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Mixed-space formalism for the dielectric response in periodic systems

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We present a useful formalism for the calculation of the polarizability and dielectric response of periodic systems. Our approach is to introduce intermediate "mixed-space" functions with the full translational periodicity of the lattice. This is a considerable advantage over existing real-space methods since the decay length of a response function [such as $\epsilon(\mathbf{r},\mathbf{r}'|\omega)$] can be significantly larger than the Wigner-Seitz cell radius. Further, we show that, in supercell calculations, these mixed-space functions decay as fast as the corresponding real-space quantities within one supercell, so that the present scheme can be combined with usual real-space cutoff techniques. The advantage of the present method compared to a standard reciprocal space approach is exemplified for the case of bulk silicon and for the case of a Si surface in a slab geometry.

We present in this paper a useful formalism for the calculation of the dielectric response of periodic systems. The present scheme is well suited for large unit cell systems, systems exhibiting large gradients of electronic density, or systems with a significant amount of vacuum in the unit cell (e.g., molecules, clusters, nanotubes, or surfaces in a supercell geometry). In these situations of growing importance in modern calculations, the standard reciprocal-space approaches[1,2] present many drawbacks related to using a plane-wave basis to describe large gradients of charge and to the fact that each region of real space is necessarily described by the same number of plane waves. On the contrary, in a real-space approach, localized objects are easily described and different basis functions can be used to describe different regions of space. Another advantage of a real-space approach is related to the decay at "large" distances of the response functions of interest [e.g., the independent-particle polarizability $\chi^0(\mathbf{r},\mathbf{r}')$ or the dielectric response $\epsilon(\mathbf{r},\mathbf{r}')$ that we study in this work]. If R is the decay length of $\chi^0(\mathbf{r},\mathbf{r}')$, then for a given $\mathbf{r}$, $\chi^0(\mathbf{r},\mathbf{r}')$ needs to be computed only for $\mathbf{r}'$ spanning a sphere of constant radius R around $\mathbf{r}$, *independent* of the size of the unit cell. Therefore, the number of $\chi^0(\mathbf{r},\mathbf{r}')$ to be calculated scales linearly with the number of atoms N_{at} in the unit cell in the large N_{at} limit. This is a considerable advantage over a reciprocal-space approach where the number of $\chi^0_{\mathbf{G},\mathbf{G}'}$ needed scales as N_{at}^2. A real-space approach of this kind has been recently investigated[3] for bulk silicon and will be referred to as the "direct" real-space method. We note, however, that if R is larger than the "average radius" R_{WS} of the Wigner-Seitz (WS) cell, then the sphere of radius R may extend over a large number of unit cells, and the direct real-space approach becomes significantly more costly than a reciprocal-space scheme. This will be exemplified in the simple case of bulk silicon.

In this work, a "mixed-space" (MS) formalism for the calculation of the dielectric response of periodic systems is developed. We show that $\chi^0(\mathbf{r},\mathbf{r}'|\omega)$ and related response functions can be written in terms of MS response functions $\chi^0_{\mathbf{q}}(\mathbf{r},\mathbf{r}'|\omega)$, where $\mathbf{q}$ is a wave vector in the first Brillouin zone (BZ). The MS response functions have the essential quality that they are fully periodic in real space. The advantage of the present method over the direct real-space approach is that we can rigorously fold the entire space into a single unit cell. In addition, we show that the decay length of the MS response functions is, within one unit cell, comparable to its real-space counterpart. Therefore, the present scheme can be combined with usual real-space cutoff techniques when it is appropriate.

In the MS formalism, we start from the expression for the independent-particle polarizability $\chi^0(\mathbf{r},\mathbf{r}'|\omega)$ in terms of the eigensolutions (ε_i,ψ_i) of a one-electron Hamiltonian [e.g., the Kohn-Sham Hamiltonian[4] in the local density approximation (LDA)],

$$\chi^0(\mathbf{r},\mathbf{r}'|\omega)=\sum_{i,j}(f_i-f_j)\,\frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i-\varepsilon_j+\omega+i\eta}, \tag{1}$$

where η is a positive infinitesimal number. Taking the (i,j) pairs of states to be the usual $(n\mathbf{k},n'\mathbf{k}')$ Bloch states, it is straightforward to show that

$$\chi^0(\mathbf{r},\mathbf{r}'|\omega)=\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}\chi^0_{\mathbf{q}}(\mathbf{r},\mathbf{r}'|\omega), \tag{2}$$

with

$$\chi^0_{\mathbf{q}}(\mathbf{r},\mathbf{r}'|\omega)=\sum_{n,n',\mathbf{k}}(f_{n,\mathbf{k}+\mathbf{q}}-f_{n',\mathbf{k}})\times\frac{u^*_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r})u_{n',\mathbf{k}}(\mathbf{r})u^*_{n',\mathbf{k}}(\mathbf{r}')u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}')}{\varepsilon_{n,\mathbf{k}+\mathbf{q}}-\varepsilon_{n',\mathbf{k}}+\omega+i\eta}, \tag{3}$$

where the u's are the periodic part of the Bloch states. Therefore, the $\chi^0_{\mathbf{q}}$'s are periodic in space with respect to both $\mathbf{r}$ and $\mathbf{r}'$ separately and need only be calculated within one unit cell. In the following, the variable ζ refers to a real-space coordinate restricted to a single unit cell. We emphasize that the combination of Eqs. (2) and (3) is just a partitioning of the double sum over states in Eq. (1) and does not introduce

any additional BZ summation. Similarly, we define a MS dielectric function $\epsilon_{\mathbf{q}}(\mathbf{r},\mathbf{r}')$ by the equation

$$\epsilon_{\mathbf{q}}(\zeta,\zeta')=\delta(\zeta-\zeta')-\int_{\Omega_{\mathrm{WS}}} d\zeta_1 \tilde{V}_{\mathbf{q}}(\zeta,\zeta_1)\chi^0_{\mathbf{q}}(\zeta_1,\zeta'), \quad (4)$$

where $\tilde{V}$ is related to the original potential[5] V through an Ewald summation,

$$\tilde{V}_{\mathbf{q}}(\zeta,\zeta_1)=\sum_{\mathbf{R}} V(\zeta+\mathbf{R},\zeta_1)e^{-i\mathbf{q}\cdot(\zeta+\mathbf{R}-\zeta_1)}, \quad (5)$$

over the lattice vectors $\mathbf{R}$. In particular, the integral in Eq. (4) is restricted to a single unit cell. Special care must be taken when using Eq. (5) in the long-wavelength limit[6] and for $|\zeta-\zeta_1|$ going to zero. The inversion of $\epsilon_{\mathbf{q}}(\zeta,\zeta')$, which may be performed entirely in real space, yields $\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')$. The MS inverse dielectric responses $\epsilon^{-1}_{\mathbf{q}}$'s are simply related to their real-space and reciprocal-space analogs via an Ewald summation or Fourier transform (FT).

The approach is first applied to bulk silicon. The electron wave functions are generated in a plane-wave basis with kinetic energy up to 14 Ry using a standard pseudopotential LDA calculation. The wave functions are then Fourier transformed into real space onto a $18\times18\times18$ grid in the unit cell. To test convergence, one grid point out of n is kept in each direction to build the real-space grid on which $\chi^0_{\mathbf{q}}(\zeta,\zeta')$, $\epsilon_{\mathbf{q}}(\zeta,\zeta')$, and $\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')$ are calculated. With $n=3$ (e.g., a $6\times6\times6$ grid in the unit cell), the dielectric response, including local-field effects, is accurately described. To check this, we Fourier transform to reciprocal space the $\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')$'s as calculated in the MS formalism and compare the resulting matrix elements $\mathcal{F}[\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}'}$ to the corresponding $\epsilon^{-1}_{\mathbf{q}}(G,G')$'s as calculated within a reciprocal-space approach.[2] In Fig. 1(a), the diagonal elements are compared for $\mathbf{q}=\mathbf{X}$. The agreement is excellent up to $|\mathbf{q}+\mathbf{G}|\leq 3$ a.u., which is the usual cutoff used to terminate the dielectric matrix in reciprocal space for bulk silicon. In Fig. 1(b), the nondiagonal elements $\mathcal{F}[\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}'}$ are plotted against the corresponding $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$'s. The resulting points land nicely on the first diagonal, indicating how accurately the MS scheme describes (with a $6\times6\times6$ grid in real space) the local-fields contribution to the screening properties.

We compare now, in the case of bulk silicon, the performances of the MS approach with respect to the reciprocal-space approach of Ref. 2. We note that the size of a $\chi^0_{\mathbf{q}}(\mathbf{G},\mathbf{G}'|\omega)$ matrix, with a $|\mathbf{q}+\mathbf{G}|\leq 3$ a.u. cutoff, is $\sim120\times120$, that is, significantly smaller than the 216×216 $\chi^0_{\mathbf{q}}(\zeta,\zeta'|\omega)$ matrix we calculate in the mixed-space approach. However, while a small cutoff ($G_{\max}=3$ a.u.) is used to truncate the dielectric matrix, in the reciprocal-space approach a larger cutoff (typically $E_{\mathrm{cut}}=10$ Ry) is needed to expand the LDA wave functions involved in the matrix elements $\langle v,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\rangle$ which couple valence bands to conduction bands.[2] In addition, such matrix elements are convolution products in reciprocal space. In contrast, as seen in Eq. (3), in the MS approach, the numerator of each $\chi^0_{\mathbf{q}}(\zeta,\zeta')$ is a direct product of wave functions and the same grid (that is, the same "cutoff") is used for the dielectric

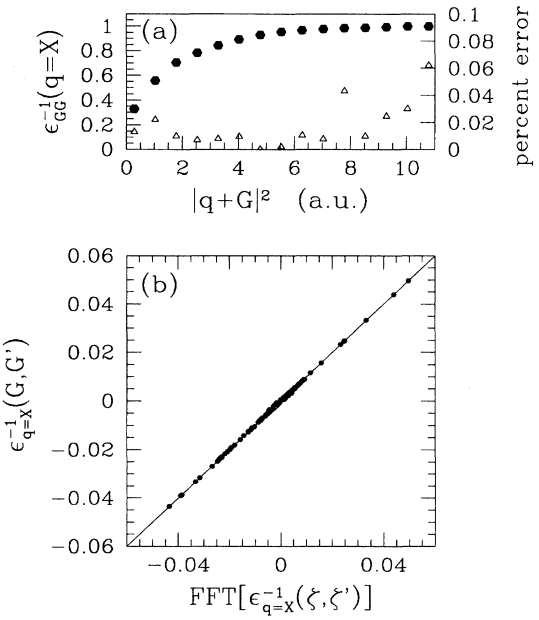

FIG. 1. (a) The diagonal elements of $\epsilon^{-1}_{q=X}$ for bulk silicon are plotted as a function of $|q+G|^2$ in a.u. (left vertical axis and filled hexagons). The corresponding error in % between $\epsilon^{-1}_{\mathbf{G},\mathbf{G}}(q=X)$ and $\mathcal{F}[\epsilon^{-1}_{q=X}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}}$ is also given (right vertical axis and empty triangles). (b) The nondiagonal elements of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(q=X)$ are plotted as a function of the corresponding $\mathcal{F}[\epsilon^{-1}_{q=X}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}'}$ nondiagonal elements. The solid line is a guide to the eye for the first diagonal.

matrix and the LDA eigenstates. We find that the calculation of an entire $\chi^0_{\mathbf{q}}(\zeta,\zeta'|\omega)$ matrix takes an average of 16 s on a Cray C-90 computer. This is comparable to the performance of our reciprocal-space code (~15 s) for the calculation of $\chi^0_{\mathbf{q}}(\mathbf{G},\mathbf{G}'|\omega)$.

To compare the present MS approach to the direct real-space approach,[3] we plot in Fig. 2 the number of $(\mathbf{r},\mathbf{r}')$ pairs needed in each approach as a function of the real-space cutoff radius selected. We use a $6\times6\times6$ grid in the unit cell that is repeated over the entire space. In the direct real-space approach, the variable $\mathbf{r}$ can be restricted to the irreducible wedge of the unit cell while $\mathbf{r}'$ spans a sphere of radius $R_{\max}$ around each $\mathbf{r}$. As a consequence, the number of $(\mathbf{r},\mathbf{r}')$ pairs needed scales as $R^3_{\max}$ in the direct real-space approach (dashed line). In the MS approach, for the calculation of $\chi^0_{\mathbf{q}}$, the variable $\mathbf{r}=\zeta$ can be restricted to the irreducible wedge of the BZ associated with the small group of $\mathbf{q}$. However, the number of $\mathbf{r}'=\zeta'$ needed saturates quickly to the maximum of grid points in the unit cell and does not increase with $R_{\max}$ as soon as $R_{\max}$ becomes larger than the average WS cell radius. This is illustrated in Fig. 2 in the three following cases: $\mathbf{q}$ is at the center of the zone Γ (lower dotted line), $\mathbf{q}$ has no symmetries (upper dotted line), and $\mathbf{q}$ samples a $4\times4\times4$ Monckhorst-Pack[7] grid (solid line). In this last case, the average number of pairs per $\mathbf{q}$ point is plotted. We note again that each $\chi^0_{\mathbf{q}}(\zeta,\zeta'|\omega)$ is associated with a single BZ summation while the calculation of $\chi^0(\mathbf{r},\mathbf{r}'|\omega)$ requires a double BZ summation. As a consequence, Fig. 2 really compares the actual computational ef-

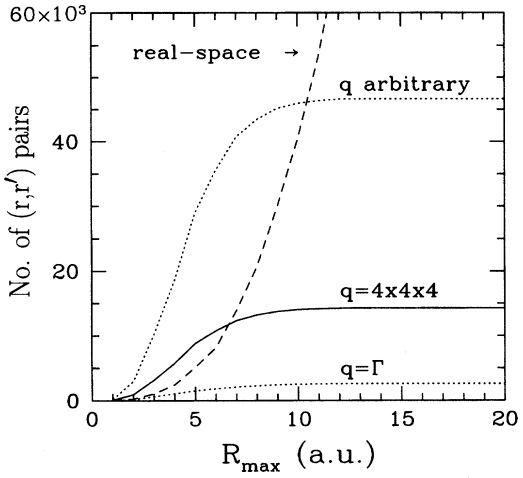

FIG. 2. Number of $(\mathbf{r},\mathbf{r}')$ needed in the case of a $6\times6\times6$ grid in the fcc Wigner Seitz (WS) cell. The long dashed line (with the label "real-space →") corresponds to the real-space approach. The solid line (labeled "$q=4\times4\times4$") corresponds, in the present MS approach, to the average number of pairs sampled for $\mathbf{q}$'s on a $4\times4\times4$ Monkhorst-Pack grid in the BZ; the upper dotted line (labeled "q arbitrary") corresponds to the case where $\mathbf{q}$ has no symmetries; and the lower dotted line (labeled "$q=\Gamma$") applies when $\mathbf{q}$ is at the center of the zone.

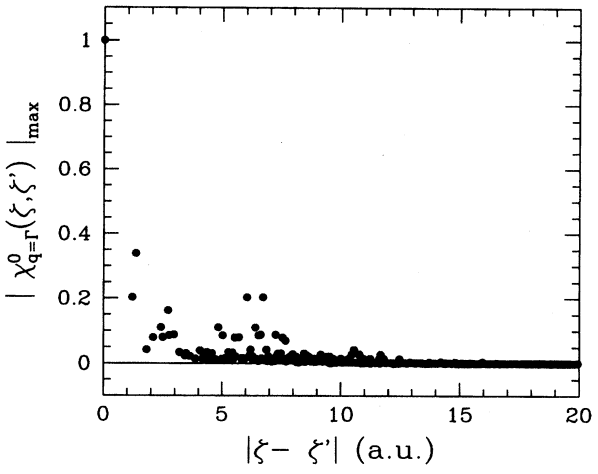

FIG. 3. Value of $|\chi^0_{q=\Gamma}(\zeta,\zeta')|_{\max}$ as a function of $|\zeta-\zeta'|$ for a H/Si(111)-(1×1) 14-layer slab. $|\chi^0_{q=\Gamma}(\zeta,\zeta')|_{\max}$ is normalized by its value at $|\zeta-\zeta'|=0$.

fort of the two methods. In the case of bulk silicon, a real-space cutoff of 18 a.u. is used (see Ref. 3 and below). For this value of $R_{\max}$, it is clear that the MS approach, in all cases of BZ summations, yields a significant saving on the number of $(\mathbf{r},\mathbf{r}')$ pairs for which the summations over valence and conduction bands must actually be performed.[8]

An important issue associated with the MS approach is the decay of the MS response functions in real space in the limit of large supercells. To address this question, we study a H/Si(111)-(1×1) surface in a 14-layer slab geometry. As in the case of bulk silicon, we obtain the LDA wave functions using a standard pseudopotential plane-wave approach and then Fourier transform these wave functions onto a grid in real space. Details for the slab geometry, energy cutoff, and pseudopotentials can be found in a previous report, where we calculated the dielectric response of the H/Si(111)-(1×1) surface using a reciprocal-space approach.[9] We find that a $6\times6\times36$ real-space grid in the unit cell is sufficient to describe the dielectric properties of this system. Further, we find that basically all of the grid points located in the vacuum between neighboring slabs can be removed from the grid. Indeed, we verify that the resulting grid yields $\mathcal{F}[\chi^0_{\mathbf{q}}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}'}$'s that are in excellent agreement with the $\chi^0_{\mathbf{q}}(\mathbf{G},\mathbf{G}')$ calculated in reciprocal space.

The absolute value of $\chi^0_{q=\Gamma}(\zeta,\zeta')$ as a function of $|\zeta-\zeta'|$ for the H/Si(111)-(1×1) surface is presented in Fig. 3. The real-space range of the MS $\chi^0_{q=\Gamma}$ is significantly smaller than the maximum distance $|\zeta-\zeta'|$ allowed by the unit cell size (~44 a.u. in the present case) and a real-space cutoff $R=18$ a.u. can be used which keeps the calculated $\mathcal{F}[\chi^0_{\mathbf{q}}(\zeta,\zeta')]_{\mathbf{G},\mathbf{G}'}$'s in excellent agreement with their original value. This cutoff is the same as the one used in Ref. 3 for bulk silicon in a direct real-space method. Thus, the decay length of the $\chi^0_{\mathbf{q}}(\zeta,\zeta')$'s is comparable to the one of $\chi^0(\mathbf{r},\mathbf{r}')$. For $\mathbf{q}=\mathbf{X}$ in the two-dimensional surface BZ, we find that it takes ~18 min on a Cray C-90 computer to obtain the entire $\chi^0_{\mathbf{q}}(\zeta,\zeta')$ matrix. In reciprocal space, the calculation of the entire $\chi^0_{\mathbf{q}}(\mathbf{G},\mathbf{G}')$ (which is a 998×998 matrix for the selected cutoff $G_{\max}=3$ a.u.) takes ~43 min. We find therefore a 2.4 ratio in favor of the present MS approach. Greater gains in efficiency are expected in the limit of larger systems.

Since in the limit of large systems the number of (ζ,ζ') pairs to be considered scales linearly with the number of atoms N_{at} in the unit cell, the summation over valence and conduction bands for all (ζ,ζ') pairs requires an overall scaling of N^3_{at} for the MS approach. This can be compared to the N^4_{at} scaling of a reciprocal-space approach. Therefore the present method has significantly better scaling properties than the reciprocal-space approach, with a crossover between the two methods which occurs for systems as small as bulk silicon. We note that a direct real-space method offers also a N^3_{at} scaling. However, as exemplified in the case of bulk silicon, the "prefactor" associated with the direct real-space method is much larger and it is not clear in practice at which system size the direct real-space approach will become preferable over a standard reciprocal-space method.

Finally, for the systems studied above, we find that the calculation of $\epsilon_{\mathbf{q}}(\zeta,\zeta')$ using Eq. (4) and the inversion needed to calculate $\epsilon^{-1}_{\mathbf{q}}(\zeta,\zeta')$ are fast as compared to the time spent to build $\chi^0_{\mathbf{q}}$. We note, however, that a standard matrix inversion yields an N^3_{at} scaling. Therefore, as noted in Ref. 3, even if an imaginary-time technique is used to decouple the summations over valence and conduction states when calculating $\chi^0_{\mathbf{q}}$, the necessity of accounting for the local-field effects in calculating $\epsilon^{-1}_{\mathbf{q}}$ would still keep the overall scaling of the method to a N^3_{at} scaling.

In conclusion, we have presented a useful approach to calculate the dielectric response in periodic systems. In the limit of large systems, the present method scales as N^3_{at}

(where N_{at} is the number of atoms in the unit cell), as compared to the N_{at}^4 scaling of a standard reciprocal-space approach. In the case of silicon, we find that the crossover between the MS and reciprocal-space methods occurs for unit cells as small as that of bulk silicon. Further, we found that a significant saving can already be gained in the case of a moderately large H/Si(111) slab system. In addition, we have shown that the present method is preferable over a direct real-space method. This scheme should allow dielectric response calculations for large-scale systems. We note that the present formalism can be straightforwardly combined with an imaginary-time technique[3] and extended to quasiparticle energy calculations in the *GW* approximation.[3,10,11]

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