Localised spherical-wave basis set for $O(N)$ total-energy pseudopotential calculations

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We consider a localised spherical-wave basis set suitable for $O(N)$ total-energy pseudopotential calculations. The basis set is conveniently truncated using a single parameter, the kinetic energy cut-off used with the plane-wave basis. We present analytic results for the overlap integrals between any two basis functions centred on different sites, as well as for the kinetic energy matrix-elements which can therefore be evaluated accurately in real-space. A method for analytically performing the projection of the basis states onto angular-momentum states required for the use of non-local pseudopotentials is also presented.

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1 Introduction

Traditional total-energy calculations using density-functional theory (DFT) require a computational effort and quantity of memory which scale as the cube and square of the system size N (i.e. the number of atoms or the volume of the system) respectively. Therefore as systems of increasing size are considered, the computational resources are rapidly exhausted, and a ten-fold increase in computing power will roughly only double the size of system which can be studied. However, the complexity of the problem within DFT scales only linearly with N, and there has therefore been considerable interest in developing new schemes for performing these calculations in which the computational effort and memory required also scale linearly: so-called $O(N)$ methods.

One elegant and popular choice of basis in $O(N^3)$ calculations has been the plane-wave basis. However, because of the extended nature of these basis functions they cannot be used in $O(N)$ calculations, and a different choice has to be made, in which the basis functions are localised in real space. Examples include truncated Gaussian orbitals, orbitals based on pseudoatomic wave functions and representing the functions on a real-space grid. An $O(N)$ method results from the combination of a localised basis set and exploitation of the fact that local properties of a system (e.g. the density $n(\mathbf{r})$) depend only upon the electronic states in the vicinity of the point of interest [1].

In this paper we present a set of localised functions which are related to the plane-wave basis set and share some of its attractive features. A significant problem associated with localised basis functions is that they are not in general orthogonal, so that as the size of the basis is increased, the overlap matrix becomes singular. We demonstrate that the basis functions introduced here are orthogonal, by construction, to others centred on the same site, and that the overlap matrix elements for functions centred on different sites can be calculated analytically, and hence evaluated efficiently and accurately when implemented computationally.

Another disadvantage of using basis functions localised in real-space arises in the calculation of the action of the kinetic energy operator. To take advantage of the localisation it is necessary to focus on real-space and calculate all quantities in that representation. However, since the kinetic energy operator is diagonal in reciprocal-space, the kinetic energy matrix elements are most naturally calculated in reciprocal-space. Methods to evaluate the kinetic energy using finite-difference schemes can be inaccurate. With this new choice of basis, the matrix-elements of the kinetic energy operator between any two functions can also be calculated analytically, thus overcoming this problem.

One final advantage arises in the inclusion of non-local pseudopotentials which traditionally required significant computational effort. We present a method of obtaining the matrix-elements of the non-local pseudopotential operator by performing the projection of the basis function onto a core angular-momentum state analytically.

2 Origin of the basis functions

In the pseudopotential approximation, the core electrons and strong ionic potential of the atom are replaced by a much weaker potential in which the remaining pseudovalence electrons move. The pseudovalence states no longer have to be orthogonal to lower-lying core states and hence are much smoother than the all-electron valence states in the core region and have less kinetic energy. Thus the pseudovalence states can be accurately represented by a much smaller set of plane-wave basis functions than the all-electron states.

The plane-wave basis state $e^{i\mathbf{q}\cdot\mathbf{r}}$ is a solution of the Helmholtz equation (the time-independent free-electron Schrödinger equation)

$$\left(\nabla^2 + q^2\right) \psi(\mathbf{r}) = 0 \tag{1}$$

subject to periodic boundary conditions, with energy $E = \frac{1}{2}q^2$ (we use atomic units throughout.)

If instead we wish to localise the basis functions, say within spherical regions of radius a, so that the function vanishes outside these regions, then appropriate conditions would be to require the functions to be finite within the regions and to vanish on the boundary. The solutions to the Helmholtz equation (1) subject to these conditions are then truncated spherical-waves

$$\psi(\mathbf{r}) = \begin{cases} j_\ell(qr)\; Y_{\ell m}(\vartheta, \varphi), & r < a \\ 0, & r \geq a \end{cases} \tag{2}$$

where (r, ϑ, φ) are spherical polar coordinates with the origin at the centre of the spherical region, ℓ is a non-negative integer, m is an integer satisfying $-\ell \leq m \leq \ell$ and q is chosen to satisfy $j_\ell(qa) = 0$. $j_\ell(x)$ is a spherical Bessel function and $Y_{\ell m}(\Omega)$ is a spherical harmonic. Solutions involving the spherical von Neumann function $n_\ell(x)$ have been rejected because they are not finite at the centre of the sphere.

We note that these functions solve the same equation as the plane-wave basis functions, so that within the pseudopotential approximation the wave functions will be well-described by a truncated set of these basis functions. Moreover, these functions are eigenstates of the kinetic energy operator within the localisation region $r < a$ (i.e. in the region in which they will be used to describe the wave functions) with eigenvalue $\frac{1}{2}q^2$ so that the same kinetic energy cut-off used to truncate the plane-wave basis can be used here to restrict the values of ℓ and q.

Since the Laplacian is a self-adjoint operator under these boundary conditions, application of Sturm-Liouville theory proves that all states within the same spherical region are mutually orthogonal.

In a calculation, the electronic states are described by covering the simulation cell with overlapping spheres, usually chosen to be centred on the ions at positions $\mathbf{R}_\alpha$, and expanding the wave functions ϕ_α within these spheres in this basis:

$$\phi_\alpha(\mathbf{r}) = \sum_{n\ell m} c^\alpha_{n\ell m}\; j_\ell(q_{n\ell}\,|\mathbf{r} - \mathbf{R}_\alpha|)\; Y_{\ell m}(\Omega_{\mathbf{r}-\mathbf{R}_\alpha}). \tag{3}$$

The notation $\Omega_{\mathbf{r}}$ is introduced as shorthand for the polar and azimuthal angles of the vector $\mathbf{r}$ used to represent that vector in spherical polar coordinates. We denote the radius of the sphere by r_α so that the $\{q_{n\ell}\}$ are defined by $j_\ell(q_{n\ell} r_\alpha) = 0$.

The expansion (3) is frequently written down formally, but rarely used computationally because of the inconvenience of using spherical Bessel functions in numerical work. However, the analytic results derived in the following sections offset this disadvantage.

$O(N)$ methods are aimed at large systems, and so the Brillouin zone sampling of the electronic states is usually restricted to the states at the Γ-point only. The wave functions can then be made real without loss of generality, and so in practice we use real linear combinations of the spherical harmonics defined below, which does not alter any of the analysis here.

$$\{Y_{\ell m}\} \rightarrow \{\bar{Y}_{\ell m}\} = \left\{ \begin{array}{c} Y_{\ell,0}(\Omega) \\ \frac{1}{\sqrt{2}}\left[Y_{\ell,-m}(\Omega) + (-1)^m Y_{\ell,m}(\Omega)\right] \\ \frac{\mathrm{i}}{\sqrt{2}}\left[Y_{\ell,-m}(\Omega) - (-1)^m Y_{\ell,m}(\Omega)\right] \end{array} \right\} \tag{4}$$

These real combinations of spherical harmonics, which we denote $\bar{Y}_{\ell m}$, can be written down as real functions of the variables $\left\{\frac{x}{r}, \frac{y}{r}, \frac{z}{r}\right\}$ where (x, y, z) are Cartesian coordinates with origin at the centre of the sphere, and are familiar as the angular components of s, p, d etc. orbitals.

We introduce $\chi^\alpha_{n\ell m}(\mathbf{r})$ to represent a truncated spherical-wave basis function centred at the origin and confined to a sphere of radius r_α:

$$\chi^\alpha_{n\ell m}(\mathbf{r}) = \begin{cases} j_\ell(q_{n\ell} r)\bar{Y}_{\ell m}(\Omega_{\mathbf{r}}), & r \le r_\alpha, \\ 0, & r > r_\alpha. \end{cases} \tag{5}$$

Equation (3) can then be written:

$$\phi_\alpha(\mathbf{r}) = \sum_{n\ell m} c^\alpha_{n\ell m}\ \chi^\alpha_{n\ell m}(\mathbf{r} - \mathbf{R}_\alpha). \tag{6}$$

3 Fourier transform of the basis functions

We define the Fourier transform of a basis function $\chi^\alpha_{n\ell m}(\mathbf{r})$ by

$$\tilde{\chi}^{\alpha}_{n\ell m}(\mathbf{k}) = \int\limits_{\text{all space}} \mathrm{d}^3 r \ \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \ \chi^{\alpha}_{n\ell m}(\mathbf{r})$$
$$= \int\limits_{0}^{r_\alpha} \mathrm{d}r \ r^2 \ j_\ell(q_{n\ell} r) \int \mathrm{d}\Omega \ \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \ \bar{Y}_{\ell m}(\Omega). \tag{7}$$

The angular integral is performed by using the expansion of $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ into spherical-waves (42, Appendix) leaving the radial integral

$$\tilde{\chi}^{\alpha}_{n\ell m}(\mathbf{k}) = 4\pi \mathrm{i}^\ell \ \bar{Y}_{\ell m}(\Omega_{\mathbf{k}}) \int\limits_{0}^{r_\alpha} \mathrm{d}r \ r^2 \ j_\ell(q_{n\ell} r) \ j_\ell(kr). \tag{8}$$

The radial integral can now be calculated using equations (43,44) given in the Appendix and the boundary conditions (that the basis functions are finite at $r = 0$ and vanish at $r = r_\alpha$) for the cases when $k \neq q_{n\ell}$ and $k = q_{n\ell}$ respectively. The final result for the Fourier transform of a basis function is then

$$\tilde{\chi}^{\alpha}_{n\ell m}(\mathbf{k}) = 4\pi \mathrm{i}^\ell \ \bar{Y}_{\ell m}(\Omega_{\mathbf{k}}) \begin{cases} \dfrac{q_{n\ell} r_\alpha^2}{k^2 - q_{n\ell}^2} j_\ell(k r_\alpha) j_{\ell-1}(q_{n\ell} r_\alpha), & k \neq q_{n\ell}, \ (a) \\[2ex] \dfrac{q_{n\ell} r_\alpha^3}{k + q_{n\ell}} j_{\ell-1}^2(q_{n\ell} r_\alpha), & k = q_{n\ell}. \ (b) \end{cases} \tag{9}$$

Equation (9b) is in fact a limiting case of (9a) which can therefore always be substituted for $\tilde{\chi}^{\alpha}_{n\ell m}(\mathbf{k})$ in an integral over reciprocal-space.

4 Overlap matrix elements

The overlap matrix for any two basis functions $\chi^{\alpha}_{n\ell m}$ and $\chi^{\beta}_{n'\ell' m'}$ centred at $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ respectively is

$$S_{\alpha\beta} = \int\limits_{\text{all space}} \mathrm{d}^3 r \ \chi^{\alpha}_{n\ell m}(\mathbf{r} - \mathbf{R}_\alpha) \chi^{\beta}_{n'\ell' m'}(\mathbf{r} - \mathbf{R}_\beta)$$
$$= \int\limits_{\text{all space}} \mathrm{d}^3 r' \ \chi^{\alpha}_{n\ell m}(\mathbf{r}') \chi^{\beta}_{n'\ell' m'}(\mathbf{r}' - \mathbf{R}_{\alpha\beta}) \tag{10}$$

where $\mathbf{R}_{\alpha\beta} = \mathbf{R}_\beta - \mathbf{R}_\alpha$. The dummy variable of integration has been changed in order to highlight the fact that $S_{\alpha\beta}$ is a function of $\mathbf{R}_{\alpha\beta}$ only. Using a variant of the convolution theorem and the fact that the basis functions are real enables the integral to be rewritten as

$$S_{\alpha\beta} = \frac{1}{(2\pi)^3} \int\limits_{\text{all space}} \mathrm{d}^3k \, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}_{\alpha\beta}} \, \tilde{\chi}^{\alpha}_{n\ell m}(\mathbf{k}) \tilde{\chi}^{\beta}_{n'\ell' m'}(-\mathbf{k}). \tag{11}$$

Using equation (9a) we obtain

$$S_{\alpha\beta} = \left(q_{n\ell} r_\alpha^2\right) \left(q_{n'\ell'} r_\beta^2\right) j_{\ell-1}(q_{n\ell} r_\alpha) j_{\ell'-1}(q_{n'\ell'} r_\beta) \; I_{\alpha\beta} \tag{12}$$

where $I_{\alpha\beta}$ is the integral

$$I_{\alpha\beta} = \frac{2}{\pi} \, \mathrm{i}^{(\ell-\ell')} \int \mathrm{d}^3k \; \frac{\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}_{\alpha\beta}} \, j_\ell(kr_\alpha) \; j_{\ell'}(kr_\beta)}{(k^2 - q_{n\ell}^2)\,(k^2 - q_{n'\ell'}^2)} \bar{Y}_{\ell m}(\Omega_{\mathbf{k}}) \bar{Y}_{\ell' m'}(\Omega_{\mathbf{k}}). \tag{13}$$

Introducing differential operators $\hat{D}_{\ell m}$, obtained from $\bar{Y}_{\ell m}$ by making the replacement

$$\left\{ \frac{x}{r}, \frac{y}{r}, \frac{z}{r} \right\} \longrightarrow \left\{ \frac{\partial}{\partial x_{\alpha\beta}}, \frac{\partial}{\partial y_{\alpha\beta}}, \frac{\partial}{\partial z_{\alpha\beta}} \right\}$$

where $\mathbf{R}_{\alpha\beta} = (x_{\alpha\beta}, y_{\alpha\beta}, z_{\alpha\beta})$ in Cartesian coordinates, equation (13) becomes

$$I_{\alpha\beta} = 4(-1)^\ell \; \hat{D}_{\ell m} \hat{D}_{\ell' m'} \int\limits_{-\infty}^{\infty} \mathrm{d}k \; \frac{j_\ell(kr_\alpha) \; j_{\ell'}(kr_\beta) \; j_0(kR_{\alpha\beta})}{k^{(\ell+\ell')}\,(k^2 - q_{n\ell}^2)\,(k^2 - q_{n'\ell'}^2)} \tag{14}$$

where we have used the fact that the integrand is an even function of k for all values of ℓ and ℓ' to change the limits of the integral. From equation (14) $I_{\alpha\beta}$ no longer appears manifestly symmetric with respect to swapping α and β. Nonetheless, it still is because under the swap $\{\alpha, \ell, m\} \leftrightarrow \{\beta, \ell', m'\}$, $\hat{D}_{\ell m} \to (-1)^{\ell'} \hat{D}_{\ell' m'}$ and $\hat{D}_{\ell' m'} \to (-1)^{\ell} \hat{D}_{\ell m}$.

The three spherical Bessel functions in equation (14) can all be expressed in terms of trigonometric functions and algebraic powers of the argument, using the recursion rules (40,41, Appendix). The product of three trigonometric functions can always be expressed as a sum of four trigonometric functions with different arguments, using well-known identities. The result is to split the integrand up into terms of the following form:

$$\frac{\sin k\,(r_\alpha \pm r_\beta \pm R_{\alpha\beta})}{k^p\,(k^2 - q_{n\ell}^2)\,(k^2 - q_{n'\ell'}^2)}, \qquad p \text{ always an odd integer,}$$

$$\frac{\cos k\,(r_\alpha \pm r_\beta \pm R_{\alpha\beta})}{k^p\,(k^2 - q_{n\ell}^2)\,(k^2 - q_{n'\ell'}^2)}, \qquad p \text{ always an even integer.} \tag{15}$$

These terms are individually singular and generally possess a pole of order p on the real axis at $k = 0$ and cannot be integrated. However, since we are integrating finite well-behaved functions we know that the total integrand cannot contain any non-integrable singularities. Therefore we can add extra contributions to each term to cancel all the singularities except simple poles, and all these extra terms must cancel when the terms are added together to obtain the whole integrand.

We shall evaluate the integrals using the calculus of residues so that the general integral to be performed is

$$I = \oint_C \mathrm{d}z\, \frac{\mathrm{e}^{\mathrm{i}Rz}}{z^p\,(z^2 - q_{n\ell}^2)\,(z^2 - q_{n'\ell'}^2)} \tag{16}$$

where $R = r_\alpha \pm r_\beta \pm R_{\alpha\beta}$ and the contour C runs along the real z-axis from $-\infty$ to $+\infty$, and is closed in either the upper or lower half z-plane, depending upon whether R is positive or negative respectively. Adding the extra terms to regularise the integral we obtain the final form of the integral

$$I = \oint_C \mathrm{d}z\, \frac{\mathrm{e}^{\mathrm{i}Rz} - \sum_{m=0}^{p-2} \frac{(\mathrm{i}Rz)^m}{m!}}{z^p\,(z^2 - q_{n\ell}^2)\,(z^2 - q_{n'\ell'}^2)}. \tag{17}$$

This integrand now has simple poles lying on the contour of integration at $z = 0, \pm q_{n\ell}, \pm q_{n'\ell'}$. The residues of these poles are

$$\begin{aligned} &\frac{(\mathrm{i}R)^{p-1}}{(p-1)!\; q_{n\ell}^2\; q_{n'\ell'}^2}, && z = 0, \\ &\frac{\mathrm{e}^{\pm\mathrm{i}q_{n\ell}R} - \sum_{m=0}^{p-2} \frac{(\pm\mathrm{i}q_{n\ell}R)^m}{m!}}{2\,(q_{n\ell}^2 - q_{n'\ell'}^2)\,(\pm q_{n\ell})^{p+1}}, && z = \pm q_{n\ell} \quad \text{(similarly for } z = \pm q_{n'\ell'}.) \end{aligned} \tag{18}$$

Summing the residues to perform the Cauchy principal value integrals, and taking real or imaginary parts as appropriate, we obtain the following results:

$$\int_{-\infty}^{\infty} \mathrm{d}k \frac{\sin kR + (\text{cancelling terms})}{k^p\left(k^2-q_{n\ell}^2\right)\left(k^2-q_{n'\ell'}^2\right)} =$$
$$\frac{\pi\ \mathrm{sgn}R}{q_{n\ell}^2-q_{n'\ell'}^2}\left[-\frac{(-1)^{\frac{p-1}{2}}\ R^{p-1}}{(p-1)!\ q_{n\ell}^2}+\frac{(-1)^{\frac{p-1}{2}}\ R^{p-1}}{(p-1)!\ q_{n'\ell'}^2}+\frac{\cos q_{n\ell}R}{q_{n\ell}^{p+1}}\right.$$
$$\left.-\frac{\cos q_{n'\ell'}R}{q_{n'\ell'}^{p+1}}-\sum_{m=0,\ \mathrm{even}}^{p-3}\left\{\frac{(-1)^{\frac{m}{2}}R^m}{m!\ q_{n\ell}^{p-m+1}}-\frac{(-1)^{\frac{m}{2}}R^m}{m!\ q_{n'\ell'}^{p-m+1}}\right\}\right], \tag{19}$$
$$\int_{-\infty}^{\infty} \mathrm{d}k \frac{\cos kR + (\text{cancelling terms})}{k^p\left(k^2-q_{n\ell}^2\right)\left(k^2-q_{n'\ell'}^2\right)} =$$
$$\frac{\pi\ \mathrm{sgn}R}{q_{n\ell}^2-q_{n'\ell'}^2}\left[-\frac{(-1)^{\frac{p}{2}}\ R^{p-1}}{(p-1)!\ q_{n\ell}^2}+\frac{(-1)^{\frac{p}{2}}\ R^{p-1}}{(p-1)!\ q_{n'\ell'}^2}-\frac{\sin q_{n\ell}R}{q_{n\ell}^{p+1}}\right.$$
$$\left.+\frac{\sin q_{n'\ell'}R}{q_{n'\ell'}^{p+1}}+\sum_{m=1,\ \mathrm{odd}}^{p-3}\left\{\frac{(-1)^{\frac{m-1}{2}}R^m}{m!\ q_{n\ell}^{p-m+1}}-\frac{(-1)^{\frac{m-1}{2}}R^m}{m!\ q_{n'\ell'}^{p-m+1}}\right\}\right] \tag{20}$$

where

$$\mathrm{sgn}R = \begin{cases} -1, & R<0, \\ +1, & R\geq 0. \end{cases} \tag{21}$$

For the case when $q_{n\ell} = q_{n'\ell'}$, we note that since the integrand in equation (17) must still only have a simple pole at $z = \pm q_{n\ell}$ we obtain a simplified form in this special case by taking the limit $q_{n'\ell'} \to q_{n\ell}$ of equations (19,20).

$$\int_{-\infty}^{\infty} \mathrm{d}k \frac{\sin kR + (\text{cancelling terms})}{k^p\left(k^2-q_{n\ell}^2\right)^2} =$$
$$\pi\ \mathrm{sgn}R\ \frac{(-1)^{\frac{p-1}{2}}R^{p-1}}{(p-1)!\ q_{n\ell}^4}-\frac{(p+1)\cos q_{n\ell}R}{2q_{n\ell}^{p+3}}-\frac{R\sin q_{n\ell}R}{2q_{n\ell}^{p+2}}$$
$$+\sum_{m=0,\ \mathrm{even}}^{p-3}\frac{(-1)^{\frac{m}{2}}(p-m+1)R^m}{2(m!)q_{n\ell}^{p-m+3}}, \tag{22}$$
$$\int_{-\infty}^{\infty} \mathrm{d}k \frac{\cos kR + (\text{cancelling terms})}{k^p\left(k^2-q_{n\ell}^2\right)^2} =$$
$$\pi\ \mathrm{sgn}R\ \frac{(-1)^{\frac{p}{2}}R^{p-1}}{(p-1)!\ q_{n\ell}^4}-\frac{(p+1)\sin q_{n\ell}R}{2q_{n\ell}^{p+3}}-\frac{R\cos q_{n\ell}R}{2q_{n\ell}^{p+2}}$$
$$+\sum_{m=1,\ \mathrm{odd}}^{p-3}\frac{(-1)^{\frac{m-1}{2}}(p-m+1)R^m}{2(m!)q_{n\ell}^{p-m+3}}. \tag{23}$$

The result for $S_{\alpha\beta}$ is obtained by summing the results in equations (19,20,22, 23) for all the terms in the expansion of the integrand (14) and then operating with the differential operators $\hat{D}_{\ell m}$.

A second special case occurs when $\mathbf{R}_{\alpha\beta} = 0$, and in this case it is simplest to perform the integral (10) in real-space using the generalised orthogonality relation for spherical Bessel functions (43) when $q_{n\ell} \neq q_{n'\ell'}$.

$$S_{\alpha\beta} = \frac{1}{q_{n\ell}^2 - q_{n'\ell'}^2}\delta_{\ell\ell'}\delta_{mm'} \begin{cases} -q_{n\ell}r_\alpha^2 j_\ell(q_{n'\ell'}r_\alpha)j_{\ell-1}(q_{n\ell}r_\alpha), \; r_\alpha < r_\beta, \\ q_{n'\ell'}r_\beta^2 j_\ell(q_{n\ell}r_\beta)j_{\ell-1}(q_{n'\ell'}r_\beta), \;\; r_\alpha \geq r_\beta. \end{cases} \tag{24}$$

There is also the case when $\mathbf{R}_{\alpha\beta} = 0$ and $q_{n\ell} = q_{n'\ell'}$ which is calculated using equation (44, Appendix).

$$S_{\alpha\beta} = \tfrac{1}{2}\delta_{\ell\ell'}\delta_{mm'} \begin{cases} r_\alpha^3 j_{\ell-1}^2(q_{n\ell}r_\alpha), & r_\alpha < r_\beta, \\ r_\beta^3 j_{\ell-1}^2(q_{n\ell}r_\beta), & r_\alpha \geq r_\beta. \end{cases} \tag{25}$$

Finally, it is obvious that the overlap matrix element must vanish when the separation of the the sphere centres exceeds the sum of their radii (i.e. $R_{\alpha\beta} > r_\alpha + r_\beta$) because then there is no region of space where both basis functions are non-zero. However, this is not obvious from the results presented above, but arises because of the change of sign of the residue sums in equations (19,20,22, 23) (denoted by sgn$R$) which occurs when $R_{\alpha\beta} = r_\alpha + r_\beta$ and results in exact cancellation of all terms.

5 Kinetic energy matrix elements

The kinetic energy matrix elements for any two basis functions $\chi_{n\ell m}^\alpha$ and $\chi_{n'\ell'm'}^\beta$ centred at $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ respectively are defined by

$$\begin{aligned} T_{\alpha\beta} &= -\tfrac{1}{2} \int\limits_{\text{all space}} \mathrm{d}^3 r \chi_{n\ell m}^\alpha(\mathbf{r} - \mathbf{R}_\alpha)\nabla^2\chi_{n'\ell'm'}^\beta(\mathbf{r} - \mathbf{R}_\beta) \\ &= \frac{1}{2(2\pi)^3}\int \mathrm{d}^3 k \; k^2 \, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}_{\alpha\beta}} \, \tilde{\chi}_{n\ell m}^\alpha(\mathbf{k})\tilde{\chi}_{n'\ell'm'}^\beta(\mathbf{k}). \end{aligned} \tag{26}$$

Because of the discontinuity in the first derivatives of the basis functions at the sphere boundaries, a delta-function arises when the Laplacian operates on a basis function. This is integrated out when the matrix element is calculated and this contribution is included when transforming the real-space integral to reciprocal-space in equation (26).

The second line of equation (26) is identical to equation (11) apart from a factor of $\frac{1}{2}k^2$. The same separation into individually regular terms can be applied here, and the result is that we need to calculate the contour integral (17) as before, except that the integer p must be replaced by $(p-2)$ and a numerical factor of $\frac{1}{2}$ is introduced. The calculation of the residues is identical to that presented in the previous section, except that the integrand no longer *always* has a pole at $z=0$ in every term.

The results for $T_{\alpha\beta}$ when $\mathbf{R}_{\alpha\beta}=0$ are

$$
\begin{array}{ll}
\dfrac{\frac{1}{2}\delta_{\ell\ell'}\delta_{mm'}}{q_{n\ell}^2-q_{n'\ell'}^2}\left\{\begin{array}{ll} -q_{n\ell}^3 r_\alpha^2 j_\ell(q_{n'\ell'}r_\alpha)j_{\ell-1}(q_{n\ell}r_\alpha), & r_\alpha < r_\beta \\ q_{n'\ell'}^3 r_\beta^2 j_\ell(q_{n\ell}r_\beta)j_{\ell-1}(q_{n'\ell'}r_\beta), & r_\alpha \geq r_\beta \end{array}\right\} q_{n\ell}\neq q_{n'\ell'}, & \\
 & (27) \\
\frac{1}{4}\delta_{\ell\ell'}\delta_{mm'}q_{n\ell}^2\left\{\begin{array}{ll} r_\alpha^3 j_{\ell-1}^2(q_{n\ell}r_\alpha), & r_\alpha < r_\beta \\ r_\beta^3 j_{\ell-1}^2(q_{n\ell}r_\beta), & r_\alpha \geq r_\beta \end{array}\right\} q_{n\ell}=q_{n'\ell'}. &
\end{array}
$$

The calculation of the kinetic energy has been checked by projecting a set of wave functions expanded in the spherical-wave basis onto the plane-wave basis using equation (9a). As the kinetic energy cut-off for the plane-wave basis is increased, so the description of the wave functions becomes more accurate. The kinetic energy calculated using the results above can then be compared against the kinetic energy calculated by a plane-wave $O(N^3)$ code [2].

From the asymptotic behaviour of the spherical Bessel functions, the Fourier transform (9a) for large k is

$$
\tilde{\chi}_{n\ell m}^{\alpha}(\mathbf{k}) \sim \frac{\sin(kr_\alpha - \frac{\ell\pi}{2})}{k^3}\,\bar{Y}_{\ell m}(\Omega_{\mathbf{k}}) \qquad (28)
$$

and so the error in the kinetic energy due to truncating the plane-wave basis with cut-off $E_{\mathrm{cut}}=\frac{1}{2}k_{\mathrm{cut}}^2$ is

$$
\Delta T \sim \int_{k_{\mathrm{cut}}}^{\infty} \mathrm{d}k\; k^2\left(\frac{1}{k^3}\right)k^2\left(\frac{1}{k^3}\right) = \frac{1}{k_{\mathrm{cut}}} \sim \frac{1}{\sqrt{E_{\mathrm{cut}}}}. \qquad (29)
$$

In figure 1 the kinetic energy as calculated by the plane-wave code has been plotted against $1/\sqrt{E_{\mathrm{cut}}}$ and yields a straight line as expected, which can then be extrapolated to obtain an estimate of the kinetic energy calculated for infinite cut-off: 60.66 ± 0.01 eV. This is in agreement with the value calculated analytically of 60.65 eV.

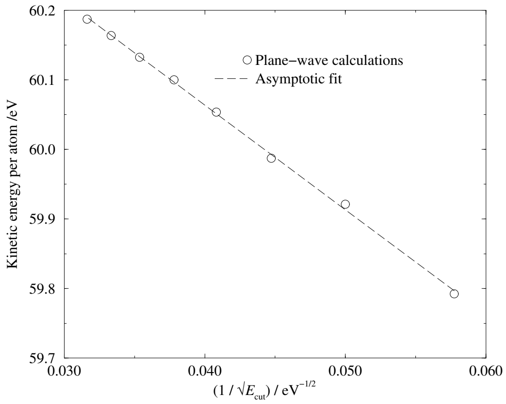

Fig. 1. Plot of asymptotic fit to kinetic energy data.

6 Non-local pseudopotential

The general form for a semi-local pseudopotential operator (i.e. one which is non-local in the angular but not radial coordinates) for an ion is

$$\hat{V}_{\mathrm{NL}} = \sum_{\ell m} |\ell m\rangle \hat{V}_\ell \langle \ell m| \tag{30}$$

where $\langle \mathbf{r}|\ell m\rangle = \bar{Y}_{\ell m}(\Omega)$ and $\bar{Y}_{\ell m}$ is centred on the ion.

The pseudopotential components V_ℓ are themselves short-ranged in real-space, and vanish beyond the core radius r_{c}. Therefore the action of the non-local pseudopotential depends only upon the form of the wave functions within this core region. We require the matrix elements of the non-local pseudopotential between localised basis functions which are not necessarily centred on the ion.

We therefore need to find an expansion of the basis functions in terms of functions localised within the pseudopotential core. Since the basis functions are all solutions of the Helmholtz equation, we invoke the uniqueness theorem which states that the expansion we seek is uniquely determined by the boundary conditions on the surface of the core region and solve the Helmholtz equation subject to these inhomogeneous boundary conditions by the standard method using the formal expansion of the Green's function. The result is

$$\chi^{\alpha}_{n\ell m}(\mathbf{r}) = \sum_{\ell' m'} f^{n\ell m}_{\ell' m'} \left[1 + \sum_{n'} a^{n\ell m}_{n'\ell'} j_{\ell'}(q_{n'\ell'} r')\right] \bar{Y}_{\ell' m'}(\Omega_{\mathbf{r}'}) \tag{31}$$

and is valid for points $\mathbf{r}' = \mathbf{r} - \mathbf{R}_{\mathrm{ion}} + \mathbf{R}_\alpha$ within the core region (i.e. for $r' \le r_{\mathrm{c}}$.)

The coefficients $f^{n\ell m}_{\ell' m'}$ and $a^{n\ell m}_{n'\ell'}$ are defined by:

$$f^{n\ell m}_{\ell' m'} = \int\limits_{r'=r_\mathrm{c}} \mathrm{d}\Omega_{\mathbf{r}'} \bar{Y}_{\ell' m'}(\Omega_{\mathbf{r}'})\ \chi^{\alpha}_{n\ell m}(\mathbf{r}' + \mathbf{R}_\mathrm{ion} - \mathbf{R}_\alpha), \tag{32}$$

$$a^{n\ell m}_{n'\ell'} = \frac{2}{r_\mathrm{c}^3\ j^2_{\ell'-1}(\lambda_{n'\ell'} r_\mathrm{c})} \left[\frac{\lambda_{n'\ell'}\ r_\mathrm{c}^2\ j_{\ell'-1}(\lambda_{n'\ell'} r_\mathrm{c})}{q^2_{n\ell} - \lambda^2_{n'\ell'}} - \int\limits_0^{r_\mathrm{c}} \mathrm{d}r\ r^2 j_{\ell'}(\lambda_{n'\ell'} r) \right]. \tag{33}$$

The $\{\lambda_{n\ell}\}$ are chosen by $j_\ell(\lambda_{n\ell} r_\mathrm{c}) = 0$ and play the same role as the $\{q_{n\ell}\}$ in the expansion of the wave functions. The integral in equation (33) is straightforward to evaluate for given ℓ'.

The surface integral in equation (32) is evaluated by first rotating the coordinate system so that the new z-axis is parallel to $\mathbf{R}_\alpha - \mathbf{R}_\mathrm{ion}$, thus mixing the spherical harmonics [5]. The elements of the orthogonal spherical harmonic mixing matrices $C^\ell_{mm'}$ are defined by the elements of the rotation matrix for the coordinate system. In the new coordinate system, the surface integral is written in terms of a one-dimensional integral

$$K_{\ell' n\ell m}(u, q_{n\ell}) = \frac{1}{2u} \left[(2\ell'+1)(2\ell+1) \frac{(\ell'-|m|)!(\ell-|m|)!}{(\ell'+|m|)!(\ell+|m|)!} \right]^{\frac{1}{2}} \times$$
$$\int\limits_{|u-1|}^{\min(u+1, r_\alpha/r_\mathrm{c})} \mathrm{d}z\ z P^{|m|}_{\ell'} \left(\frac{1+u^2-z^2}{2u} \right) j_\ell(q_{n\ell} r_\mathrm{c} z) P^{|m|}_{\ell} \left(\frac{1-u^2-z^2}{2uz} \right) \tag{34}$$

in which the dimensionless variable $u = \frac{|\mathbf{R}_\alpha - \mathbf{R}_\mathrm{ion}|}{r_\mathrm{c}}$ is introduced. $P^{|m|}_\ell(x)$ denotes an associated Legendre polynomial, and these integrals can all be calculated indefinitely using elementary methods once the integrand is expanded into trigonometric functions.

The final result for $f^{n\ell m}_{\ell' m'}$ is then

$$f^{n\ell m}_{\ell' m'} = \sum_{m''=-\min(\ell,\ell')}^{\min(\ell,\ell')} C^{\ell'}_{m''m'} K_{\ell' n\ell m} C^{\ell}_{m''m}. \tag{35}$$

Defining the core matrix elements

$$V^{\ell}_{nn'} = \begin{cases} \int_0^{r_c} \mathrm{d}r\ r^2\ j_\ell(\lambda_{n\ell} r) V_\ell(r) j_\ell(\lambda_{n'\ell}) & n, n' \neq 0 \\ \int_0^{r_c} \mathrm{d}r\ r^2\ j_\ell(\lambda_{n\ell} r) V_\ell(r) & n \neq 0, n' = 0 \\ \int_0^{r_c} \mathrm{d}r\ r^2\ V_\ell(r) & n = n' = 0 \end{cases} \tag{36}$$

the matrix element of the non-local pseudopotential operator between any two basis functions overlapping the core ($\chi^{\alpha}_{n\ell m}$ and $\chi^{\beta}_{n'\ell' m'}$) can be written as the sum:

$$V_{\mathrm{NL},\alpha\beta} = \sum_{\ell'' m''} f^{n\ell m}_{\ell'' m''} f^{n'\ell' m'}_{\ell'' m''} \left[V^{\ell''}_{00} + \sum_{n''} \left(a^{n\ell m}_{n''\ell''} + a^{n'\ell' m'}_{n''\ell''} \right) V^{\ell''}_{n''0} \right.$$
$$\left. + \sum_{n'' n'''} a^{n\ell m}_{n''\ell''} a^{n'\ell' m'}_{n'''\ell''} V^{\ell''}_{n'' n'''} \right] . \tag{37}$$

The non-local pseudopotential data is therefore stored in terms of the core matrix elements defined in equation (37). In figure 2 we plot the non-local pseudopotential energy against the number of core Bessel functions for an s-local silicon pseudopotential generated according to the scheme of Troullier and Martins [3]. We see that the energy converges rapidly with the number of core Bessel functions used (the dashed line is the energy calculated with fifty core functions.) Increasing the number of core functions only increases the number of $a^{n\ell m}_{n'\ell'}$ coefficients required, and the separable nature of the calculation means that even using fifty core functions requires very little computational effort.

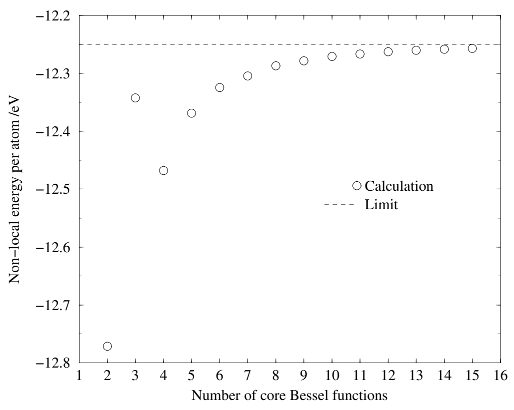

Fig. 2. Non-local pseudopotential energy against number of core Bessel functions.

7 Computational implementation

The results in equations (19,20,22, 23) have been written in a form which shows that in general each term can be represented by a real numerical prefactor, integers which are the powers of $\{R, q_{n\ell}, q_{n'\ell'}\}$ and one further integer to signify the presence of one of the terms $\{\sin q_{n\ell}R, \sin q_{n'\ell'}R, \cos q_{n\ell}R, \cos q_{n'\ell'}R\}$. When these terms are combined and differentiated by the $\hat{D}_{\ell m}$, the general term also needs integers to represent powers of $\{x_{\alpha\beta}, y_{\alpha\beta}, z_{\alpha\beta}, R_{\alpha\beta}, r_\alpha, r_\beta\}$. Therefore a general term in the expressions for $S_{\alpha\beta}$ and $T_{\alpha\beta}$ could be represented by a data structure consisting of one real variable g and ten integer variables I_{1-10} as follows:

$$g\frac{x_{\alpha\beta}^{I_1} y_{\alpha\beta}^{I_2} z_{\alpha\beta}^{I_3} R^{I_4} f(R)}{q_{n\ell}^{I_5} q_{n'\ell'}^{I_6} r_\alpha^{I_7} r_\beta^{I_8} R_{\alpha\beta}^{I_9}} \to \{g, I_1, I_2, I_3, I_4, I_5, I_6, I_7, I_8, I_9, I_{10}\} \qquad (38)$$

with the following correspondence between $f(R)$ and I_{10}:

$$\begin{aligned} & f(R) = \{1, \sin q_{n\ell}R, \sin q_{n'\ell'}R, \cos q_{n\ell}R, \cos q_{n'\ell'}R\} \\ & \to I_{10} = \{0, 1, 2, 3, 4\}\,. \end{aligned} \qquad (39)$$

A recursive function can be written to manipulate these encoded terms and perform the differentiation by the $\hat{D}_{\ell m}$, which can themselves be generated using the recursion rules for the associated Legendre polynomials. Thus it is straightforward to write a code which starts from equation (14) and generates the results up to arbitrary values of ℓ for $S_{\alpha\beta}$ and $T_{\alpha\beta}$ for the cases when $\mathbf{R}_{\alpha\beta} \neq 0$. The results for $\mathbf{R}_{\alpha\beta} = 0$ are simple enough to be coded within the program which uses this basis.

We have successfully implemented this basis set in a total-energy pseudopotential code and are currently performing preliminary calculations. For a given ionic configuration the matrix elements between the basis states can be calculated initially and stored on disk for use during the calculation.

8 Conclusions

We have shown that it is possible to construct a set of basis functions which are solutions of the free-electron Schrödinger equation, subject to being localised in spherical regions. Basis functions within the same region are mutually orthogonal, avoiding the problem of the overlap matrix becoming singular when the size of the basis set is increased. It is also possible to truncate the basis set using the kinetic energy cut-off used to truncate the plane-wave basis.

We have shown in detail how to obtain analytic results for the overlap integral between any two basis functions, and presented these in a form which can be implemented computationally.

The same results can be adapted to obtain matrix elements of the kinetic energy operator, providing an efficient and accurate method of computing the kinetic energy in real space and avoiding the use of finite difference methods.

The projection of basis functions onto ionic core angular momentum states can also be performed analytically so that non-local pseudopotentials can be used.

Appendix

In this section we list some standard results used in the analysis in this paper [4].

$$j_{\ell+1}(x) = \frac{\ell}{x} j_\ell(x) - j'_\ell(x) \tag{40}$$

$$j_{\ell-1}(x) = \frac{\ell+1}{x} j_\ell(x) + j'_\ell(x) \tag{41}$$

$$\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \mathrm{i}^\ell \; j_\ell(kr) \; \bar{Y}_{\ell m}(\Omega_{\mathbf{k}}) \; \bar{Y}_{\ell m}(\Omega_{\mathbf{r}}) \tag{42}$$

$$\begin{aligned} &\int_a^b j_\ell(mx) j_\ell(nx) x^2 \, \mathrm{d}x \\ &\qquad = \frac{1}{m^2 - n^2} \left[x^2 \left\{ n j_\ell(mx) j_{\ell-1}(nx) - m j_{\ell-1}(mx) j_\ell(nx) \right\} \right]_a^b \end{aligned} \tag{43}$$

$$\begin{aligned} \int_a^b j_\ell^2(mx) x^2 \, \mathrm{d}x = \tfrac{1}{2} \Bigg[x^2 \Bigg\{ & x j_\ell^2(mx) + x j_{\ell-1}^2(mx) \\ & - \frac{2\ell+1}{m} j_{\ell-1}(mx) j_\ell(mx) \Bigg\} \Bigg]_a^b \end{aligned} \tag{44}$$

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