

Dielectric matrix scheme for fast convergence in self-consistent electronic-structure calculations

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A scheme is devised which drastically reduces the number of iterations required to reach self-consistency in electronic-structure calculations. This scheme is particularly helpful in calculations for systems with large unit cells.

In a self-consistent electronic-structure calculation, the one-electron wave functions are obtained from the Schrödinger equation

$$(-\nabla^2 + V)\psi_{n\vec{k}} = E_{n\vec{k}}\psi_{n\vec{k}}, \quad (1)$$

where the crystal potential V is constructed as the sum of three components V_{ion} , V_H , and V_{xc} . V_{ion} is the superposition of the potentials due to the bare ions on the various atomic sites. V_{ion} is screened by the Hartree potential V_H and a local exchange-correlation potential V_{xc} . They are obtained from the electronic density ρ by

$$\nabla^2 V_H(\vec{r}) = -4\pi e^2 \rho(\vec{r}), \quad (2)$$

$$V_{\text{xc}}(\vec{r}) = -\beta e^2 (3/\pi)^{1/3} \rho(\vec{r})^{1/3}, \quad (3)$$

where β can be constant or a function of $\rho(\vec{r})$.¹

Starting with an initial guess V_{in} for $V_H + V_{\text{xc}}$ (V_{ion} is given), the electronic wave functions are obtained from (1) and hence the electron density,

$$\rho(\vec{r}) = 2 \sum_{n\vec{k}} f_{n\vec{k}} |\psi_{n\vec{k}}(\vec{r})|^2, \quad (4)$$

where $f_{n\vec{k}}$ is the occupation factor and 2 is the spin factor.

An output potential V_{out} is then constructed using (2) and (3). Self-consistency requires that this procedure be repeated until V_{in} is equal to V_{out} . Usually this is achieved by putting in a new V_{in} constructed by mixing the old V_{in} and V_{out} . In the following let us concentrate on cases where the po-

tentials are represented in reciprocal space. Thus,

$$V_{\text{in}}^{\text{new}}(\vec{G}) = c V_{\text{in}}^{\text{old}}(\vec{G}) + (1-c) V_{\text{out}}^{\text{old}}(\vec{G}). \quad (5)$$

Improved convergence is obtained if the mixing coefficient c is allowed to be a function of \vec{G} . This actually corresponds to screening the charge-density oscillations by a Fermi-Thomas-type dielectric function.² However, for calculations with large unit cells (e.g., surfaces, interfaces, defects, frozen phonons) the low \vec{G} components of the potential converge very slowly and, furthermore, the various Fourier components are found to be strongly coupled so that the simple mixing scheme above is no longer adequate. In the following we will outline an alternate approach that proved to be much more efficient. Self-consistency within 10^{-3} Ry is achieved in three to four iterations whereas about ten iterations are required with Eq. (5) even with very judicious choices for the mixing coefficients.

Suppose the input and output potentials for the n th iteration are V_{in} and V_{out} , respectively. We want δV_{in} such that

$$V_{\text{in}} + \delta V_{\text{in}} = V_{\text{out}} + \delta V_{\text{out}}. \quad (6)$$

δV_{out} can be expressed in terms of δV_{in} using perturbation theory,

$$\delta \rho(\vec{G}) = \frac{1}{\Omega_c} \sum_{\vec{G}'} \chi(\vec{G}, \vec{G}') \delta V_{\text{in}}(\vec{G}'), \quad (7)$$

where Ω_c is the cell volume and

$$\chi(\vec{G}, \vec{G}') = -2 \sum_{n, n', \vec{k}} (f_{n\vec{k}} - f_{n'\vec{k}}) \frac{\langle n\vec{k} | e^{-i\vec{G}\cdot\vec{r}} | n'\vec{k} \rangle \langle n'\vec{k} | e^{i\vec{G}'\cdot\vec{r}} | n\vec{k} \rangle}{E_{n'\vec{k}} - E_{n\vec{k}}}. \quad (8)$$

This is a matrix version (i.e., local-field effects included) of the self-consistent-field dielectric function.³ Transforming Eq. (2) to reciprocal space, we get

$$\delta V_H(\vec{G}) = \frac{4\pi e^2}{G^2} \delta \rho(\vec{G}). \quad (9)$$

Likewise, $\delta V_{xc}(\vec{G})$ is obtained, assuming a constant β ,

$$\delta V_{xc}(\vec{G}) = \frac{-\beta e^2}{3} \left[\frac{3}{\pi} \right]^{1/3} \sum_{\vec{G}'} \rho^{-2/3}(\vec{G} - \vec{G}') \delta \rho(\vec{G}'). \quad (10)$$

Putting (7), (9), and (10) into (6), we get

$$\sum_{\vec{G}'} \epsilon(\vec{G}, \vec{G}') \delta V_{in}(\vec{G}') = V_{out}(\vec{G}) - V_{in}(\vec{G}), \quad (11)$$

$$\epsilon(\vec{G}, \vec{G}') = \delta_{\vec{G}, \vec{G}'} - \frac{4\pi e^2}{\Omega_c G^2} \chi(\vec{G}, \vec{G}') + \frac{\beta e^2}{3} \left[\frac{3}{\pi} \right]^{1/3} \sum_{\vec{G}''} \rho^{-2/3}(\vec{G} - \vec{G}'') \chi(\vec{G}'', \vec{G}'). \quad (12)$$

Thus, given V_{out} , and V_{in} in Eq. (11), we can obtain δV_{in} by a matrix inversion.

Since only the low Fourier components are strongly coupled, it is only necessary to compute $\epsilon(\vec{G}, \vec{G}')$ for the first 50 or so reciprocal-lattice vectors. The higher Fourier components can be dealt with effectively using Eq. (5). Frequently, it is enough to couple only those reciprocal-lattice vectors which are perpendicular to the surface or interface. Calculation of the $\epsilon(\vec{G}, \vec{G}')$ matrix is not time consuming. If the wave functions are represented as plane waves, for a typical surface calculation the computer time for calculating $\epsilon(\vec{G}, \vec{G}')$ is roughly one-tenth of the corresponding time for one iteration. For a mixed basis representation,⁴ this rises to one-third of one iteration. Moreover, since $\epsilon(\vec{G}, \vec{G}')$ changes by less than 10% upon iteration, after the first or second iteration, there is no need to recalculate $\epsilon(\vec{G}, \vec{G}')$.

In Table I we illustrate the above iteration

scheme with an example from a nine-layer silver-surface calculation. Note that the predicted values for several components of $V_{in}(n+1)$ do not lie between $V_{in}(n)$ and $V_{out}(n)$. This "overshooting" is caused by the strong coupling between the various long-wavelength Fourier components of the potential. The Fermi-Thomas dielectric function $\epsilon(\vec{G})$ which is always greater than one cannot "guess" this overshooting. Table II shows an application of the present scheme to a semiconductor surface, namely, the GaAs (110) surface. Six layers of GaAs and a vacuum region equivalent to five layers in thickness are assumed in the unit cell. It again indicates a very rapid achievement of self-consistency. In this case, $V(\vec{G})$ and $\epsilon(G, G')$ are complex because of the lack of inversion symmetry in the unit cell. The imaginary part of $\epsilon(\vec{G}, \vec{G}')$ here does *not* represent the absorption term. Instead it provides a coupling between the real and imaginary parts of the $V(\vec{G})$'s. It is again clear

TABLE I. Fourier components of $V_{in}^{(n)}$, $V_{out}^{(n)}$, and $V_{in}^{(n+1)}$ as predicted by the dielectric matrix scheme and the resulting $V_{out}^{(n+1)}$ examples from a nine-layer Ag surface calculation. \hat{z} is the surface normal and the potentials are in rydbergs. First five components are shown.

\vec{G}_{xyz}	$V_{in}^{(n)}$	$V_{out}^{(n)}$	$V_{in}^{(n+1)}$	$V_{out}^{(n+1)}$
001	2.6627	2.6177	2.6472	2.6346
002	-0.1600	-0.1544	-0.1504	-0.1509
003	-0.0608	-0.0640	-0.0653	-0.0643
004	0.0188	0.0189	0.0181	0.0194
005	0.0076	0.0077	0.0084	0.0085

TABLE II. Second example of fast achievement of self-consistency for the GaAs(110) surface (semiconductor). Notations and units are the same as in Table I. Relaxations for two surfaces in the unit cell are assumed different and $V(\vec{G})$'s are complex in general. For each potential the first and the second subcolumns are the real and the imaginary parts, respectively. Only five strongly coupled components are shown here.

\vec{G}	$V_{\text{in}}^{(n)}$		$V_{\text{out}}^{(n)}$		$V_{\text{in}}^{(n+1)}$		$V_{\text{out}}^{(n+1)}$		$V_{\text{in}}^{(n+2)}$		$V_{\text{out}}^{(n+2)}$	
001	-0.0161	7.0463	-0.0323	7.0599	-0.0183	7.0462	-0.0133	7.0464	-0.0171	7.0469	-0.0170	-7.0481
002	0.4528	0.0094	0.4507	0.0148	0.4514	0.0110	0.4511	0.0070	0.4521	0.0097	0.4515	0.0103
003	-0.0102	0.1408	-0.0115	0.1462	-0.0099	0.1430	-0.0095	0.1411	-0.0103	0.1419	-0.0100	0.1419
004	0.0596	-0.0016	0.0608	-0.0002	0.0609	-0.0012	0.0603	-0.0022	0.0602	-0.0015	0.0604	-0.0014
005	-0.0033	0.0071	-0.0035	0.0093	-0.0030	0.0073	-0.0029	0.0074	-0.0032	0.0074	-0.0030	0.0075

that the Fermi-Thomas $\epsilon(\vec{G})$, real by definition, cannot produce results as good as the dielectric matrix approach. These examples illustrate that the present scheme is valid for both metals and semiconductors. Applications to frozen phonon calculations for Nb and Mo, not presented here, have also been successful.

To summarize, the main advantages of the dielectric matrix screening method are as follows.

(1) Self-consistency for the electronic-structure calculation is achieved extremely fast and no efforts to "guess" the mixing coefficients are necessary.

(2) We obtain the dielectric matrix for sophisticated systems such as surfaces or interfaces, which is an important physical quantity by itself and useful for study of surface or interface responses (e.g.,

phonons, plasmons).

(3) The apparent instability in the self-consistent iteration for these systems disappears. There is no intrinsic instability for such systems; it is simply that the dielectric matrix for them is different from that of bulk materials.

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