Wavelets in Electronic Structure Calculations

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A three-dimensional wavelet analysis is employed to develop a new formalism for electronic structure calculations. The wavelet formalism provides a systematically improvable and tractable description of electronic wave functions and overcomes limitations of conventional basis expansions. The potential power of the wavelet formalism for *ab initio* electronic structure calculations is demonstrated by a calculation of 1*s* states for all the naturally occurring nuclei on the periodic table and the interaction energies of the hydrogen molecule ion.

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Spectral analysis using the Fourier transform (FT) is a powerful method for solving many problems in science and engineering. This method, however, is not appropriate for problems that require a localized description in real space *and* in Fourier space. Although several techniques, such as the windowed Fourier transform, have been invented to attempt to overcome this limitation, by far the most promising new technique is the wavelet transform (WT) [1]. Unlike the plane wave (PW) basis functions of the FT, the wavelet basis functions are localized both in real space *and* in Fourier space [1-4]. Furthermore, multiresolution analysis (MRA) of the WT provides a systematic successive approximation scheme for practical applications [1,2]. Applications of the WT have focused primarily on digital signal processing (1D), compact image coding (2D), and related fast mathematical algorithms [3]. Most recently the WT has been applied to the analysis of chaotic behavior and turbulence in 2D, the coherent states of quantum optics and quantum field theory, and to real space renormalization group theory [4].

In this Letter, we introduce a new method for the application of WT, in 3D, to electronic structure investigations of material properties. The traditional *ab initio* total energy density functional pseudopotential methods for electronic structure calculations use either LCAO-type (linear combination of atomic orbitals) (e.g., atomic, Gaussian, or Slater) basis sets or PW basis sets [5]. LCAO-type basis sets typically are capable of describing the electronic structure with a small number of basis functions, but lack an explicit and well-defined procedure for systematic improvement [6], and generally complicate the calculation of forces because of the presence of large Pulay terms [7] which must be compensated through explicit calculation. On the other hand, PW basis sets provide a systematic expansion of electronic wave functions, introduce no Pulay terms for supercells of fixed size (thus considerably simplifying the calculation of forces), but suffer from the same limitations as the FT method. Specifically, the description of the rapid variations of the electronic wave function close to the atomic nuclei (atomic core) requires a large number of PW functions even though the volume of the atomic core is only a small part of the total volume of the system. In addition PW basis sets are, in principle, not well suited for the description of isolated molecules and surfaces. This is because the periodic nature of the basis introduces unnecessary periodic images and a redundant high resolution description of the vacuum regions.

The "best of all worlds" then would be to have a basis set that, unlike a PW basis, can zoom into the atomic core regions and does not introduce unnecessary periodic images, *and*, unlike an LCAO-type basis, does not introduce Pulay terms which must be calculated explicitly, and provides an explicit prescription for complete expansion of the electronic wave functions. The wavelet basis has all these desired properties: multiscale decomposition of the wave function, the localized description of the rapid variations, and systematically complete expansion similar to the PW expansion. Therefore, as we demonstrate in this Letter, the wavelet basis overcomes the limitations of both conventional basis sets and retains only their advantages.

The wavelet transform and multiresolution analysis.—Given a square integrable function space $L^2(R^3)$, wavelets impose a hierarchical structure of subspaces with different resolutions, which forms a multiresolution analysis. The space of functions at resolution 2^{-j} (or more simply at resolution j) is represented by $V_j(R^3)$, and spanned by the basis set of *scaling functions* at resolution j, $\{\phi_{j,\mathbf{n}}(\mathbf{r})\}$, where $\mathbf{n}$ specifies the center of the basis function. The hierarchical structure is then

$$\cdots V_{-2} \subset V_{-1} \subset V_0 \subset V_1 \subset V_2 \cdots . \tag{1}$$

The *approximation* space V_j is decomposed into a sum of the coarser approximation space V_{j-1} and the *wavelet* space W_{j-1} which describes the detail at resolution j ($V_j = V_{j-1} \oplus W_{j-1}$) and is spanned by the basis set of the *wavelet functions* at resolution j, $\{\psi_{j,\mathbf{n}}(\mathbf{r})\}$. With a repetition of this decomposition, the $L^2(R^3)$ space can be

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expressed as either the sum of the wavelet spaces of all resolutions or the sum of one approximation space and the wavelet spaces of higher resolutions:

$$\bigoplus_{j} W_j = V_{j_0} \oplus \bigoplus_{j \geq j_0} W_j = L^2(R^3) . \tag{2}$$

Therefore, any square integrable function $f(\mathbf{r})$ can be expanded either as a sum of the wavelet functions of all resolutions or as a sum of the scaling functions at resolution $j = j_0$ and the wavelet functions of all finer resolutions $j \geq j_0$. In this work, we will use the latter expansion because it introduces approximations only at the high resolution cutoff in practical applications.

With the introduction of two projection operators, $\hat{A}_j$ (approximation operator) and $\hat{D}_j$ (detail operator), which project a function into V_j and W_j, respectively, one may express $f(\mathbf{r})$ as

$$f(\mathbf{r}) = \hat{A}_{j_0} f(\mathbf{r}) + \sum_{j \geq j_0} \hat{D}_j f(\mathbf{r}) . \tag{3}$$

The approximation and the detail of a function $f(\mathbf{r})$ at resolution j are expanded in terms of the basis functions,

$$\hat{A}_j f(\mathbf{r}) = \sum_{\mathbf{n}} a_{j,\mathbf{n}} \phi_{j,\mathbf{n}}(\mathbf{r}) , \tag{4}$$

$$\hat{D}_j f(\mathbf{r}) = \sum_{\mathbf{n}} d_{j,\mathbf{n}} \psi_{j,\mathbf{n}}(\mathbf{r}) . \tag{5}$$

Combination of Eqs. (3)-(5) and truncation at the finest resolution $j_{\max}$ leads to the wavelet expansion of $f(\mathbf{r})$ as

$$f(\mathbf{r}) = \sum_{\mathbf{n}} a_{j_0,\mathbf{n}} \phi_{j_0,\mathbf{n}}(\mathbf{r}) + \sum_{j=j_0}^{j_{\max}} \sum_{\mathbf{n}} d_{j,\mathbf{n}} \psi_{j,\mathbf{n}}(\mathbf{r}) . \tag{6}$$

This expansion still contains an infinite number of basis functions associated with the lattice $\{\mathbf{n}\}$. Since the scaling functions and the wavelet functions are spatially localized, one may retain only the basis functions that have significantly large coefficients in Eq. (6) for the problem at hand. This leads to an expansion with a finite number of basis functions and allows one to use different resolutions for different spatially localized regions. In particular, for the description of the rapid oscillations of the electronic wave function in an atomic core region, one need add higher resolution scales *only* to the core region and thereby systematically improve the calculation.

Construction of the wavelet basis set.— Although the wavelet and scaling functions are far from unique, we found that the following forms are particularly convenient in practical applications. The wavelet functions $\psi_{j,\mathbf{n}}(\mathbf{r})$ are chosen to be the Mexican-hat functions (the Laplacians of Gaussians) which form a fairly tight frame [1]. The scaling function $\phi_{0,\mathbf{n}}(\mathbf{r})$ corresponding to the Mexican-hat function is chosen to be a Gaussian function. Both the Mexican-hat functions and the Gaussian functions are spherically symmetric. The relationship between the Gaussian scaling function and the Mexican-hat wavelet function is not exact, but is quite a good approximation as discussed in Ref. [1]. These localized basis functions are spatially arranged so that their centers form a simple cubic lattice [8]. This is shown schematically in the top panel of Fig. 1. The lattice spacing d_0 at resolution $j = 0$ is chosen small enough to give a fairly tight frame [1,9]. The basis functions with resolution j are arranged correspondingly on the lattice sites with lattice spacing $d_0/2^j$. The centers of basis functions for different resolutions are selected so as not to overlap, and the centers of *all* the basis functions form a simple cubic lattice with spacing $d_0/2^{j_{\max}}$. In order to construct a *finite* basis set we collect the most important basis functions by introducing spheres of finite support radii at each nuclear center. This is illustrated schematically at the bottom panel of Fig. 1. Correspondingly smaller support radii are chosen for correspondingly higher resolutions so that deep core regions have more resolution scales. We designate this finite basis set as $\{\phi_{0,\mathbf{n}}(\mathbf{r}), \psi_{j,\mathbf{n}}(\mathbf{r}); j_{\max} \geq j \geq 0\}$.

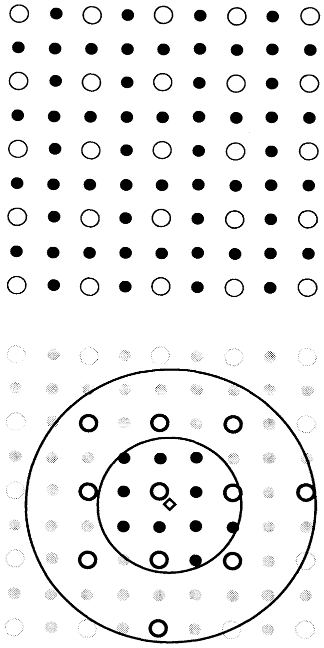

FIG. 1. Top panel shows a two-dimensional arrangement of the centers of basis functions on a simple square lattice. Open circles are the centers of the basis functions at resolution $j = 0$, and filled circles are the centers of the basis functions at resolution $j = 1$. Bottom panel shows the basis functions that lie within each support radius that is centered on an atomic position (diamond symbol). The larger (smaller) radius corresponds to $j = 0$ ($j = 1$) resolution.

The hydrogen atom.— In order to gain a sense of the optimal values of the various parameters of the formalism, we chose to study the hydrogen atom as a simple test case. After performing calculations using many different resolution scales and different support radii, we find that a satisfactory minimal basis set for the hydrogen atom contains 25 basis functions with four resolution scales (7 scaling functions for $j = 0$, plus 6 wavelets for $j = 0$, plus

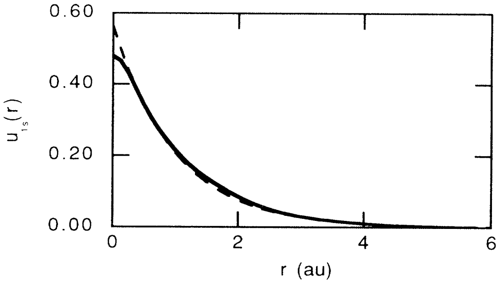

FIG. 2. The 1*s* radial wave function of a hydrogen atom calculated with 25 basis functions (7+ three 6's). The continuous line is from the wavelet calculation, and the broken line is the exact wave function.

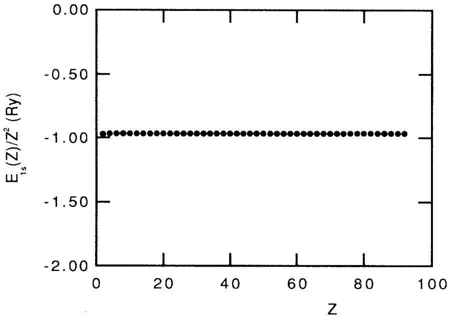

FIG. 3. The filled circles are the 1*s* eigenenergies of all the nuclei with even atomic numbers on the periodic table ($Z = 2,4,\ldots,92$) calculated with the fixed 67 basis function set.

6 wavelets for $j=1$, plus 6 wavelets for $j=2$) which we designate simply as (7+three 6's). These correspond respectively to support radii of 1, 0.5, 0.25, and 0.125 a.u. The calculated 1*s* eigenenergy is within 2% of the exact value, and the calculated 1*s* radial wave function is shown in Fig. 2. The calculated wave function differs from the exact one primarily near the origin (within the resolution limit $j_{\max}$). The small difference at $r=2$ a.u. is due to the finite support radii used for the basis set. By changing the basis set to 85 functions with three resolution scales (33+two 26's, with corresponding support radii of 2, 1, and 0.5 a.u.), this difference reduces to 0.3%, and we can obtain the 1*s* eigenenergy to within 0.5% of the exact value.

Hydrogen to uranium.— By adding more resolution scales, one can calculate the wave functions of heavier nuclei *within the same accuracy* as follows. As the atomic number increases, the Coulomb potential becomes stronger, and consequently higher resolution scales are needed in the core region. However, only *one* additional resolution scale needs to be added each time the atomic number doubles. Therefore, for the description of 1*s* wave functions from hydrogen to uranium, one needs to use a basis set with eleven resolution scales (7+ten 6's). Using this fixed basis set consisting of *only* 67 basis functions, one can calculate (to within 3%) the 1*s* eigenvalues of all the naturally occurring nuclei on the periodic table. The results are shown in Fig. 3 and include, for simplicity, only the even nuclei. Note that the eigenvalue for each nucleus is larger than the exact value by very nearly a constant percentage so that the results appear to lie on a straight line as expected.

The hydrogen molecule ion.— We now investigate the efficiency of the wavelet basis for the description of chemical bonds. As a simple example, we consider the energy of an $H_2{}^+$ molecule as a function of the separation R between the two protons. The total energy (electronic eigenenergy plus the Coulomb potential energy) is plotted as a function of R in Fig. 4. The basis set for the calculation is selected using the same support radii as for the hydrogen atom calculation with the larger basis set (33+two 26's), and the total number of basis functions varies between 141 and 167 [10] depending on R. We note that the calculated values in Fig. 4 are very close to the exact values [11] and are larger than them by a nearly constant amount of 1%. This implies that the wavelet basis gives an efficient representation of the chemical bond and also gives an excellent representation of interionic forces.

Comment on Pulay forces.— It is important to note that the centers of the basis functions do not follow the nuclei as they move; the *underlying* basis set is not correlated to the ionic positions. Just as in the plane wave case, this ensures that the finite underlying wavelet basis

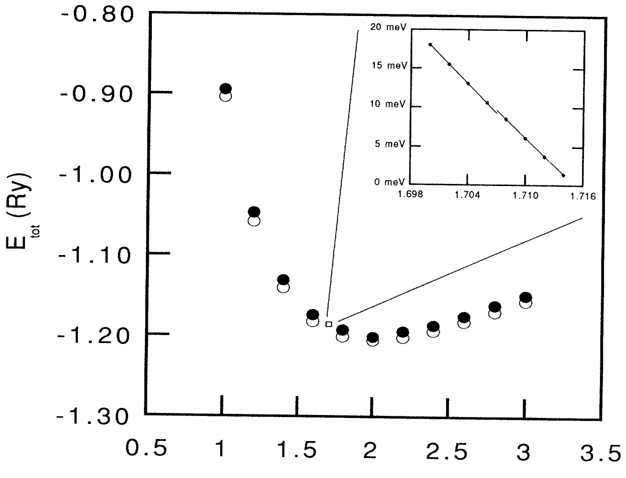

FIG. 4. The total energy of a molecular hydrogen ion is shown as a function of the separation between the nuclei. The filled circles are the calculations with 141 to 167 basis functions depending on the separation R while the open circles are the exact values. The inset shows fine detail of the calculation in the vicinity of a change in basis, illustrating that basis-change effects are at less than the meV level.

introduces no Pulay terms for a fixed calculational cell. Although, in practice, it *is* possible to use the full underlying basis, it is much more convenient to introduce the support spheres as we have done above. This does introduce a position dependence into the basis by selecting the basis set as illustrated in the bottom panel of Fig. 1. However, simply increasing the size of the support radii to where the wave function coefficients for the wavelets near the edges of their respective spheres are near zero controls the magnitude of resulting Pulay corrections and eliminates the need for their explicit calculation. Designing the basis to give a good representation of the wave functions and their eigenenergies imposes this condition on the coefficients automatically, making the treatment of Pulay forces very simple in the wavelet formalism, as our molecular ion calculation illustrates. Although the cutoff radii for this calculation were chosen only with the representation of the atomic wave functions in mind, the effect on the calculation from sudden changes in the basis set is extremely small, as the inset in Fig. 4 shows. The inset displays a representative example of the detailed behavior of the wavelet calculation on either side of a change in basis set. The discontinuity in the energy is extremely small (0.3 meV) as is the jump in force/slope (≈ 1 meV/Å).

Conclusions.—To extend this approach to many-electron systems within the local density approximation, one can simply use traditional techniques for the inclusion of Hartree and exchange-correlation interactions, expanding the charge density and other relevant fields in the wavelet basis as well. In particular, schemes developed for localized basis sets [12] provide one possible framework for this extension. It is not clear at the moment that the inherent advantages of the wavelet basis will make it more attractive for practical calculations *strictly* within LCAO-type computational frameworks because, at present, the wavelet expansion of atomic states still requires more functions per atom than do corresponding LCAO-type representations. The same is true of plane wave expansions, which nonetheless are competitive with traditional local basis schemes because of the efficiency of the fast Fourier transform. There exists an analogous fast wavelet transform, and work currently is underway to investigate its exploitation and the competitiveness of the resulting computational framework with both LCAO-type basis and plane wave approaches.

In comparison to the plane wave approach, we expect wavelets to prove most advantageous in situations which require a spatial resolution which varies significantly throughout space, including systems involving first row elements or transition metals. Also, the local nature of the wavelet basis ensures that the wavelet transform maps far more naturally than does the fast Fourier transform onto the latest generation of massively parallel computer architectures. On the other hand, it is unlikely that multiple resolutions will benefit systems such as pseudopotential silicon *directly* in terms of numbers of basis functions.

Finally, multigrid approaches provide another possible avenue toward spatially variable resolution. We have not explored this direction in depth, and we do not know what will be the advantages and disadvantages of this approach over the wavelets. It is noteworthy, however, that the basic difference between the two is that wavelets are a set of basis functions whereas multigrid is a method for solving a discretized set of equations.

In conclusion, the trivial process of introducing a Bloch transformation of the wavelet functions extends straightforwardly the current analysis to periodic systems [13]. With the extensions to many-electron systems and periodic systems, the wavelet formalism way open a completely new direction of development for *ab initio* total energy calculations.

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