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Comments

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Efficient iteration scheme for self-consistent pseudopotential calculations

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It is shown that an iteration technique introduced by Manninen *et al.* for self-consistent jellium-model calculations can be easily extended to provide a simple and very efficient iteration scheme for the self-consistent pseudopotential method.

Self-consistent electronic-structure calculations imply the solution of the field equations

$$[-\nabla^2 + V(\vec{r},\rho(\vec{r})) - E_i]\psi_i(\vec{r}) = 0\,, \tag{1}$$

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \Theta(E_F - E_i)\,, \tag{2}$$

where E_F is the Fermi level and V denotes an effective one-particle potential

$$V = V_{\rm ion} + V_{\rm Coul} + V_{\rm xc}\,. \tag{3}$$

$V_{\rm ion}$ is the potential generated by the positive ions. $V_{\rm Coul}$ is the repulsive Coulomb potential seen by an electron moving in the field of the other electrons. It depends on the electron density $\rho(\vec{r})$ through Poisson's equation

$$\nabla^2 V_{\rm Coul}(\vec{r}) = -4\pi e^2 \rho(\vec{r})\,. \tag{4}$$

$V_{\rm xc}$ is an exchange-correlation potential which is usually taken to be a local function of $\rho(\vec{r})$. As a consequence, finding the solution of Eqs. (1) and (2) requires the iteration of these equations until the electron density generated by the potential is identical to the one used to construct the potential.

It is well known that using the output potential of an iteration step as a new input for the subsequent iteration might lead to instabilities in the iteration process. An input potential which deviates from the truly self-consistent potential contains spurious Coulomb contributions which cause the electronic charge to overshoot from iteration to iteration. This effect is particularly large in systems where long-range density fluctuations exist, for example, at interfaces, surfaces, defects, impurities, and in thin films. The effect is also observed in periodic bulk systems having a large unit cell with many atoms. The conventional procedure to damp the charge-density oscillations and to enforce convergence is to use an "attenuated mixing" scheme for the potential or the charge density. At each iteration step n a new input potential $V_{\rm in}^{(n+1)}$ for the $(n+1)$th iteration is obtained by mixing the input potential $V_{\rm in}^{(n)}$ and the output potential $V_{\rm out}^{(n)}$ as follows:

$$V_{\rm in}^{(n+1)}(\vec{x}) = \alpha V_{\rm in}^{(n)}(\vec{x}) + (1-\alpha) V_{\rm out}^{(n)}(\vec{x})\,, \quad 0 \leq \alpha \leq 1\,. \tag{5}$$

The potential may be given in real space $\vec{x} = \vec{r}$ or in reciprocal space $\vec{x} = \vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector. Convergence can be considerably improved by making the mixing parameter α $\vec{x}$ dependent. For example, in periodic slab calculations[1] α has to be chosen close to 1.0 for the long-wavelength Fourier components of the potential to avoid large overshoots in $V_{(\rm out)}$. For the short-wavelength Fourier components α can be made smaller, because no instabilities occur.

The major drawback of this method is the lack of an easy and efficient algorithm to compute the mixing coefficients. Such an algorithm would have to take into account that in general the value of the potential at the point $\vec{x}$ is coupled nonlinearly to the value of the potential at a different point $\vec{x}'$. To select a mixing parameter by trial and error does not result in a convenient method to obtain rapid convergence.

Manninen *et al.*[2] have proposed an alternative iteration scheme which turned out to give rapid convergence in self-consistent jellium-model calculations. They start by rewriting Eq. (4) as follows:

$$(\nabla^2 - \lambda^2) V_{\rm Coul}(\vec{r}) = -4\pi e^2 \left(\rho(\vec{r}) + \frac{\lambda^2}{4\pi e^2} V_{\rm Coul}(\vec{r})\right), \tag{6}$$

where λ is an arbitrary constant greater than zero. Assuming that the right-hand side (rhs) is known, the solution is

$$V_{\text{Coul}}(\vec{r}) = \int \frac{\exp(-\lambda|\vec{r}-\vec{r}\,'|)}{|\vec{r}-\vec{r}\,'|} \times \left(\rho(\vec{r}) + \frac{\lambda^2}{4\pi e^2} V_{\text{Coul}}(\vec{r})\right) d^3r' . \tag{7}$$

Equation (7) can be used to obtain a new Coulomb potential from a guess of the charge density and the Coulomb potential. To exploit Eq. (7) in the iteration process we insert at a given iteration step the total electron density obtained from Eq. (2) and the Coulomb part of the effective one-particle potential used in Eq. (1) into the rhs of Eq. (7). The left-hand side (lhs) then represents the Coulomb part of the potential for the subsequent iteration step. We note that $V_{\text{Coul}}(\vec{r})$ is essentially determined by the values of $V_{\text{Coul}}(\vec{r}\,')$ and $\rho(\vec{r}\,')$ in a sphere around the space point $\vec{r}$ with a radius equal to $1/\lambda$. The exponential kernel in the integrand eliminates any distant contributions from $\rho(\vec{r}\,')$ and $V_H(\vec{r}\,')$. Manninen *et al.* chose a value of the constant λ around the Thomas-Fermi screening constant

$$\lambda \sim (4k_F/\pi)^{1/2} , \tag{8}$$

where k_F is the Fermi vector.

In the self-consistent pseudopotential method potentials and charge densities are usually given in reciprocal space. Equation (7), which is rather difficult to handle numerically for arbitrary charge densities, transforms into the much simpler equation

$$V_{\text{Coul}}^{(n+1)}(\vec{G}) = 4\pi e^2 \left(\rho^{(n)}(\vec{G}) + \frac{\lambda^2}{4\pi e^2} V_{\text{Coul}}^{(n)}(\vec{G})\right) (|\vec{G}|^2 + \lambda^2) , \tag{9}$$

where $\vec{G}$ denotes a vector in reciprocal space. It is easy to verify that at self-consistency the constant λ drops out. For vectors with $\lambda^2 \ll |\vec{G}|^2$ we obtain

$$V_{\text{Coul}}^{(n+1)}(\vec{G}) \simeq \frac{4\pi e^2}{|G|^2} \rho^{(n)}(\vec{G}) , \tag{10}$$

which means that for wavelengths shorter than the screening length $2\pi/\lambda$ the new Coulomb potential is essentially generated from the (output) charge density. Similarly, for vectors with $\lambda^2 \gg |G|^2$ we find

$$V_{\text{Coul}}^{(n+1)}(\vec{G}) \simeq V_{\text{Coul}}^{(n)}(\vec{G}) + \frac{4\pi e^2}{\lambda^2} \rho^{(n)}(\vec{G}) , \tag{11}$$

that is, for wavelengths larger than the screening length only a small amount of output information is mixed into the new Coulomb potential.

The scheme also provides a new treatment of the exchange-correlation potential. From the Coulomb potential $V_{\text{Coul}}^{(n+1)}$ one can formally define a charge density

$$n^{(n+1)}(\vec{G}) = \frac{V_{\text{Coul}}^{(n+1)}(\vec{G})}{4\pi e^2} |\vec{G}|^2 , \tag{12}$$

which can then be used to calculate a new exchange-correlation potential $V_{\text{xc}}^{(n+1)}(\vec{G})$. Finally, the new screening potential $V_{\text{scr}}^{(n+1)} = V_{\text{Coul}}^{(n+1)} + V_{\text{xc}}^{(n+1)}$ is added to the core pseudopotential to give an effective potential for the next iteration step. The parameter λ which is the only variable in this scheme is chosen such that large fluctuations in the long-wavelength components of V_{scr} are suppressed. Near self-consistency λ can be made smaller to speed up the convergence. This procedure keeps the electron-charge density from overshooting, and its long-range behavior is successively stabilized. The charge relaxes locally toward its self-consistent distribution.

To illustrate the efficiency of the scheme we have applied it to calculate the electronic structure of a seven-layer film of Ca(001) self-consistently within the pseudopotential method using the repeated-slab technique.[1] We omit the details of the calculation here which will be published elsewhere[3] and discuss the self-consistency cycle only. Calcium is a free-electron-like metal, its charge density is mostly *sp*-like, and the electrons react very sensitively to changes in the potential. If we start the iteration loop with V being a superposition of neutral atomic pseudopotentials, we need approximately 30 iterations within the mixing scheme to achieve

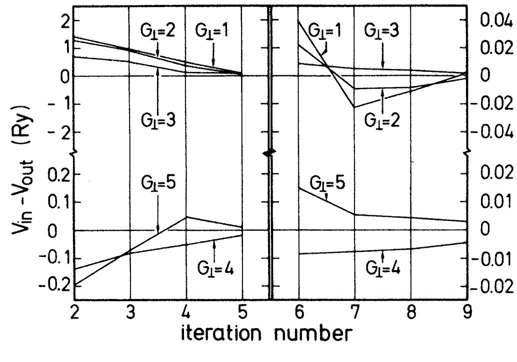

FIG. 1. Difference $V_{\text{in}} - V_{\text{out}}$ versus iteration number for a seven-layer Ca (001) film in reciprocal space. Only contributions to the most sensitive Fourier components are plotted. $G_\perp$ is a reciprocal-lattice vector component given in units of $2\pi/L$, where L is the spatial extent of the unit cell perpendicular to the slab. Note that for iteration numbers 2–5 the lh vertical scale applies whereas for iteration numbers 6–9, $V_{\text{in}} - V_{\text{out}}$ is quoted with respect to the rh vertical scale.

a satisfactory convergence. This is not too surprising because this choice for V represents a poor starting potential for a nearly-free-electron metal. However, using the above prescription self-consistency was reached after nine iteration steps. The "history" of the self-consistency cycle is plotted in Fig. 1 in terms of the difference between the total input and output potential as a function of the iteration number. By "output" potential we mean the effective one-electron potential generated from the charge density defined in Eq. (2). The potential differences are given in reciprocal space. Only contributions to the most sensitive Fourier components are plotted. A screening length of $2\pi/\lambda = 7.3$ a.u. is used, which is found from Eq. (8), assuming an average electron density equivalent to $r_s = 3.3$ a.u. At the last iteration λ is decreased by one-fourth of its value. The spatial extent of the slab unit cell perpendicular to the atomic layers is 67 a.u., and the thickness of the material slab is 36.5 a.u. The charge is confined in a box of length $l = 48$ a.u. approximately comprising the slab. As one can see from the figure the plotted differences tend to maintain the same sign during iteration. The electronic charge no longer overshoots in the attempt to find its equilibrium distribution.

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[1] M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).

[2] M. Manninen, R. Nieminen, and P. Hautojävri, Phys. Rev. B 12, 4012 (1975); see also J. Arponen, P. Hautojärvi, R. Nieminen, and E. Pajanne, J. Phys. F 3, 2092 (1973) and R. M.Nieminen, J. Phys. F 7, 375 (1977).

[3] L. Ley, G. P. Kerker, and N. Martensson (unpublished).