{7.10}$$

Comparison with (6.35) reveals that the derivative of W_{pL} with respect to γ is the negative of H_{pL}. Using (6.35) to write $H_L(\mathbf{r})$ in the form (3.6) we can get

$$\dot{H}_L(\mathbf{r}) = \frac{1}{(2\pi)^3} \int e^{i\mathbf{q}\cdot\mathbf{r}} \left[\frac{4\pi}{(\varepsilon - q^2)^2}\, \mathscr{Y}_L(-i\mathbf{q}) e^{\gamma(\varepsilon - q^2)} + \gamma \frac{-4\pi}{\varepsilon - q^2}\, \mathscr{Y}_L(-i\mathbf{q}) e^{\gamma(\varepsilon - q^2)} \right] d^3q. \tag{7.11}$$

By comparing this with (7.10) and (6.35) we obtain

$$W_{0L}(\mathbf{r}) = \dot{H}_L(\mathbf{r}) - \gamma H_L(\mathbf{r}). \tag{7.12}$$

Furthermore, one can prove the relation

$$W_{p+1,L}(\mathbf{r}) = -\varepsilon W_{pL}(\mathbf{r}) - H_{pL}(\mathbf{r}) \quad \text{for } p \geqslant 0 \tag{7.13}$$

by using (6.35) and (7.10) to show that the Fourier transforms of the right- and left-hand sides are equal. In sum, the $W_{pL}(\mathbf{r})$ can be obtained recursively from (7.12) and (7.13) if the $\dot{H}_L(\mathbf{r})$ and $H_{pL}(\mathbf{r})$ are calculated from (7.2) to (7.7) and (6.33)/(6.34), respectively.

VIII. OVERLAP AND HAMILTONIAN INTEGRALS IN THE NONPERIODIC CASE

In this section we discuss for the nonperiodic case the calculation of the overlap, kinetic energy, and potential integrals which are needed to evaluate the overlap and Hamiltonian matrix elements for the smoothed Hankel functions. As mentioned in Sec. I, these are the critical quantities when using the smoothed Hankel functions as basis set in any type of electronic structure calculation.

As preparation, we note the following important relationship. Let $P(\mathbf{r})$ and $Q(\mathbf{r})$ be two functions belonging to $\mathscr{S}(\mathscr{R}^3)$. Using Green's second identity (see, e.g., p. 350 in Ref. 15) for the case of a sphere around the origin and letting the radius of the sphere go to infinity shows

$$0 = \int [P(\mathbf{r})\Delta Q(\mathbf{r}) - Q(\mathbf{r})\Delta P(\mathbf{r})] d^3r. \tag{8.1}$$

In the following we treat the H_L and G_L as complex functions although they are actually real. We use this notation in order to be able to treat periodic structures involving Bloch sums of H_L and G_L in an analogous way as in the nonperiodic case. Moreover, where it is helpful we explicitly note the parameters $\gamma = 1/4a^2$ and $\varepsilon = -\kappa^2$ which define the Hankels and Gaussians.

First we consider the overlap integral $\int H_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r} - \mathbf{R}_1)^* H_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r} - \mathbf{R}_2) d^3r$ where H_{L_1} and H_{L_2} are smoothed Hankel functions centered at $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, and $\varepsilon_1 \neq \varepsilon_2$. Due to (6.11) and (6.4), both $H_L(\mathbf{r})$ and $H_L(\mathbf{r} - \mathbf{R})$ belong to $\mathscr{S}(\mathscr{R}^3)$. By applying (8.1) and using (6.13) we obtain

$$\begin{aligned} &\int H_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r} - \mathbf{R}_1)^* H_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r} - \mathbf{R}_2) d^3r \\ &\quad = \frac{4\pi}{\varepsilon_1 - \varepsilon_2} \left\{ \begin{array}{l} \displaystyle\int H_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r} - \mathbf{R}_1)^* G_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r} - \mathbf{R}_2) d^3r \\ \displaystyle -\int G_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r} - \mathbf{R}_1)^* H_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r} - \mathbf{R}_2) d^3r \end{array} \right\}. \end{aligned} \tag{8.2}$$

The integral over a smoothed Hankel function times a Gaussian can be evaluated using (3.15), (3.14), (6.35), (5.8), (2.4), (2.9), (3.6) and again (6.35). The idea is to perform the integral in reciprocal space, by rewriting the product of the Fourier transforms of the two factors as a sum of Fourier transforms of smoothed Hankel functions. The phase factors for the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ combine and we are left with back transforms at the vector $\mathbf{R}_1 - \mathbf{R}_2$. In detail:

$$\int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= \frac{1}{(2\pi)^3}\int \frac{-4\pi}{\varepsilon_1-q^2}(-1)^{\ell_1}\mathscr{Y}_{L_1}(-i\mathbf{q})e^{\gamma_1(\varepsilon_1-q^2)}e^{i\mathbf{q}\cdot\mathbf{R}_1}\mathscr{Y}_{L_2}(-i\mathbf{q})e^{\gamma_2(\varepsilon_2-q^2)}e^{-i\mathbf{q}\cdot\mathbf{R}_2}d^3q$$

$$= e^{\gamma_2(\varepsilon_2-\varepsilon_1)}(-1)^{\ell_1}\frac{1}{(2\pi)^3}\int \frac{-4\pi}{\varepsilon_1-q^2}e^{(\gamma_1+\gamma_2)(\varepsilon_1-q^2)}e^{i\mathbf{q}\cdot(\mathbf{R}_1-\mathbf{R}_2)}$$

$$\times\sum_M C_{L_1L_2M}(-q^2)^{(\ell_1+\ell_2-m)/2}\mathscr{Y}_M(-i\mathbf{q})d^3q$$

$$= e^{\gamma_2(\varepsilon_2-\varepsilon_1)}(-1)^{\ell_1}\sum_M C_{L_1L_2M}H_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_1;\mathbf{R}_1-\mathbf{R}_2) \tag{8.3}$$

and similarly

$$\int G_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= e^{\gamma_1(\varepsilon_1-\varepsilon_2)}(-1)^{\ell_1}\sum_M C_{L_1L_2M}H_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_2;\mathbf{R}_1-\mathbf{R}_2). \tag{8.4}$$

These two relations also hold for $\varepsilon_1=\varepsilon_2$. From (8.2) to (8.4) we obtain the final result that the overlap integral for $\varepsilon_1\neq\varepsilon_2$ is given in closed form as

$$\int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= 4\pi(-1)^{\ell_1}\sum_M C_{L_1L_2M}\left\{\begin{array}{l} \dfrac{e^{\gamma_2(\varepsilon_2-\varepsilon_1)}}{\varepsilon_1-\varepsilon_2}H_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_1;\mathbf{R}_1-\mathbf{R}_2) \\ +\dfrac{e^{\gamma_1(\varepsilon_1-\varepsilon_2)}}{\varepsilon_2-\varepsilon_1}H_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_2;\mathbf{R}_1-\mathbf{R}_2)\end{array}\right\}. \tag{8.5}$$

The values of the $H_{(\ell_1+\ell_2-m)/2,M}$ can be calculated from (6.33) and (6.34) because

$$C_{L_1L_2M} \text{ vanishes unless } \frac{\ell_1+\ell_2-m}{2}\in\mathscr{N}_0. \tag{8.6}$$

Equations (8.3), (8.4), and (8.5) are examples of an important general property: *Two-center integrals involving any combination of smoothed Hankel functions and Gaussians can be expressed analytically using functions of the same families, evaluated for the connecting vector between the two centers.* This is still the case when the kinetic energy operator or a Coulomb kernel is included in the integral. Furthermore, the analytical expressions are equally valid for Bloch-summed functions. These points are discussed below and in Sec. XI.

We still need the overlap integral in the case $\varepsilon_1=\varepsilon_2=:\varepsilon$ which involves, not surprisingly, the energy derivatives. It can be obtained by using (3.15), (3.14), (6.35), (2.4), (2.9), (3.6), and (7.10):

$$\int H_{L_1}(\gamma_1,\varepsilon;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= \frac{1}{(2\pi)^3}\int \frac{(4\pi)^2}{(\varepsilon-q^2)^2}e^{(\gamma_1+\gamma_2)(\varepsilon-q^2)}(-1)^{\ell_1}\mathscr{Y}_{L_1}(-i\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_1}\mathscr{Y}_{L_2}(-i\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}_2}d^3q$$

$$= (-1)^{\ell_1}\frac{4\pi}{(2\pi)^3}\int \frac{4\pi e^{(\gamma_1+\gamma_2)(\varepsilon-q^2)}}{(\varepsilon-q^2)^2}e^{i\mathbf{q}\cdot(\mathbf{R}_1-\mathbf{R}_2)}\sum_M C_{L_1L_2M}(-q^2)^{(\ell_1+\ell_2-m)/2}\mathscr{Y}_M(-i\mathbf{q})d^3q$$

$$= 4\pi(-1)^{\ell_1}\sum_M C_{L_1L_2M}W_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon;\mathbf{R}_1-\mathbf{R}_2). \tag{8.7}$$

The functions $W_{(\ell_1+\ell_2-m)/2,M}$ can be calculated from (7.12) and (7.13).

Next, the kinetic energy integrals follow almost immediately from our previous results. Using (6.13) we obtain

$$\begin{aligned}\int & H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^*(-\Delta)H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \\ &= \varepsilon_2 \int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r + 4\pi \\ &\quad \times \int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \end{aligned} \tag{8.8}$$

as well as an equivalent expression obtained when the Laplace operator is moved to the first function in the integrand. This reduces the integral to cases which have already been handled in (8.2)–(8.7).

Finally, we discuss the potential integrals $\int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* V(\mathbf{r}) H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$ where $V(\mathbf{r})$ is a smooth potential. In an augmentation method, this will be the interstitial potential, extended smoothly through the muffin-tin spheres. In a pseudopotential method, it might be a smooth local potential defined in all of space to which nonlocal atomic terms are added later on. The evaluation of these integrals cannot be discussed before the representation of the potential has been chosen, but in any case will require careful thought. One sensible approach is to represent the smooth potential on a real-space mesh and to evaluate the integrals numerically. This exploits the advantage that realistic basis functions are often strongly smoothed, so that a relatively coarse mesh is adequate. For crystals, this approach has been successfully implemented as described in Ref. 5. A key step is to evaluate the smoothed Hankel functions efficiently on the real-space mesh. This is done by setting up the Fourier transforms (6.35) and applying a fast Fourier transform routine. In a similar manner, the output density can be calculated.

IX. EVALUATION OF BLOCH SUMS

In this section, we discuss the evaluation of the Bloch sums

$$H^b_{pL}(\gamma,\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H_{pL}(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}), \tag{9.1}$$

$$W^b_{pL}(\gamma,\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} W_{pL}(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}), \tag{9.2}$$

where H_{pL} and W_{pL} have been introduced in the Secs. VI and VII, respectively, and $\mathbf{r}$ is some point in $\mathscr{R}^3$. These Bloch sums will be needed in Sec. X for the evaluation of the overlap and Hamiltonian matrix elements involving Bloch versions of smoothed Hankel functions.

As we will see below, for the calculation of the $H^b_{pL}(\gamma,\varepsilon;\mathbf{r})$ we also need the Gaussian Bloch sums

$$G^b_{pL}(\gamma,\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} G_{pL}(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}), \tag{9.3}$$

where the G_{pL} were defined in Sec. V. These can be evaluated by direct summation, whereby the $G_{pL}(\gamma,\varepsilon;\mathbf{r}-\mathbf{R})$ are obtained from (5.11), (5.14), (5.15), and (5.19). The sums converge rapidly because the G_{pL} are well-localized functions and therefore only a few terms in the sum (9.3) must be included.

The basic idea for the evaluation of the more slowly convergent sums is Ewald summation: Each term is split into a localized and a smooth part, and the corresponding sums are done in real

and reciprocal space, respectively. In the present case, the sum over the smoothed Hankels H_L [Eq. (9.1) for the case $p=0$] can by virtue of (3.18) and (6.35) be written as

$$H_L^b(\gamma,\varepsilon;\mathbf{r}) = H_L^b(\gamma',\varepsilon;\mathbf{r}) + (H_L^b(\gamma,\varepsilon;\mathbf{r}) - H_L^b(\gamma',\varepsilon;\mathbf{r}))$$
$$= \frac{1}{\Omega}\sum_{\mathbf{G}} \frac{-4\pi}{\varepsilon-|\mathbf{k}+\mathbf{G}|^2}\mathscr{Y}_L(-i(\mathbf{k}+\mathbf{G}))e^{\gamma'(\varepsilon-|\mathbf{k}+\mathbf{G}|^2)}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$
$$+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}(H_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}) - H_L(\gamma',\varepsilon;\mathbf{r}-\mathbf{R})). \tag{9.4}$$

Here $\gamma'>\gamma$ is chosen to enable the rapid convergence of both $\Sigma_{\mathbf{G}}$ and $\Sigma_{\mathbf{R}}$ simultaneously. The first sum converges rapidly if γ' is large enough for a fast decay of the factor $e^{\gamma'(\varepsilon-|\mathbf{k}+\mathbf{G}|^2)}$ in reciprocal space. Convergence of the second sum comes about because the function $H_L(\gamma,\varepsilon;\mathbf{r})-H_L(\gamma',\varepsilon;\mathbf{r})$ is localized, since $H_L(\gamma,\varepsilon;\mathbf{r})$ and $H_L(\gamma',\varepsilon;\mathbf{r})$ coincide as soon as $|\mathbf{r}|$ becomes moderately large. The $H_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R})$ and $H_L(\gamma',\varepsilon;\mathbf{r}-\mathbf{R})$ in (9.4) are evaluated using (6.18)–(6.24). The values of the $H_{pL}^b(\gamma,\varepsilon;\mathbf{r})$ [Eq. (9.1)] for all $p\in\mathscr{N}_0$ can then be obtained from the recurrence relation

$$H_{0L}^b(\gamma,\varepsilon;\mathbf{r}) = H_L^b(\gamma,\varepsilon;\mathbf{r}), \tag{9.5}$$

$$H_{p+1,L}^b(\gamma,\varepsilon;\mathbf{r}) = -\varepsilon H_{pL}^b(\gamma,\varepsilon;\mathbf{r}) - 4\pi G_{pL}^b(\gamma,\varepsilon;\mathbf{r}) \tag{9.6}$$

following directly from the recurrence relation (6.33)/(6.34) for the H_{pL}, where the G_{pL}^b are obtained from (9.3).

In order to calculate W_{pL}^b of Eq. (9.2), we will require Bloch sums of the energy derivative:

$$\dot{H}_L^b(\gamma,\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\dot{H}_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}) \tag{9.7}$$

[see (7.1)] which can be evaluated by choosing a suitable parameter $\gamma'>\gamma$ in the Ewald sum

$$\dot{H}_L^b(\gamma,\varepsilon;\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{G}} \frac{4\pi}{\varepsilon-|\mathbf{k}+\mathbf{G}|^2}\left(\frac{1}{\varepsilon-|\mathbf{k}+\mathbf{G}|^2}-\gamma'\right)\mathscr{Y}_L(-i(\mathbf{k}+\mathbf{G}))e^{\gamma'(\varepsilon-|\mathbf{k}+\mathbf{G}|^2)}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$
$$+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}(\dot{H}_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}) - \dot{H}_L(\gamma',\varepsilon;\mathbf{r}-\mathbf{R})). \tag{9.8}$$

This formula can be obtained by taking the derivative of formula (9.4) with respect to the energy parameter ε. Again, if γ' is chosen suitably, both sums in (9.8) converge rapidly. The energy derivatives $\dot{H}_L(\mathbf{r}-\mathbf{R})$ are evaluated according to (7.2)–(7.7).

After this preparation, we obtain W_{pL}^b from the recurrence relation

$$W_{0L}^b(\gamma,\varepsilon;\mathbf{r}) = \dot{H}_L^b(\gamma,\varepsilon;\mathbf{r}) - \gamma H_L^b(\gamma,\varepsilon;\mathbf{r}), \tag{9.9}$$

$$W_{p+1,L}^b(\gamma,\varepsilon;\mathbf{r}) = -\varepsilon W_{pL}^b(\gamma,\varepsilon;\mathbf{r}) - H_{pL}^b(\gamma,\varepsilon;\mathbf{r}), \tag{9.10}$$

which follows from (7.12)/(7.13), whereby the $H_{pL}^b(\gamma,\varepsilon;\mathbf{r})$ are calculated using (9.4)–(9.6).

X. OVERLAP AND HAMILTONIAN INTEGRALS IN THE PERIODIC CASE

In this section we show how to calculate the overlap and kinetic energy integrals for Bloch sums H_L^b of smoothed Hankel functions. As was discussed in Sec. VIII, the evaluation of the potential matrix elements is a separate problem which can, for example, be treated reasonably efficiently by numerical integration. This will not be considered further here. Exactly as in the nonperiodic case, two-center integrals can be expressed analytically using functions evaluated for the connecting vector between the centers. We recover the same expressions as before except that all appearing functions are now Bloch sums with the same wave vector **k**.

We require some preliminary considerations: Let

$$K^b(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} K(\mathbf{r}-\mathbf{R}) \tag{10.1}$$

and

$$L^b(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} L(\mathbf{r}-\mathbf{R}) \tag{10.2}$$

be Bloch sums for the same wave vector $\mathbf{k}$ where $K(\mathbf{r})$ and $L(\mathbf{r}) \in \mathscr{S}(\mathscr{R}^3)$. According to Green's second identity (see, e.g., p. 350 of Ref. 15) we have

$$\int_{\mathrm{UC}} (K^b(\mathbf{r})^* \Delta L^b(\mathbf{r}) - L^b(\mathbf{r}) \Delta K^b(\mathbf{r})^*) d^3r = \int_{\partial(\mathrm{UC})} \left(K^b(\mathbf{r})^* \frac{\partial}{\partial n} L^b(\mathbf{r}) - L^b(\mathbf{r}) \frac{\partial}{\partial n} K^b(\mathbf{r})^* \right) d^2r, \tag{10.3}$$

where the first integral is taken over a unit cell of the direct lattice and the second integral is taken over its surface, and where $\partial/\partial n$ denotes derivation in the direction of the outer normal on the unit cell surface. To every point $\mathbf{r}_0$ on the unit cell surface (with the exception of a finite number of vertex points) there corresponds some point

$$\mathbf{r}' = \mathbf{r}_0 + \mathbf{R}' \tag{10.4}$$

on the unit cell surface for a suitable direct lattice vector $\mathbf{R}' \neq \mathbf{0}$, such that the outer normal at $\mathbf{r}'$ is the negative of that in $\mathbf{r}_0$. This is a consequence of the fact that a unit cell, when translated through all direct lattice vectors, fills all of the space without either overlapping periodic images of itself or leaving voids. From (10.1) and (10.2) we have the Bloch property

$$K^b(\mathbf{r}+\mathbf{R}') = e^{i\mathbf{k}\cdot\mathbf{R}'} K^b(\mathbf{r}), \tag{10.5}$$

$$L^b(\mathbf{r}+\mathbf{R}') = e^{i\mathbf{k}\cdot\mathbf{R}'} L^b(\mathbf{r}) \tag{10.6}$$

for all $\mathbf{r} \in \mathscr{R}^3$. Consequently the contributions from opposite parts of the unit cell surface cancel in the right-hand side of (10.3), giving

$$\int_{\mathrm{UC}} K^b(\mathbf{r})^* \Delta L^b(\mathbf{r}) d^3r = \int_{\mathrm{UC}} L^b(\mathbf{r}) \Delta K^b(\mathbf{r})^* d^3r. \tag{10.7}$$

We are now able to proceed in straightforward analogy to the nonperiodic case [see (8.2)–(8.8)] whereby we use (10.7) in place of (8.1), (3.21) in place of (3.15), and (3.18) in place of (3.6). The two functions in question are again centered at the points $\mathbf{R}_1$ and $\mathbf{R}_2$ [not to be confused with the lattice vectors $\mathbf{R}$ used to write out Bloch sums as in (10.1)]. We obtain

$$\int_{\mathrm{UC}} H^b_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r}-\mathbf{R}_1)^* G^b_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r}-\mathbf{R}_2) d^3r$$

$$= (-1)^{\ell_1} e^{\gamma_2(\varepsilon_2-\varepsilon_1)} \sum_M C_{L_1 L_2 M} H^b_{(\ell_1+\ell_2-m)/2, M}(\gamma_1+\gamma_2, \varepsilon_1; \mathbf{R}_1-\mathbf{R}_2), \tag{10.8}$$

$$\int_{\mathrm{UC}} G^b_{L_1}(\gamma_1, \varepsilon_1; \mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2, \varepsilon_2; \mathbf{r}-\mathbf{R}_2) d^3r$$

$$= (-1)^{\ell_1} e^{\gamma_1(\varepsilon_1-\varepsilon_2)} \sum_M C_{L_1 L_2 M} H^b_{(\ell_1+\ell_2-m)/2, M}(\gamma_1+\gamma_2, \varepsilon_2; \mathbf{R}_1-\mathbf{R}_2), \tag{10.9}$$

giving the overlap integral in the case $\varepsilon_1 \neq \varepsilon_2$:

$$\int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= 4\pi(-1)^{\ell_1}\sum_M C_{L_1L_2M}\left(\begin{array}{l} \dfrac{e^{\gamma_2(\varepsilon_2-\varepsilon_1)}}{\varepsilon_1-\varepsilon_2} H^b_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_1;\mathbf{R}_1-\mathbf{R}_2) \\ + \dfrac{e^{\gamma_1(\varepsilon_1-\varepsilon_2)}}{\varepsilon_2-\varepsilon_1} H^b_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon_2;\mathbf{R}_1-\mathbf{R}_2) \end{array}\right). \tag{10.10}$$

The overlap integral in the case $\varepsilon_1=\varepsilon_2=:\varepsilon$ is given by:

$$\int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= 4\pi(-1)^{\ell_1}\sum_M C_{L_1L_2M} W^b_{(\ell_1+\ell_2-m)/2,M}(\gamma_1+\gamma_2,\varepsilon;\mathbf{R}_1-\mathbf{R}_2). \tag{10.11}$$

The required Bloch sums H^b_{pM} and W^b_{pM} can be evaluated as described in the preceding section. Finally, the kinetic energy integral is

$$\int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^*(-\Delta) H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= \varepsilon_2 \int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$+ 4\pi \int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* G^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r. \tag{10.12}$$

XI. COULOMB INTEGRALS

Up to now, the smoothed Hankel functions were mainly considered as a basis to represent the wave function. Once a localized representation is available, these functions are also useful to describe other quantities. For example, the implementation of Ref. 5 uses a combination of smoothed Hankel functions and Gaussians to represent the charge density of an atomic core. One important task is then to calculate the associated Coulomb integrals. That is, we need the integrals $\int\int P(\mathbf{r})Q(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d^3r d^3r'$ where $P(\mathbf{r})Q(\mathbf{r}')$ is any combination of Gaussians and smoothed Hankels. We first discuss this problem for the nonperiodic case, then for periodic functions. The latter case is not fundamentally different but somewhat more complicated because of the long-range nature of the Coulomb interaction.

We are interested in Coulomb integrals of the following general form (written in atomic Rydberg units):

$$U = \int\int \frac{n_1(\mathbf{r})n_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' \tag{11.1}$$

where n_1 and n_2 are two charge densities. We can rewrite U as

$$U = \frac{1}{2}\int n_1(\mathbf{r})\phi_2(\mathbf{r})d^3r = \frac{1}{2}\int \phi_1(\mathbf{r})n_2(\mathbf{r})d^3r, \tag{11.2}$$

where $\phi_j(\mathbf{r})$ is the potential generated at point $\mathbf{r}$ by the charge distribution n_j, given by Coulomb's law as

$$\phi_j(\mathbf{r}) = 2\int \frac{n_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'. \tag{11.3}$$

This potential satisfies Poisson's equation

$$\Delta \phi_j(\mathbf{r}) = -8\pi n_j(\mathbf{r}). \tag{11.4}$$

Turning to the nonperiodic case first, our aim is to calculate the integral

$$U_{PQ} = \int\int \frac{P_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* Q_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}'-\mathbf{R}_2)}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' \tag{11.5}$$

for all combinations $P,Q \in \{G,H\}$. We will do this using the potential generated by one of the two functions as in (11.2). To determine this potential, we first note that according to (6.13) and (5.7) we have

$$\Delta H_L(\gamma,\varepsilon;\mathbf{r}) = -4\pi e^{\gamma\varepsilon} G_L(\gamma,0;\mathbf{r}) - \varepsilon H_L(\gamma,\varepsilon;\mathbf{r}), \tag{11.6}$$

$$\Delta H_L(\gamma,0;\mathbf{r}) = -4\pi G_L(\gamma,0;\mathbf{r}). \tag{11.7}$$

Here $G_L(\gamma,0;\mathbf{r})$ denotes the function $G_L(\gamma,\varepsilon;\mathbf{r})$ for $\varepsilon=0$ and $H_L(\gamma,0;\mathbf{r})$ denotes the function $\lim_{\varepsilon\to 0} H_L(\gamma,\varepsilon;\mathbf{r})$. We see that the two potentials of interest are

$$\phi_{G_L}(\gamma,\varepsilon;\mathbf{r}) = 2e^{\gamma\varepsilon} H_L(\gamma,0;\mathbf{r}), \tag{11.8}$$

$$\phi_{H_L}(\gamma,\varepsilon;\mathbf{r}) = \frac{8\pi}{\varepsilon}(H_L(\gamma,\varepsilon;\mathbf{r}) - e^{\gamma\varepsilon} H_L(\gamma,0;\mathbf{r})) \tag{11.9}$$

since these functions satisfy Poisson's equation for the corresponding densities and go to zero at infinity. Inserting these expressions in (11.2) yields

$$U_{GG} = e^{\gamma_1\varepsilon_1} \int H_{L_1}(\gamma_1,0;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r, \tag{11.10}$$

$$U_{GH} = e^{\gamma_1\varepsilon_1} \int H_{L_1}(\gamma_1,0;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r, \tag{11.11}$$

$$U_{HH} = \frac{4\pi}{\varepsilon_1}\left\{ \begin{array}{l} \displaystyle\int H_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r \\ \displaystyle -e^{\gamma_1\varepsilon_1} \int H_{L_1}(\gamma_1,0;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r \end{array} \right\}. \tag{11.12}$$

This reduces all three Coulomb integrals to the integrals over products of Gaussians and smoothed Hankels for which we can use the expressions (8.3), (8.7), and (8.5), whereby the necessary values of the type $H_{pM}(\gamma,0;\mathbf{r}) = \lim_{\varepsilon\to 0} H_{pM}(\gamma,\varepsilon;\mathbf{r})$ occurring therein can be evaluated from:

$$H_{0M}(\gamma,0;\mathbf{r}) = H_M(\gamma,0;\mathbf{r}) = \left(\lim_{\varepsilon\to 0} \chi_m(\gamma,\varepsilon;r)\right) r^m Y_M(\hat{\mathbf{r}}), \tag{11.13}$$

$$\lim_{\varepsilon\to 0} \chi_0(\gamma,\varepsilon;r) = \frac{\mathrm{erf}(ar)}{r}, \tag{11.14}$$

$$\lim_{\varepsilon\to 0} \chi_1(\gamma,\varepsilon;r) = \frac{\mathrm{erf}(ar)}{r^3} - \frac{2a}{\sqrt{\pi} r^2} e^{-a^2r^2}, \tag{11.15}$$

$$\lim_{\varepsilon\to 0} \chi_{m+1}(\gamma,\varepsilon;r) = \frac{2m+1}{r^2} \lim_{\varepsilon\to 0} \chi_m(\gamma,\varepsilon;r) - \frac{4\pi}{r^2}\left(\frac{a^2}{\pi}\right)^{3/2} (2a^2)^{m-1} e^{-a^2r^2} \quad \text{for } m \geq 1, \tag{11.16}$$

for $\mathbf{r}\neq\mathbf{0}$,

$$H_M(\gamma,0;\mathbf{0}) = \frac{a}{\pi}\delta_{M0} \tag{11.17}$$

[cf. (6.18)–(6.21), (6.23), (6.24)] and

$$H_{p+1,M}(\gamma,0;\mathbf{r}) = -4\pi G_{pM}(\gamma,0;\mathbf{r}) \quad \text{for } p\geqslant 0 \tag{11.18}$$

[cf. (6.34)].

In the remainder of this section, we discuss the Coulomb integrals involving smoothed Hankels and Gaussians for the periodic case. Because of the long-ranged nature of the electrostatic potential, we must be careful about the way in which the limit $\varepsilon\to 0$ is done. We introduce new functions $F^b_{pL}(\gamma;\mathbf{r})$ by subtracting a homogeneous background from the Bloch function before taking the limit:

$$F^b_L(\gamma;\mathbf{r}) := \lim_{\varepsilon\to 0}\{H^b_L(\gamma,\varepsilon;\mathbf{r}) - \overline{H}^b_L(\gamma,\varepsilon)\}, \tag{11.19}$$

$$F^b_{pL}(\gamma;\mathbf{r}) := \Delta^p F^b_L(\gamma;\mathbf{r}), \tag{11.20}$$

where H^b_L is the previously defined Bloch sum of smoothed Hankels for the case $\mathbf{k}=\mathbf{0}$ and $\varepsilon<0$:

$$H^b_L(\gamma,\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} H_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}) \tag{11.21}$$

and the constant $\overline{H}^b_L$ is the average value of this Bloch sum over a unit cell:

$$\overline{H}^b_L(\gamma,\varepsilon) := \frac{1}{\Omega}\int_{\mathrm{UC}} H^b_L(\gamma,\varepsilon;\mathbf{r})d^3r. \tag{11.22}$$

In other words, we define the function $F^b_L(\gamma;\mathbf{r})$ by subtracting the average value from the Bloch sum over the smooth Hankels when $\varepsilon<0$ and then taking the limit for $\varepsilon\to 0$. In a representation as a Fourier sum over the reciprocal lattice, this is equivalent to simply leaving away the divergent term for $\mathbf{G}=\mathbf{0}$ and setting ε to zero in all others: Following (11.21), (3.18), and (6.35) the Fourier series for H^b_L is

$$H^b_L(\gamma,\varepsilon;\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{G}} \frac{-4\pi}{\varepsilon-G^2}\mathscr{Y}_L(-i\mathbf{G})e^{\gamma(\varepsilon-G^2)}e^{i\mathbf{G}\cdot\mathbf{r}} \tag{11.23}$$

and hence we obtain from (11.22) and (3.20) the average value

$$\overline{H}^b_L(\gamma,\varepsilon) = \frac{1}{\Omega}\widehat{H_L}(\mathbf{0}) = \frac{-4\pi}{\Omega}\frac{e^{\gamma\varepsilon}}{\varepsilon}Y_0\delta_{L0} = \frac{-\sqrt{4\pi}}{\Omega}\frac{e^{\gamma\varepsilon}}{\varepsilon}\delta_{L0}. \tag{11.24}$$

The factor δ_{L0} arises from $\mathscr{Y}_L(-i\mathbf{G}) = (-i)^{\ell}G^{\ell}Y_L(\mathbf{G})$, which is zero whenever $\mathbf{G}=\mathbf{0}$ and $L\neq 0$. From (11.19), (3.18), (11.24), and (6.35) we obtain the Fourier series for F^b_L:

$$F^b_L(\gamma;\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{G}\neq\mathbf{0}} \frac{4\pi}{G^2}\mathscr{Y}_L(-i\mathbf{G})e^{-\gamma G^2}e^{i\mathbf{G}\cdot\mathbf{r}}. \tag{11.25}$$

We see from (11.19), (11.21), (11.24), (11.25) that we can evaluate $F^b_L(\gamma;\mathbf{r})$ by Ewald summation in practice, using the formula

$$F_L^b(\gamma;\mathbf{r}) = F_L^b(\gamma';\mathbf{r}) + (F_L^b(\gamma;\mathbf{r}) - F_L^b(\gamma';\mathbf{r}))$$
$$= \frac{1}{\Omega}\sum_{\mathbf{G}\neq\mathbf{0}} \frac{4\pi}{G^2}\,\mathscr{Y}_L(-i\mathbf{G})e^{-\gamma' G^2}e^{i\mathbf{G}\cdot\mathbf{r}}$$
$$+\sum_{\mathbf{R}} (H_L(\gamma,0;\mathbf{r}-\mathbf{R}) - H_L(\gamma',0;\mathbf{r}-\mathbf{R})) + \frac{\sqrt{4\pi}}{\Omega}(\gamma-\gamma')\,\delta_{L0} \tag{11.26}$$

with some suitable $\gamma' > \gamma$. Here the last term is obtained from $\lim_{\varepsilon\to 0}\{\bar{H}_L^b(\gamma',\varepsilon) - \bar{H}_L^b(\gamma,\varepsilon)\}$ [cf. (11.24)] using the rule of de l'Hospital. The preceding expression involves terms of the type $H_L(\gamma,0,\mathbf{r}) = \lim_{\varepsilon\to 0} H_L(\gamma,\varepsilon,\mathbf{r})$, to be calculated according to (11.13)–(11.17).

Finally, to obtain the $F_{pL}^b(\gamma;\mathbf{r})$ for $p>0$ we first note that due to (11.20), (11.19), (6.13) and (11.23) we have

$$F_{1L}^b(\gamma;\mathbf{r}) = \lim_{\varepsilon\to 0}\{-\varepsilon H_L^b(\gamma,\varepsilon;\mathbf{r}) - 4\pi G_L^b(\gamma,\varepsilon;\mathbf{r})\} = \frac{\sqrt{4\pi}}{\Omega}\delta_{L0} - 4\pi G_L^b(\gamma,0;\mathbf{r}), \tag{11.27}$$

where G_L^b denotes the Bloch sum of the G_L for $\mathbf{k}=\mathbf{0}$. Using (11.27) we immediately get the result

$$F_{p+1,L}^b(\gamma,\mathbf{r}) = -4\pi G_{pL}^b(\gamma,0;\mathbf{r}) \quad \text{for } p\geqslant 1. \tag{11.28}$$

The $G_{pL}^b(\gamma,0;\mathbf{r})$ for $p\in\mathscr{N}_0$ are evaluated by direct summation as described in (9.3) with $\mathbf{k}$ set to zero. Using (11.26), (11.27), and (11.28), the $F_{pL}^b(\gamma;\mathbf{r})$ for all $p\in\mathscr{N}_0$ can be calculated.

After this somewhat tedious excursion to define the functions F_{pL}^b and to supply a method to calculate them, we can return to the Coulomb integrals in the case of periodic systems. For their evaluation we will need the integrals

$$\int_{\mathrm{UC}} F_{L_1}^b(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)\,d^3r, \tag{11.29}$$

$$\int_{\mathrm{UC}} G_{L_1}^b(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* F_{L_2}^b(\gamma_2;\mathbf{r}-\mathbf{R}_2)\,d^3r, \tag{11.30}$$

and

$$\int_{\mathrm{UC}} F_{L_1}^b(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* H_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)\,d^3r, \tag{11.31}$$

which are discussed next. For the evaluation of (11.29) and (11.30) we use Eq. (11.25) for F_L^b, proceed in the same manner as in Sec. X to evaluate the integrals (10.8) and (10.9), and obtain the first two integrals in closed form:

$$\int_{\mathrm{UC}} F_{L_1}^b(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)\,d^3r$$
$$= e^{\gamma_2\varepsilon_2}(-1)^{\ell_1}\sum_M C_{L_1L_2M} F_{(\ell_1+\ell_2-m)/2,M}^b(\gamma_1+\gamma_2;\mathbf{R}_1-\mathbf{R}_2), \tag{11.32}$$

$$\int_{\mathrm{UC}} G_{L_1}^b(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* F_{L_2}^b(\gamma_2;\mathbf{r}-\mathbf{R}_2)\,d^3r$$
$$= e^{\gamma_1\varepsilon_1}(-1)^{\ell_1}\sum_M C_{L_1L_2M} F_{(\ell_1+\ell_2-m)/2,M}^b(\gamma_1+\gamma_2;\mathbf{R}_1-\mathbf{R}_2). \tag{11.33}$$

Since H_L^b and F_L^b are Bloch functions for the same wave vector $\mathbf{k}=\mathbf{0}$ we have following (10.7) the relation

$$\int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* \Delta H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r = \int_{\mathrm{UC}} H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)\Delta F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* d^3r. \tag{11.34}$$

As before, we use this expression to reduce the third required integral (11.31) to the previous cases. Applying (6.13) and (11.27) gives

$$\int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= \frac{1}{\varepsilon_2}\left\{ \begin{array}{c} 4\pi \int_{\mathrm{UC}} G^b_{L_1}(\gamma_1,0;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \\ -4\pi \int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* G^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \\ -(\sqrt{4\pi}/\Omega)\,\delta_{L_1 0}\int_{\mathrm{UC}} H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \end{array} \right\}. \tag{11.35}$$

From (3.18), (3.20), (6.35) we see

$$\int_{\mathrm{UC}} H^b_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R})d^3r = \widehat{H_L}(\mathbf{0}) = -\sqrt{4\pi}\,\frac{e^{\gamma\varepsilon}}{\varepsilon}\,\delta_{L0} \tag{11.36}$$

giving the final expression for the integral (11.31) in terms of the previous cases (10.9) and (11.32):

$$\int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r$$

$$= \frac{4\pi}{\varepsilon_2}\left\{ \begin{array}{c} \int_{\mathrm{UC}} G^b_{L_1}(\gamma_1,0;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \\ -\int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* G^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r \\ +\frac{1}{\Omega}\,\frac{e^{\gamma_2\varepsilon_2}}{\varepsilon_2}\,\delta_{L_1 0}\delta_{L_2 0} \end{array} \right\}. \tag{11.37}$$

Finally, the two-center Coulomb integrals for the periodic case can be formulated. As before, we want to calculate the potential for one of the factors, then integrate over the product with the other factor. However, if $P(\mathbf{r})$ is any function representing a periodic charge density, then we can find a *periodic* potential ϕ_P satisfying $\Delta\phi_P = -8\pi P$ only if the neutrality condition is satisfied:

$$\int_{\mathrm{UC}} P(\mathbf{r})d^3r = 0. \tag{11.38}$$

Therefore, a sensible aim is to derive expressions for the integrals

$$\int_{\mathrm{UC}}\int_{\mathrm{UC}} \frac{\tilde{P}_{L_1}(\mathbf{r}-\mathbf{R}_1)^* \tilde{Q}_{L_2}(\mathbf{r}'-\mathbf{R}_2)}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r', \tag{11.39}$$

where $P(\mathbf{r})$ and $Q(\mathbf{r})$ are Bloch sums of smoothed Hankels or Gaussians, and $\tilde{P}$ and $\tilde{Q}$ are the corresponding functions with a possible constant term subtracted:

$$\tilde{P}_L(\mathbf{r}) := P_L(\mathbf{r}) - \frac{1}{\Omega}\int_{\mathrm{UC}} P_L(\mathbf{r})d^3r, \tag{11.40}$$

$$\tilde{Q}_L(\mathbf{r}) := Q_L(\mathbf{r}) - \frac{1}{\Omega}\int_{\mathrm{UC}} Q_L(\mathbf{r})d^3r. \tag{11.41}$$

In a properly formulated application of the resulting expressions, the various additional homogeneous terms will cancel in the final result. Our plan is therefore to calculate the integral

$$U = \frac{1}{2}\int_{\mathrm{UC}} \phi_{\tilde{P}_{L_1}}(\mathbf{r}-\mathbf{R}_1)^* \tilde{Q}_{L_2}(\mathbf{r}-\mathbf{R}_2)d^3r, \tag{11.42}$$

where $\phi_{\tilde{P}_L}(\mathbf{r})$ satisfies Poisson's equation

$$\Delta\phi_{\tilde{P}_L}(\mathbf{r}) = -8\pi\tilde{P}_L(\mathbf{r}). \tag{11.43}$$

Of course, the potential $\phi_{\tilde{P}_L}$ is determined only up to an additive constant. But since $\tilde{Q}_{L_2}(\mathbf{r})$ satisfies the neutrality condition by construction, adding an arbitrary constant to $\phi_{\tilde{P}_L}$ will not change the value of the integral (11.42). We therefore need not impose any additional condition besides (11.43) on $\phi_{\tilde{P}_L}$ in order to obtain the correct value of U.

First, we subtract the average values from G_L^b and H_L^b to make functions which satisfy the neutrality condition [cf. (3.18), (3.20), (5.8) and (11.36)]:

$$\tilde{G}_L^b(\gamma,\varepsilon;\mathbf{r}) = G_L^b(\gamma,\varepsilon;\mathbf{r}) - \frac{1}{\Omega}\frac{e^{\gamma\varepsilon}}{\sqrt{4\pi}}\delta_{L0} \tag{11.44}$$

and

$$\tilde{H}_L^b(\gamma,\varepsilon;\mathbf{r}) = H_L^b(\gamma,\varepsilon;\mathbf{r}) + \frac{\sqrt{4\pi}}{\Omega}\frac{e^{\gamma\varepsilon}}{\varepsilon}\delta_{L0}. \tag{11.45}$$

Next, we obtain two potentials which satisfy the Poisson equation for G_L^b and H_L^b, using (11.27), (5.7), (11.44) for the first and (6.13), (11.27), (5.7), (11.45) for the second:

$$\phi_{\tilde{G}_L^b}(\gamma,\varepsilon;\mathbf{r}) = 2e^{\gamma\varepsilon}F_L^b(\gamma;\mathbf{r}), \tag{11.46}$$

$$\phi_{\tilde{H}_L^b}(\gamma,\varepsilon;\mathbf{r}) = \frac{8\pi}{\varepsilon}(H_L^b(\gamma,\varepsilon;\mathbf{r}) - e^{\gamma\varepsilon}F_L^b(\gamma;\mathbf{r})). \tag{11.47}$$

Finally, we exploit that $F_L^b(\gamma;\mathbf{r})$ satisfies the neutrality condition according to the definition (11.19) and assemble the final expressions for the two-center Coulomb integrals by means of (11.42), the previous equations, and (11.36):

$$\begin{aligned} U_{GG} &= \int_{\mathrm{UC}}\int_{\mathrm{UC}} \frac{\tilde{G}_{L_1}^b(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^*\tilde{G}_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}'-\mathbf{R}_2)}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r' \\ &= \frac{1}{2}\int_{\mathrm{UC}} \phi_{\tilde{G}_{L_1}^b}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^*\left(G_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) - \frac{1}{\Omega}\frac{e^{\gamma_2\varepsilon_2}}{\sqrt{4\pi}}\delta_{L_20}\right)d^3r \\ &= e^{\gamma_1\varepsilon_1}\int_{\mathrm{UC}} F_{L_1}^b(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* G_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2)d^3r, \end{aligned} \tag{11.48}$$

$$U_{GH} = \int_{\mathrm{UC}}\int_{\mathrm{UC}} \frac{\tilde{G}_{L_1}^b(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^*\tilde{H}_{L_2}^b(\gamma_2,\varepsilon_2;\mathbf{r}'-\mathbf{R}_2)}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'$$

$$= \frac{1}{2} \int_{\mathrm{UC}} \phi_{\tilde{G}^b_{L_1}}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* \left(H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) + \frac{\sqrt{4\pi}}{\Omega} \frac{e^{\gamma_2\varepsilon_2}}{\varepsilon_2} \delta_{L_2 0} \right) d^3r$$

$$= e^{\gamma_1\varepsilon_1} \int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r, \tag{11.49}$$

$$U_{HH} = \int_{\mathrm{UC}} \int_{\mathrm{UC}} \frac{\tilde{H}^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* \tilde{H}^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}'-\mathbf{R}_2)}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'$$

$$= \frac{1}{2} \int_{\mathrm{UC}} \phi_{\tilde{H}^b_{L_1}}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* \left(H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) + \frac{\sqrt{4\pi}}{\Omega} \frac{e^{\gamma_2\varepsilon_2}}{\varepsilon_2} \delta_{L_2 0} \right) d^3r$$

$$= \frac{4\pi}{\varepsilon_1} \left\{ \begin{array}{c} \displaystyle\int_{\mathrm{UC}} H^b_{L_1}(\gamma_1,\varepsilon_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r \\ \displaystyle -e^{\gamma_1\varepsilon_1} \int_{\mathrm{UC}} F^b_{L_1}(\gamma_1;\mathbf{r}-\mathbf{R}_1)^* H^b_{L_2}(\gamma_2,\varepsilon_2;\mathbf{r}-\mathbf{R}_2) d^3r \end{array} \right\}$$

$$- \frac{\Omega}{\varepsilon_1} \frac{4\pi e^{\gamma_1\varepsilon_1}}{\Omega\varepsilon_1} \frac{4\pi e^{\gamma_2\varepsilon_2}}{\Omega\varepsilon_2} \delta_{L_1 0} \delta_{L_2 0}. \tag{11.50}$$

As usual, the integrals in these expressions can be calculated using functions evaluated for the connecting vector $\mathbf{R}_1 - \mathbf{R}_2$. The relevant equations are (11.32), (11.37), (10.10), and (10.11).

XII. EXPANSION OF A SMOOTH FUNCTION AROUND A SITE

Modern electronic structure calculations often use either augmentation or nonlocal pseudopotentials to introduce atomic detail at the atomic sites. In either approach it is neccessary to expand the basis functions as a sum of angular-momentum components around the various atomic sites. In this section, we present a method to do this, based on biorthogonal polynomials to the Gaussian family $G_{kL}(\mathbf{r})$. This approach can be applied to any smooth function, in particular to the smoothed Hankel functions and to plane waves. The result will be to approximate a given smooth function $F(\mathbf{r})$ by a finite expansion of the form

$$F(\mathbf{r}) \sim \sum_{kL} a_{kL} P_{kL}(\mathbf{r}). \tag{12.1}$$

The expansion functions P_{kL} are polynomials in x, y, and z which will be defined using the radial functions $\varphi_{k\ell}$ of the generalized Gaussians (5.11). The advantage over a Taylor series is that the expansion (12.1) converges evenly over some chosen range, making it significantly more useful in practical applications.

In Sec. V, the Gaussians $G_{kL}(\gamma,\varepsilon;\mathbf{r})$ were defined with an energy-dependent factor $e^{\gamma\varepsilon}$ in order to simplify expressions involving Gaussians and smoothed Hankel functions. Throughout this section, ε is zero and will be suppressed in the notation. Gaussians are therefore specified by one parameter γ which gives the decay of the functions as $e^{-a^2r^2}$ with $a^2 = 1/(4\gamma)$. Equivalently, we speak of the smoothing radius $R_{\mathrm{sm}} = 1/a$ which is the width of the Gaussian. As preparation, we prove two relationships for the functions G_{kL}.

(a) The radial functions $\varphi_{k\ell}(r)$ which define the generalized Gaussians as in (5.11) by

$$G_{kL}(\gamma;\mathbf{r}) = \varphi_{k\ell}(r) \left(\frac{a^2}{\pi} \right)^{3/2} e^{-a^2r^2} r^\ell Y_L(\hat{\mathbf{r}}) \tag{12.2}$$

are related to the generalized Laguerre polynomials $L_n^{(\alpha)}(x)$ (see Chapter 22 in Ref. 9) by

$$\varphi_{k\ell}(r) = (-1)^k (2a^2)^{k+\ell} 2^k k! L_k^{(\ell+1/2)}(a^2r^2). \tag{12.3}$$

Proof: We proceed by induction over $k \in \mathcal{N}_0$. For $k \leqslant 1$, Eq. (12.3) can be confirmed by comparing the explicit expressions for $L_0^{(\ell+1/2)}(x)$ and $L_1^{(\ell+1/2)}(x)$ (see 22.3.9 in Ref. 9) with expressions (5.14) and (5.15) for $\varphi_{0\ell}(r)$ and $\varphi_{1\ell}(r)$, respectively. Assume we have already shown (12.3) for all $k<k_0$ where $k_0 \geqslant 2$. By applying the recurrence relation for $L_n^{(\alpha)}(a^2r^2)$ (22.7.12 in Ref. 9) and the induction hypothesis, the right-hand side of (12.3) for $k=k_0$ is transformed into the right-hand side of the recurrence relation for the $\varphi_{p\ell}(r)$ (Eq. (5.19)) with p replaced by k_0. This completes the proof for all $k \in \mathcal{N}_0$. ◇

(b) The functions G_{kL} are orthogonal in both k and L in the following sense:

$$\int G_{kL}(\gamma;\mathbf{r}) G_{k'L'}(\gamma;\mathbf{r}) e^{a^2r^2} d^3r = \frac{1}{4\pi}\left(\frac{a^2}{\pi}\right)^{3/2} (2a^2)^{2k+\ell} 2^k k!(2k+2\ell+1)!!\,\delta_{kk'}\delta_{LL'}. \tag{12.4}$$

Proof: In the case $L \neq L'$ the orthogonality follows immediately from (12.2) and the orthogonality of the spherical harmonics $Y_L(\hat{\mathbf{r}})$. For the case $L=L'$, the result is obtained using (12.2), Eq. (2.9) for the case $K=L$, the orthogonality of the $Y_M(\hat{\mathbf{r}})$, $C_{LL0}=1/\sqrt{4\pi}$, (12.3) and the orthogonality relation of the generalized Laguerre polynomials

$$\int_0^\infty e^{-u} u^{\ell+1/2} L_k^{(\ell+1/2)}(u) L_{k'}^{(\ell+1/2)}(u)\,du = \frac{\Gamma(k+\ell+3/2)}{k!}\,\delta_{kk'} \tag{12.5}$$

(cf. 22.2.12 in Ref. 9) with the substitution $u=a^2r^2$. ◇

Returning to the desired expansion (12.1), we define the polynomials $P_{kL}(\gamma;\mathbf{r})$ by scaling $\varphi_{k\ell}(r)$ in a convenient way:

$$P_{kL}(\gamma;\mathbf{r}) = p_{k\ell}(\gamma;r) Y_L(\hat{\mathbf{r}}), \tag{12.6}$$

$$p_{k\ell}(\gamma;r) = \varphi_{k\ell}(r)\,\frac{a^\ell (2\ell+1)!!}{(2a^2)^{k+\ell}(2k+2\ell+1)!!}\,r^\ell. \tag{12.7}$$

The radial functions $\varphi_{k\ell}$ [see (5.16)] as well as the $r^\ell Y_L(\hat{\mathbf{r}}) = \mathscr{Y}_L(\mathbf{r})$ are polynomials in x,y,z. Therefore, we see that the P_{kL} are indeed polynomials in the Cartesian coordinates of $\mathbf{r}$. The $P_{kL}(\gamma;\mathbf{r})$ are biorthogonal to the G_{kL} as follows from Eqs. (12.6)/(12.7), (12.2), and (12.4):

$$\int G_{kL}(\gamma;\mathbf{r}) P_{k'L'}(\gamma;\mathbf{r})\,d^3r = \frac{1}{4\pi}(2a^2)^k a^\ell 2^k k!(2\ell+1)!!\,\delta_{kk'}\delta_{LL'}. \tag{12.8}$$

The significance of the biorthogonality is that, in order to expand a function as a linear combination of the P_{kL}, we can use the Gaussians G_{kL} to project out the coefficients. Consider some function $F(\mathbf{r})$ and assume that

$$\int_0^{2\pi}\int_0^{\pi} |F(r,\theta,\varphi)|^2 \sin\theta\, d\theta\, d\varphi < \infty \quad \text{for all } r \geqslant 0. \tag{12.9}$$

Such a function can be written in the form

$$F(\mathbf{r}) = \sum_L f_L(r) r^\ell Y_L(\hat{\mathbf{r}}) \tag{12.10}$$

because the $Y_L(\hat{\mathbf{r}})$ form a complete basis of $\mathscr{S}_2(S)$ [cf.(2.5)]. Now, if $f_L(r)$ satisfies the condition

$$\int_0^\infty e^{-u} u^{\ell+1/2}\left[f_L\left(\frac{\sqrt{u}}{a}\right)\right]^2 du < \infty$$

$$\text{where } u=a^2r^2, \tag{12.11}$$

we can expand $f_L(r)$ in terms of the generalized Laguerre polynomials $L_k^{(\ell+1/2)}(u)$ by using (12.5):

$$f_L\left(\frac{\sqrt{u}}{a}\right) \sim \sum_{k=0}^{\infty} c_{kL}(\gamma) L_k^{(\ell+1/2)}(u), \tag{12.12}$$

$$c_{kL}(\gamma) = \frac{k!}{\Gamma(k+\ell+3/2)} \int_0^{\infty} e^{-u} u^{\ell+1/2} f_L\left(\frac{\sqrt{u}}{a}\right) L_k^{(\ell+1/2)}(u) du. \tag{12.13}$$

For a finite approximation obtained by truncating the sum at some $n \in \mathcal{N}_0$ we have the property

$$\int_0^{\infty} e^{-u} u^{\ell+1/2} \left[f_L\left(\frac{\sqrt{u}}{a}\right) - \sum_{k=0}^{n} c_{kL}(\gamma) L_k^{(\ell+1/2)}(u) \right]^2 du = \min_{\zeta \in \Pi_n} \int_0^{\infty} e^{-u} u^{\ell+1/2} \left[f_L\left(\frac{\sqrt{u}}{a}\right) - \zeta(u) \right]^2 du, \tag{12.14}$$

where Π_n is the set of all polynomials of degree $\leqslant n$ (see, e.g., pp. 98–101 in Ref. 16). Using (12.3) and (12.7), expansion (12.12) translates to a linear combination of the radial functions $p_{k\ell}(r)$:

$$f_L(r) r^{\ell} \sim \sum_{k=0}^{\infty} a_{kL}(\gamma) p_{k\ell}(\gamma; r) \tag{12.15}$$

for suitable coefficients $a_{kL}(\gamma)$. By multiplying through with $Y_L(\hat{\mathbf{r}})$ we obtain the desired expansion (12.1) of $F(\mathbf{r})$, which is valid provided (12.11) holds for all angular-momentum components L. Because of the biorthogonality relation (12.8), the expansion coefficients $a_{kL}(\gamma)$ can be obtained by integration:

$$a_{kL}(\gamma) = \frac{4\pi}{(2a^2)^k a^{\ell} 2^k k! (2\ell+1)!!} \int G_{kL}(\gamma; \mathbf{r}) F(\mathbf{r}) d^3 r. \tag{12.16}$$

As a specific instance, the aim might be to expand the smoothed Hankel function $H_{L'}(\gamma', \varepsilon'; \mathbf{r}-\mathbf{R}')$ centered at $\mathbf{R}'$ around some other site $\mathbf{R}$. We obtain an expansion in the polynomials $P_{kL}(\gamma; \mathbf{r}-\mathbf{R})$ centered at $\mathbf{R}$:

$$H_{L'}(\gamma', \varepsilon'; \mathbf{r}-\mathbf{R}') \sim \sum_{k,L} a_{kL}(\gamma, \mathbf{R}-\mathbf{R}') P_{kL}(\gamma; \mathbf{r}-\mathbf{R}) \tag{12.17}$$

whereby the coefficients are

$$\begin{aligned} a_{kL}(\gamma, \mathbf{R}-\mathbf{R}') &= \frac{4\pi}{(2a^2)^k a^{\ell} 2^k k! (2\ell+1)!!} \int G_{kL}(\gamma; \mathbf{r}-\mathbf{R}) H_{L'}(\gamma', \varepsilon'; \mathbf{r}-\mathbf{R}') d^3 r \\ &= \frac{4\pi}{(2a^2)^k a^{\ell} 2^k k! (2\ell+1)!!} e^{-\gamma\varepsilon'} (-1)^{\ell} \\ &\quad \times \sum_{M} C_{LL'M} H_{(\ell+\ell'-m)/2+k, M}(\gamma+\gamma', \varepsilon'; \mathbf{R}-\mathbf{R}') \end{aligned} \tag{12.18}$$

[compare (8.4)], i.e., the involved integral reduces to a sum of smoothed Hankel functions of the connecting vector $\mathbf{R}-\mathbf{R}'$. Altogether we obtain an analytical expansion theorem for the smoothed Hankel functions around an arbitrary point in space. In contrast to the well-known structure-constant expansion[17] for the standard Hankel functions, the present expression can be applied even when point $\mathbf{R}$ lies close to or is identical with the center of the function at $\mathbf{R}'$. Furthermore, analogous expressions can be used to expand a Bloch-summed function $H_{L'}^{b}(\gamma', \varepsilon'; \mathbf{r}-\mathbf{R}')$. Hereby the integral over all space as in (12.18) is reduced to an integral over the unit cell which

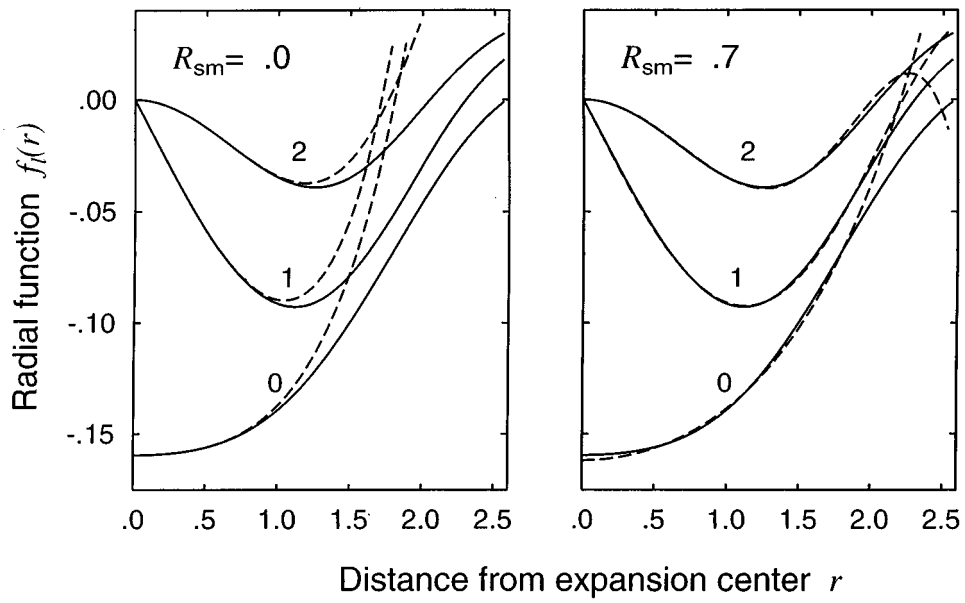

FIG. 3. Expansion of a smoothed Hankel function centered at point $\mathbf{R}'=(0,0,2)$ as a sum of the polynomials P_{kL} around the origin. The Hankel function has angular momentum $(\ell',m_{\ell'})=(1,0)$, energy $\varepsilon'=-1$, and smoothing radius $R'_{\rm sm}=1/a'=1$. Shown are the radial components for $(\ell,m_\ell)=(0,0)$, (1,0), and (2,0) for two choices of the smoothing radius $R_{\rm sm}=1/a$ when expanded up to $k_{\max}=2$. For $R_{\rm sm}=0$, the expansion reduces to a Taylor series, which is accurate near the center but deviates in an uncontrolled manner already at moderate distances. For $R_{\rm sm}=0.7$ the error in the expansion is spread evenly over the range where the Gaussian is large, here approximately to $r=1.5$.

is then evaluated analytically following (10.9). On the other hand, if the aim is to expand a plane wave, the coefficients are given by integrals over the plane wave times $G_{kL}(\gamma;\mathbf{r}-\mathbf{R})$. This simply picks out the corresponding Fourier coefficient of G_{kL}.

For a discussion of the convergence of the expansion (12.1), the central quantity is the width $R_{\rm sm}$ of the underlying Gaussian $g_0(r)=e^{-a^2r^2}=e^{-r^2/R_{\rm sm}^2}$ which defines the family $G_{kL}(\mathbf{r})$. By calculating the expansion coefficients according to (12.16), we are projecting out information about the function $F(\mathbf{r})$ in that part of volume where g_0 is non-negligible. Correspondingly, we obtain a representation which is accurate there but deviates where g_0 is small. When the extent of g_0 is made larger by increasing $R_{\rm sm}$, the resulting expansion is valid over a larger part of space but is less accurate overall for a fixed level of truncation. This is in contrast to a Taylor series, which places all emphasis on the (comparatively irrelevant) point at the center of expansion. Figure 3 illustrates the dependence of the convergence on the smoothing radius.

In order to formalize the discussion of convergence, we have chosen the normalization of the functions P_{kL} (12.6)/(12.7) such that

$$|p_{k\ell}(\gamma;r)|\leqslant 1 \quad \text{for all} \quad r\leqslant R_{\rm sm}$$

and

$$|p_{0\ell}(\gamma;R_{\rm sm})|=1. \tag{12.19}$$

Typical radial functions $p_{k\ell}(r)$ are shown in Fig. 4. The characteristic behavior is that the polynomials oscillate in a well-behaved manner up to a range of approximately $R_{\rm sm}$ and somewhat beyond, then quickly increase to large values. If we truncate (12.15) in order to approximate $f_L(r)r^\ell$ by the finite sum $\Sigma_{k\leqslant k_{\max}}a_{kL}(\gamma)p_{k\ell}(\gamma;r)$, then an upper bound for the approximation error on $r\leqslant R_{\rm sm}$ is given by

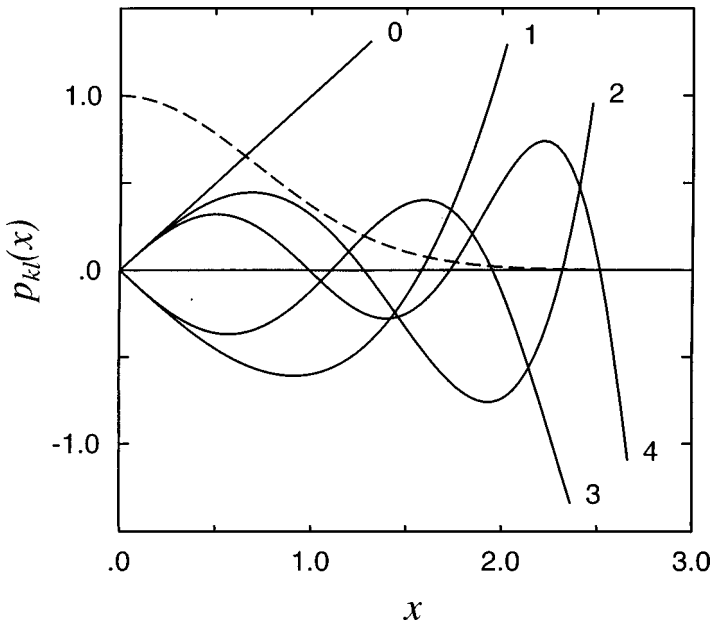

FIG. 4. Radial polynomials $p_{k\ell}(r)$ for $\ell=1$ and $R_{\rm sm}=1/a=1.0$, plotted for $0\leqslant k\leqslant 4$. The Gaussian $g_0(r)=\exp(-r^2/R_{\rm sm}^2)$ is also shown (dashed line). Note that the polynomials are well-behaved where g_0 is large, then increase rapidly outside this range.

$$\left| f_L(r) r^{\ell} - \sum_{k\leqslant k_{\max}} a_{kL}(\gamma) p_{k\ell}(\gamma;r) \right| = \left| \sum_{k>k_{\max}} a_{kL}(\gamma) p_{k\ell}(\gamma;r) \right| \leqslant \sum_{k>k_{\max}} |a_{kL}(\gamma)|. \quad (12.20)$$

In close analogy to the expansion of a function over a finite interval using Chebyshev poynomials,[18] the absolute values of the expansion coefficients generally decrease rapidly by orders of magnitude. The approximation error on $r\leqslant R_{\rm sm}$ is then bounded by the coefficient of the first neglected term, i.e.,

$$\left| f_L(r) r^{\ell} - \sum_{k\leqslant k_{\max}} a_{kL}(\gamma) p_{k\ell}(\gamma;r) \right| \leqslant |a_{k_{\max}+1,L}(\gamma)|. \quad (12.21)$$

XIII. SUMMARY

In this paper, we have presented a set of functions which combine many of the best features of Hankel functions and Gaussians as a basis for electronic structure calculations. These ''smoothed Hankel functions'' equal the standard Hankel functions at large distances, showing the same exponential decay. At smaller radii, the functions bend over smoothly until they approach the origin as $r^{\ell} Y_L(\hat{\mathbf{r}})$. The resulting object is nonsingular and analytical in all parts of space. The shape of each function is characterized by two separate parameters. The first is an energy which defines the decay at large distances, exactly as in the case of the standard Hankel functions. The second parameter is a smoothing radius which determines how strongly the singularity has been smoothed out, i.e., at what distance the smoothed Hankel function starts to deviate significantly from the standard function. A major advantage is that by adjusting these two parameters, basis functions can be made which closely resemble the true wave function outside the core regime. This is an improvement over both Gaussians and standard Hankel functions. A second advantage is that the resulting basis set is reasonably well suited to a direct numerical evaluation of the unavoidable three-center integrals, since a coarse mesh can be used. Furthermore, Bloch sums of the functions can be handled in a very similar way, leading to a unified description for crystals and molecules. In Ref. 5, a successful implementation of a density-functional crystal program based on these features was presented.

To use a given set of functions as a basis set, a number of calculational steps must be performed. To provide the neccessary formalism for the smoothed Hankel functions, we have first

introduced some families of auxiliary functions. These as well as the smoothed Hankel functions themselves are generated in compact form from simple root functions by differential operators. Using these results, we have derived analytical expressions for overlap and kinetic-energy two-center matrix elements as well as Coulomb integrals involving two such functions. To evaluate the expressions in practice, suitable recurrence relations were found. Finally, we have presented a general procedure by which an arbitrary smooth function can be expanded as a sum of polynomials around some point in space, whereby the approximation converges evenly over a chosen range as higher terms are included. Such a local representation is a necessary step when the functions are used in the context of augmentation methods or norm-conserving pseudopotentials. In sum, we believe the functions presented here have a high potential as a local basis set in electronic structure calculations and have derived expressions to perform the various calculational steps needed for such an application.

ACKNOWLEDGMENTS

We thank the Fonds der Chemischen Industrie for financial support.

APPENDIX A: DERIVATION OF AN EXPLICIT INTEGRAL REPRESENTATION FOR THE $\chi_\ell(r)$

Here, we make the connection to an explicit integral representation for the radial functions $\chi_\ell(r)$, related to the smoothed Hankel functions by $H_L(\mathbf{r})=\chi_\ell(r)r^\ell Y_L(\hat{\mathbf{r}})$ [see Eq. (6.18)]. Such representations are used in standard formulations of Ewald summation[19] and in Ref. 20. This representation is mainly of theoretical interest; for the calculation of the χ_ℓ it is more efficient to use the recurrence relations (6.19)–(6.21).

For $\chi_0(r)$ we obtain from (6.19) and (6.6) the representation

$$\chi_0(r)=\frac{1}{2r}\left[e^{-\kappa r}\frac{2}{\sqrt{\pi}}\int_{(\kappa/2a)-ar}^{\infty}e^{-t^2}dt-e^{\kappa r}\frac{2}{\sqrt{\pi}}\int_{(\kappa/2a)+ar}^{\infty}e^{-t^2}dt\right]. \tag{A1}$$

By making the substitutions

$$\xi=\frac{-t+\sqrt{t^2+2\kappa r}}{2r},\quad t=\frac{\kappa}{2\xi}-r\xi,\quad \frac{dt}{d\xi}=-\frac{\kappa}{2\xi^2}-r, \tag{A2}$$

and

$$\xi=\frac{t-\sqrt{t^2-2\kappa r}}{2r},\quad t=\frac{\kappa}{2\xi}+r\xi,\quad \frac{dt}{d\xi}=-\frac{\kappa}{2\xi^2}+r \tag{A3}$$

in the first and second integral, respectively, we obtain

$$\begin{aligned}\chi_0(r)&=\frac{1}{2r}\frac{2}{\sqrt{\pi}}\left[\int_a^0 e^{-\kappa^2/4\xi^2}e^{-r^2\xi^2}\left(-\frac{\kappa}{2\xi^2}-r\right)d\xi-\int_a^0 e^{-\kappa^2/4\xi^2}e^{-r^2\xi^2}\left(-\frac{\kappa}{2\xi^2}+r\right)d\xi\right]\\&=\frac{2}{\sqrt{\pi}}\int_0^a e^{\varepsilon/4\xi^2}e^{-r^2\xi^2}d\xi.\end{aligned} \tag{A4}$$

Finally, by applying (4.10) and (4.11) we see that

$$\chi_\ell(r)=\frac{2}{\sqrt{\pi}}2^\ell\int_0^a \xi^{2\ell}e^{\varepsilon/4\xi^2}e^{-r^2\xi^2}d\xi\quad\text{for all }\ell\in\mathcal{N}_0. \tag{A5}$$

APPENDIX B: EVALUATION OF BLOCH SUMS OF ORDINARY (UNSMOOTHED) HANKEL FUNCTIONS

The standard Ewald method[19] for evaluating lattice sums of Hankel functions is equivalent to splitting off a smoothed-Hankel part which is summed in reciprocal space. Here, we show how to do this in our formalism, whereby the inconvenient integrals to represent $\chi_\ell(r)$ are avoided (see Appendix A).

The aim is the evaluation of the Bloch sum

$$\check{H}_L^b(\varepsilon;\mathbf{r}) := \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \check{H}_L(\varepsilon;\mathbf{r}-\mathbf{R}) \tag{B1}$$

of unsmoothed Hankel functions at some point $\mathbf{r}$. This point cannot be a direct lattice point $\mathbf{R}'$ since $\check{H}_L^b(\mathbf{r})$ is undefined there. For a suitable parameter $\gamma>0$, we split (B1) up into two parts, which are evaluated as sums over reciprocal and direct space lattice vectors, respectively:

$$\begin{aligned}\check{H}_L^b(\varepsilon;\mathbf{r}) &= H_L^b(\gamma,\varepsilon;\mathbf{r}) + (\check{H}_L^b(\varepsilon;\mathbf{r}) - H_L^b(\gamma,\varepsilon;\mathbf{r})) \\ &= \frac{1}{\Omega}\sum_{\mathbf{G}} \frac{-4\pi}{\varepsilon-|\mathbf{k}+\mathbf{G}|^2}\, \mathscr{Y}_L(-i(\mathbf{k}+\mathbf{G}))\, e^{\gamma(\varepsilon-|\mathbf{k}+\mathbf{G}|^2)} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\ &\quad + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} (\check{H}_L(\varepsilon;\mathbf{r}-\mathbf{R}) - H_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R}))\end{aligned} \tag{B2}$$

[cf. (3.18), (6.35)]. In the real-space sum, the values $H_L(\gamma,\varepsilon;\mathbf{r}-\mathbf{R})$ can be calculated from (6.18) to (6.24). Furthermore, the values $\check{H}_L(\varepsilon;\mathbf{r}-\mathbf{R})$ can be obtained as follows in view of (6.27) and (6.18)–(6.24):

$$\check{H}_L(\mathbf{r}) = \check{\chi}_\ell(r) r^\ell Y_L(\hat{\mathbf{r}}), \tag{B3}$$

$$\check{\chi}_0(r) = \frac{e^{-\kappa r}}{r}, \tag{B4}$$

$$\check{\chi}_1(r) = \frac{e^{-\kappa r}}{r^3} + \frac{\kappa e^{-\kappa r}}{r^2}, \tag{B5}$$

$$\check{\chi}_{\ell+1}(r) = \frac{2\ell+1}{r^2}\,\check{\chi}_\ell(r) - \frac{\varepsilon}{r^2}\,\check{\chi}_{\ell-1}(r) \quad \text{for } \ell \geqslant 1. \tag{B6}$$

[1] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
[2] G. B. Bachelet, D. R. Haman, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[3] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[5] M. Methfessel and M. van Schilfgaarde (unpublished); M. Methfessel, *NFP Manual* [Institute for Semiconductor Physics, Frankfurt (Oder), 1997].
[6] J. Spanier and K. B. Oldham, *An Atlas of Functions* (Springer, Berlin, 1987).
[7] Z. Szmydt, *Fourier Transformation and Linear Differential Equations* (PNW, Warszawa, 1977).
[8] E. Bott, Diplomarbeit, Technische Universität Darmstadt, 1997.
[9] M. Abramowitz and I. A. Stegun, *Pocketbook of Mathematical Functions* (Harri Deutsch, Thun, 1984).
[10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, Philadelphia, 1976).
[11] M. Methfessel, Ph.D. thesis, Katholieke Universiteit de Nijmegen, 1986, pp. 22, 118–125.
[12] P. C. Schmidt and K. G. Weil, *Atom- und Molekülbau* (Thieme, Stuttgart, 1982).
[13] R. Daudel, G. Leroy, D. Peeters, and M. Sana, *Quantum Chemistry* (Wiley, Chichester, 1983), p. 160.
[14] M. Springborg and O. K. Andersen, J. Chem. Phys. **87**, 7125 (1987).
[15] I. N. Bronstein and K. A. Semendjajew, *Taschenbuch der Mathematik* (Harri Deutsch, Thun, 1985), 22. Aufl.
[16] H. Werner and R. Schaback, *Praktische Mathematik II Methoden der Analysis* (Springer, Berlin, 1972).
[17] R. J. Nozawa, J. Math. Phys. **7**, 1841 (1966).
[18] W. H. Press *et al.*, *Numerical Recipes in FORTRAN; the Art of Scientific Computing*, 2nd ed. (Cambridge University Press, Cambridge, 1992).
[19] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).
[20] S. Y. Savrasov, Phys. Rev. B **54**, 16470 (1996).