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Conjugate gradient minimization of the energy functional: A new method for electronic structure calculation

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A new robust iterative method for electronic structure calculations based on a convenient adaptation of the conjugate gradient minimization of the energy functional is presented. The method is compared with some other techniques using the direct minimization of the density functional and with a more traditional Davidson approach. Numerical results for silicon and carbon are used to compare the different schemes. The new method is shown to be rapidly convergent, irrespective of the system under consideration, thus providing an efficient solution to a variety of large-scale electronic structure calculations.

I. INTRODUCTION

There is great current interest in large-scale electronic structure calculations, based on the local-density approximation (LDA) of density-functional theory (DFT).[1] Within DFT the electronic ground state is given by the minimum of the energy functional and is usually obtained by solving the Kohn-Sham (KS) equations,[2] i.e., the Euler equations associated with the minimum problem. In the conventional numerical approaches the KS equations are converted into self-consistent matrix eigenvalue equations, which are then solved by repeated matrix diagonalization. Such an approach is rather costly in large-scale problems, since it requires $O(M^3)$ floating-point operations for each diagonalization of a matrix of order M. M is the size of the basis set used to expand the electronic wave functions and can be very large, particularly, in plane-wave pseudopotential calculations. In order to achieve self-consistency the diagonalization must be repeated for a number of I_{sc} of iterations. Using an efficient mixing scheme such as e.g., Ref. (3) I_{sc} can vary from ~ 5 up to a few tens, depending on the system under study.

In order to reduce the calculation to more manageable size, two different approaches have been followed. Both of them exploit the fact that only the lowest N occupied KS orbitals are required to find the ground-state energy within DFT. Usually, and particularly in plane-wave schemes, N is much smaller than M.

The first of these approaches retains the self-consistent structure described above but replaces the full matrix diagonalization, yielding all M eigenstates, with a partial diagonalization scheme which yields only the lowest N eigenstates. This is acheived by iteratively improving some trial eigenfunctions which are usually provided by the previous self-consistent iteration. In this way the numerical cost of the diagonalization can be made as small as $O(N^2M)$ for very large systems in plane-wave pseudopotential calculations. Various such methods have been proposed which differ among themselves mainly in the way in which they compute the corrections to the trial wave functions.[4,5] In general, such schemes have comparable efficiencies even though some may be more effective in particular applications. We take as representative of this class of methods the block Davidson iterative scheme (DI) as implemented for LDA plane-wave pseudopotential calculations by one of us (S.B.).[6]

A different approach has been recently proposed by two of us (R.C. and M. P.) in the wider context of performing molecular-dynamics (MD) simulations with interatomic forces having LDA accuracy.[7] Such an approach regards the minimization of the energy functional as an optimization problem and will be referred to hereafter as the MD method. This allows one to achieve simultaneously self-consistency and diagonalization. The resulting algorithm grows with size as N^2M similarly to the DI approach discussed above. However, the actual numerical cost of the MD scheme can vary significantly, depending on the procedure used to achieve the minimization. In its original formulation the MD approach was mostly focused on the coupled electron-ion problem, and the optimization procedure was based on the simulated annealing[8] ideas. This was necessary, since when the ions are allowed to move, several local minima are possible and one needs a global search method which allows also for uphill moves like simulated annealing. This approach has been highly successful in a variety of applications.[9] However, if the ions are kept fixed, experience has shown that only a single minimum is encountered.[10] In this case use of simulated annealing techniques may considerably slow down the approach to the minimum. It was therefore realized that, in the context of total energy calculations at fixed ionic positions, the efficiency of the method improves considerably by adopting an approach based on very fast quench or on steepest descent (SD),[11-13] which allow only for downhill moves and expedite convergence to the minimum. It is well known that straightforward SD methods suffer from various drawbacks and can be improved significantly if one uses minimization techniques that take also into account information on the second derivatives of the function to be minimized.[14] Although not originally formulated in this way, Payne *et al.*,[11] Williams and Soler,[12] and some of us[13] made attempts at including partial information on the second derivatives. As we shall see, these schemes can be useful at times but they still retain some of the negative aspects of SD methods.

We want to propose here that by conveniently adapting the well-known conjugate gradient (CG) minimization method,[14] one can construct a powerful scheme that overcomes the limitations previously described. An important advantage of CG methods over other approaches is that they take full advantage of the matrix of the second derivatives without explicitly inverting or calculating it. The resulting method appears efficient and robust. In particular, it is always more efficient than straightforward SD methods and it is usually better than SD schemes using the Payne *et al.*[11-13] integration algorithm. The advantage is significant, particularly in difficult low-symmetry situations, where the CG approach reduces the numerical cost of the minimization by an order of magnitude compared to the above methods. The comparison with the more traditional DI approach is less overwhelming but still favorable. In fact, the CG approach usually requires an equal or smaller number of steps than the DI method to converge and the cost of a CG step in terms of the number of operations required is slightly smaller than that of a DI step. Such an advantage is more pronounced in situations that require a large number of self-consistent iterations $I_{\rm sc}$ in the traditional approach. A further advantage of the CG method is that it does not require parameters to control the convergence rate, such as the mixing parameter between input and output potentials in conventional self-consistent schemes, or the integration time step in SD schemes.

The paper is organized as follows. The basic notation is introduced in Sec. II as well as the concepts of the total energy minimization. Section III contains a description of the CG method for the electronic minimization problem. A comparison between the different schemes based on various numerical examples is presented in Sec. IV, which also contains our conclusions. Some numerical details useful for plane-wave nonlocal pseudopotential calculations are given in the Appendix.

II. TOTAL ENERGY MINIMIZATION

According to DFT, the total ground-state energy $\Phi[\{\mathbf{R}_I\}]$ of a system of interacting electrons and ions, corresponding to the ionic configuration $\{\mathbf{R}_I\}$, is a unique functional of the electronic density $n(\mathbf{r})$.[1] If we express $n(\mathbf{r})$ in terms of N occupied single-particle orbitals, i.e.,

$$n(\mathbf{r})=\sum_i^{\rm occ}|\psi_i(\mathbf{r})|^2 , \tag{1}$$

then the ground-state energy can be found by minimizing the functional $E[\{\psi_i\},\{\mathbf{R}_I\}]$ with respect to the "*electronic degrees of freedom*" $\{\psi_i\}$, i.e.,

$$\Phi[\{\mathbf{R}_I\}]=\min_{\{\psi_i\}}E[\{\psi_i\},\{\mathbf{R}_I\}] . \tag{2}$$

The functional $E[\{\psi_i\},\{\mathbf{R}_I\}]$ is given by

$$\begin{aligned}E[\{\psi_i\},\{\mathbf{R}_i\}]=&\sum_i^{\rm occ}\int d\mathbf{r}\,\psi_i^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\psi_i(\mathbf{r})\\&+\int d\mathbf{r}\,V^{\rm ext}(\mathbf{r})n(\mathbf{r})\\&+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\&+E^{\rm xc}[n]+\tfrac{1}{2}\sum_{I\neq J}\frac{Z_IZ_J}{|\mathbf{R}_I-\mathbf{R}_J|} .\end{aligned} \tag{3}$$

Atomic units $e=\hbar=m_e=1$ are used throughout the paper. $E^{\rm xc}[n]$ is the exchange-correlation energy[1] and $V^{\rm ext}$ is the total external potential felt by the electrons. In a pseudopotential formulation $V^{\rm ext}$ is a sum of ionic pseudopotentials and Z_I are the charges of the ionic cores. For simplicity, we will treat here the case of local pseudopotentials and leave the discussion of nonlocal pseudopotentials to the Appendix. In Eq. (3) the single-particle orbitals $\{\psi_i\}$ are subject to the orthonormality constraints:

$$\int d\mathbf{r}\,\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})=\delta_{ij} . \tag{4}$$

Note that we are here assuming that all the occupation numbers can be taken as equal.

The standard way of solving Eq. (2), subject to the constraints of Eq. (4), consists in solving the associated Euler-Lagrange equations, i.e.,

$$\begin{aligned}&H\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) ,\\&H=-\tfrac{1}{2}\nabla^2+V^{\rm ext}(\mathbf{r})+V^H(\mathbf{r})+\mu^{\rm xc}(\mathbf{r}) ,\end{aligned} \tag{5}$$

where $V^H(\mathbf{r})=\int d\mathbf{r}'\,[n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]$ is the Hartree potential and $\mu^{\rm xc}(\mathbf{r})=\delta E^{\rm xc}[n]/\delta n(\mathbf{r})$ is the exchange-correlation potential. The Schrödinger-type equations (5) are called Kohn-Sham equations and provide the theoretical framework of most self-consistent electronic structure calculations. By expanding the $\{\psi_i\}$ in terms of a basis set the KS equations are converted into a matrix eigenvalue problem. In the plane-wave pseudopotential formalism[15] we have

$$\psi_i(\mathbf{r})=\psi_{n\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{G}}c_{\mathbf{G}}^{n\mathbf{k}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} , \tag{6}$$

and the Hamiltonian matrix is given by

$$H_{\mathbf{G}\mathbf{G}'}^{\mathbf{k}}=\tfrac{1}{2}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G},\mathbf{G}'}+V_{\mathbf{G}-\mathbf{G}'}^{H}+\mu_{\mathbf{G}-\mathbf{G}'}^{\rm xc}+V_{\mathbf{G}-\mathbf{G}'}^{\rm ext} . \tag{7}$$

In practical applications the sum over $\mathbf{G}$ in Eq. (6) is truncated to include only M plane waves defined by the conditions $\frac{1}{2}(k+G)^2<E_{\rm cut}$, where the energy cutoff $E_{\rm cut}$ determines the accuracy of the calculation.

In the conventional approach for very large systems, the Hamiltonian matrix is diagonalized via iterative methods such as DI. The basic ingredient of Davidson-like schemes is the generation for any trial wave function ψ of a correction vector $\Delta\psi$ and the variational determination of the mixing coefficient between them by diagonalizing the Hamiltonian in the subspace spanned by $\{\psi,\Delta\psi\}$. The correction vectors $\{\Delta\psi\}$ are given by

$$\Delta\psi_i(\mathbf{r})=\frac{1}{H_d-\varepsilon_i}(H-\varepsilon_i)\psi_i(\mathbf{r}) \,, \tag{8}$$

where $\varepsilon_i=\langle\psi_i|H|\psi_i\rangle$, and H_d is the diagonal part of the Hamiltonian matrix. A single iteration of the Davidson algorithm consists of the followng steps: (i) generation of the correction vectors, where the computationally time-consuming part is the calculation of $H\psi$; (ii) each correction vector must be orthogonalized to all the trial vectors and the remaining correction vectors; (iii) to calculate the projection of H onto the $\{\psi,\Delta\psi\}$ subspace one has to calculate $H\Delta\psi$, which requires roughly the same cost as step (i); (iv) the eigenvectors of the projected Hamiltonian (which are the input for the next iteration) must then be transformed into the full plane-wave basis set. In the original Davidson scheme, the dimension of the $\{\psi,\Delta\psi\}$ subspace is increased at each iteration. In the body of a self-consistent calculation, where high accuracy is not required, this dimension can be kept as small as $2N$ and allowed to grow only in the very last self-consistent iterations. The number of operations necessary to perform the above four steps is αN^2M plus twice the operations needed to calculate $H\psi$. The cost of computing efficiently $H\psi$ will be discussed later. It turns out that $\alpha\geq\frac{11}{2}$ when the dimensions of the $\{\psi,\Delta\psi\}$ subspace is kept at its minimum $(2N)$.

In what follows, we will focus mostly on a different approach, namely the direct minimization of the functional in Eq. (3) without using the KS equations. Perhaps the simplest way to find a minimum of a function with many variables is provided by the steepest-descent approach, which in the present case can be formulated in terms of the equations

$$\dot{\psi}_i(\mathbf{r},t)=-\frac{\bar{\delta}E}{\bar{\delta}\psi_i^*(\mathbf{r},t)} \,, \tag{9}$$

where the dot indicates the derivative with respect to a fictitious time variable t, and $\bar{\delta}$ indicates the constrained functional derivative that preserves the orthonormality. The orthonormality constraints [Eq. (4)] must be added to Eq. (9) when an unconstrained functional derivative is used. Equation (9) defines a trajectory in the space of the electronic degrees of freedom in which at each step one moves a little bit down the "gradient" $-\bar{\delta}E/\bar{\delta}\psi_i^*$. The end product is the self-consistent minimization of E. The "time" dependence is fictitious, since in the SD procedure only the end product matters and the time is just a parameter used to label different configurations in the space of the $\{\psi_i\}$. The functional derivatives in Eq. (9) are obtained by adding the orthogonality constraints to the unconstrained functional derivatives:

$$\frac{\delta E}{\delta\psi_i^*(\mathbf{r},t)}=H\psi_i(\mathbf{r},t) \,, \tag{10}$$

where H depends nonlinearly on the $\{\psi_i\}$, [Eqs. (5)]. When a minimum is attained at the end of the SD procedure, $\{\dot{\psi}_i=0\}$ and Eqs. (9) are equivalent, within a unitary transformation, to the KS equations. From this point of view the SD procedure is just an alternative way of solving the KS equations without treating them as a self-consistent eigenvalue problem. If one neglects the constraints, Eq. (9) is formally equivalent to a time-dependent Schrödinger equation in imaginary time. The SD procedure can be thought of as a way of projecting onto the ground state an initial trial state by propagating it in imaginary time. In practice the SD step consists of the following:

$$\psi_i(\mathbf{r},t+\Delta)=\psi_i(\mathbf{r},t)-\Delta H\psi_i(\mathbf{r},t)+\text{constraints} \,. \tag{11}$$

The elementary time step Δ in Eq. (11) is a parameter that fixes the time scale and therefore governs the convergence rate of the SD scheme: it is the analog of the mixing parameter in a self-consistent diagonalization scheme. The $\{\psi_i(t=0)\}$ constitute the initial trial state. This must be nonorthogonal to the ground state in order for the SD procedure to work correctly. Also it has been pointed out that hidden symmetries in $\{\psi_i(t=0)\}$ coupled to a nonsymmetry breaking orthogonalization scheme can prevent the system from reaching the correct ground state,[16] This danger can be avoided by either adding some random component to the wave function or by adopting a symmetry-breaking orthogonalization scheme, such as Gram-Schmidt. In general, the final $\{\psi_i\}$ obtained with the SD procedure do not necessarily coincide with the KS eigenstates but are unitarily equivalent to them. This depends on the scheme used to impose the constraints. In particular, if the Gram-Schmidt orthogonalization method is used then the $\{\psi_i(t\rightarrow\infty)\}$ coincide with KS eigenstates[16] and the corresponding eigenvalues may be simply calculated by taking the expectation values of the Hamiltonian H. Note also that since physical quantities are invariant with respect to unitary transformations among occupied states, the orthogonalization scheme chosen is in this context largely arbitrary.

The basic step in the iterative schemes discussed here (SD, DI, CG described below) consists of acting on the $\{\psi_i\}$ with the Hamiltonian H followed by an orthonormalization of the new $\{\psi_i\}$ so obtained. In a plane-wave approach the action of the Hamiltonian on the wave functions requires $O(NM^2)$ floating-point operations, whereas the orthonormalization requires $O(N^2M)$. Such a counting can be improved as follows. The Hamiltonian H consists of a kinetic- plus a potential-energy term. The kinetic-energy term is diagonal in reciprocal space so that its action on the wave functions requires only $O(NM)$ operations. If the potential is local its action on the Fourier coefficients of the wave functions is a convolution that can be conveniently calculated in real space by means of fast-Fourier-transform (FFT) techniques.[7] This requires $O(NM'\log_2M')$ operations, where $M'=xM$ is the number of points used to evaluate the Fourier transform. The actual value of x depends on the number of nonzero Fourier cofficients of the potential and on the accuracy that we require for the convolution $V\psi$. Equation (7) requires a cutoff $2G_{\max}$ for the potential if $G_{\max}$ is the cutoff imposed to the wave functions. Then $x\sim2^3$ is required in order to obtain exactly the first M Fourier components of the convolution product $V\psi$. Note, however, that the assumption of a unique cutoff $G_{\max}$ for all expansions in plane waves also represents a physically sound approximation.[17] In such a case, $x \sim 1$. In the applications described in the present paper we have always used $x \sim 2^3$: with this choice the results obtained with the iterative approaches coincide with those of standard diagonalization methods using the same cutoff.

The result of all this is that the big dimension M enters only linearly or via $M' \log_2 M'$ in the count of the operations. This gives a significant improvement over standard diagonalization techniques where M enters as M^3. Of course for sufficiently large systems the terms growing as $N^2 M$ dominate and the numerical cost of the algorithm still grows as the cube of the system. An additional advantage of the iterative techniques (SD, DI, and CG) is that the Hamiltonian H is never explicitly required. One needs only its action on the wave functions, permitting a significant saving in memory occupation. If the FFT techniques described above are employed, the SD procedure requires the storage of the wave functions, i.e., NM words, plus the storage of the potential, which requires M' words for a local pseudopotential. In the Appendix we show that only an additional yM words are required for the nonlocal pseudopotential, where $y \lesssim 10$ in typical applications.

The efficiency of the SD scheme that we have just described is controlled by the number of steps that are necessary to achieve convergence. This can be quite large, especially in low-symmetry situations, as will be shown in Sec. IV. The straightforward SD method is known not to be the most efficient minimization algorithm,[14] and it may be improved in several ways. An obvious limiting factor is the maximum time integration step Δ that can be safely used in Eq. (11). In order to increase it and therefore accelerate convergence, one may exploit some properties of the total energy minimization problem, such as the fact that the Hamiltonian matrix is diagonally dominated for sufficiently large G. If we assume it to be diagonally dominated for all G's then in Eq. (9) we can separate the action on the wave functions of the diagonal part of the Hamiltonian from that of the off-diagonal part. We obtain

$$\dot{c}^{\,i}_{\mathbf{G}} = -(\tfrac{1}{2}|\mathbf{k}+\mathbf{G}|^2 + V_{\mathbf{G}-\mathbf{G}} - \varepsilon^i_p)c^i_{\mathbf{G}} - \sum_{\mathbf{G}' \neq \mathbf{G}} V_{\mathbf{G}-\mathbf{G}'} c^i_{\mathbf{G}'}$$
$$= -\omega_{\mathbf{G}} c^i_{\mathbf{G}} - R \ . \tag{12}$$

In Eq. (12) we have subtracted a constant ε^i_p from the diagonal part of H. By explicitly integrating the diagonal term and treating the off-diagonal one as a perturbation we obtain

$$c^i_{\mathbf{G}}(t+\Delta)$$
$$= \exp(-\omega_{\mathbf{G}}\Delta)\{c^i_{\mathbf{G}}(t) + (R/\omega_{\mathbf{G}})[1-\exp(\omega_{\mathbf{G}}\Delta)]\}$$
$$+\text{constraints} \ . \tag{13}$$

It is convenient to use $\varepsilon^i_p = \langle \psi_i(t)|H(t)|\psi_i(t)\rangle$. Equation (13) replaces Eq. (11) of the ordinary SD. Such a procedure was suggested by Williams and Soler[12] and by two of us,[13] by adapting to the SD scheme an idea originally introduced by Payne *et al.*[11] for the MD equations of Ref. 7. We call the algorithm of Eq. (13) the modified steepest-descent (MSD) scheme. In practice it is very similar to the minimization scheme of Payne *et al.*,[11] who calculate the ground-state electronic energy by performing a very fast quench with the MD equations of Ref. 7. In some cases the MSD method constitutes a definite improvement over the SD scheme, by allowing a significantly larger time integration step Δ and requiring a consistently smaller number of steps to converge. However, in many important cases and particularly in low-symmetry situations the MSD algorithm does not improve over the SD algorithm and it may even result in being less stable as we shall show with numerical examples in Sec. IV. This may be a consequence of the rather crude assumption of diagonal dominance of H for all G's. A better approximation can be obtained as follows. We write $H = H_0 + H_1$, where H_0 contains the diagonal part of H plus the off-diagonal elements up to some maximum $G = \tilde{G}$. $\tilde{G}$ is supposed to be much smaller than the cutoff that fixes the size of the plane-wave basis set. All the remaining off-diagonal elements are part of H_1. Typically the diagonalization of H_0 will require the diagonalization of a "small" matrix of order mN, where m is a small integer of order unity. Then the scheme of Eq. (13) can be easily generalized by integrating "exactly" the time dependence due to H_0 and by treating H_1 as a perturbation. Such a procedure is reminiscent of that followed in the DI scheme, and we expect that it should improve significantly the efficiency of the MSD algorithm. However, we have not implemented it and therefore in the numerical comparison between the various methods that will be presented in Sec. IV only the simpler version of the MSD scheme will be considered.

We remark that the Hamiltonian matrix H coincides with the matrix of the second derivatives of E with respect to the electronic degrees of freedom if the dependence of the self-consistent potential on the $\{\psi_i\}$ is neglected. From this point of view the MSD method is an attempt to include information on the second derivatives within the SD approach.

III. CONJUGATE GRADIENT MINIMIZATION OF THE ENERGY FUNCTIONAL

We summarize here the basic idea of the CG minimization technique. Let us suppose that the function to be minimized is roughly approximated by a multidimensional quadratic form around some point P taken as the origin of the coordinates

$$f(x) \approx c - \langle b|X\rangle + \tfrac{1}{2}\langle X|A|X\rangle \ , \tag{14}$$

where

$$X \equiv (x_1, x_2, \ldots, x_L), \quad c = f(P), \quad b \equiv -\nabla f|_P \ ,$$
$$A_{ij} \equiv \left.\frac{\partial^2 f}{\partial x_i \partial x_j}\right|_P \tag{15}$$

with a symmetric positive-definite $L \times L$ Hessian matrix A. An iterative minimization procedure is then defined by the sequence

$$P^{(n+1)} = P^{(n)} + \lambda^{(n)} h^{(n)}, \quad n = 0, 1, 2, \ldots \tag{16}$$

where $\lambda^{(n)}$ is a scalar and $h^{(n)}$ is a vector in multidimensional space. In SD schemes one chooses

$$h^{(n)}=-\nabla f(P^{(n)}) \ , \tag{17}$$

and $\lambda^{(n)}$ is either a fixed scalar sufficiently small to ensure convergence or it is chosen in such a way as to minimize the function f along the line defined by the direction $h^{(n)}$. The procedure defined in Eqs. (16) and (17) is usually far from being optimal even with functions that are nearly quadratic. The reason is that SD steps are often orthogonal or nearly orthogonal to one another and this may easily result in the need for very many steps in the case of canyon-shaped functions.[14] Such a drawback can be avoided by using the information contained in the matrix of the second derivatives A, since in this case a single operation is sufficient to minimize a perfectly quadratic function. However, for large L it is impractical to deal with the large matrix A both in terms of storage and computer time. In the CG method information on A is only used implicitly to define an optimal set of directions $h^{(n)}$ in the sequence of Eq. (16), where the scalar $\lambda^{(n)}$ is obtained by a one-dimensional minimization along the line defined by $h^{(n)}$. The directions $h^{(n)}$ are given by

$$h^{(n)}=\begin{cases} g^{(n)}, & n=0 \\ g^{(n)}+\gamma^{(n-1)}h^{(n-1)}, & n=1,2,3,\ldots \end{cases} \tag{18}$$

where

$$\begin{aligned} g^{(n)}&=-\nabla f(P^{(n)}) \ , \\ \gamma^{(n)}&=\frac{\langle g^{(n+1)}|g^{(n+1)}\rangle}{\langle g^{(n)}|g^{(n)}\rangle} \ . \end{aligned} \tag{19}$$

The directions $h^{(n)}$ are said to be conjugate. One can show[14] that for a quadratic function like the one in Eq. (14), the following conjugacy property is satisfied:

$$\langle h^{(n)}|A|h^{(m)}\rangle=0 \quad \forall n\neq m \ . \tag{20}$$

This property guarantees that each step is actually an improvement over all the preceding ones. By virtue of Eq. (20) the difficulty of SD with a canyonlike quadratic function is overcome. Notice that the Hessian matrix A is never explicitly required. The CG method is widely used in optimization problems: the simple CG step defined in Eq. (16) is not much more costly than the SD step but the method is much more efficient. The efficiency is in fact roughly the same as in methods using explicitly the Hessian matrix A, like Newton or quasi-Newton methods.[14]

We have seen in Sec. II that the electronic minimization problem within DFT can be successfully solved by means of SD methods. It is therefore natural to apply the CG procedure to it. A difficulty arises in this respect because of the existence of orthonormality constraints in the electronic problem. These originate forces of constraint that must be taken into account when the line minimizations are done. In order to deal with such constraints it is convenient to reformulate the electronic problem in terms of linearly independent but not orthonormal orbitals $\{\varphi_i\}$. The orthonormal orbitals $\{\psi_i\}$ may be related to the $\{\varphi_i\}$ via

$$\psi_i=\sum_j S_{ij}^{-1/2}\varphi_j \ , \tag{21}$$

where $S_{ij}=\langle\varphi_j|\varphi_i\rangle$ is the overlap matrix. In terms of the $\{\varphi_i\}$ the functional E in Eq. (3) can be rewritten as

$$\begin{aligned} E=&\sum_{ij}^{\text{occ}} S_{ij}^{-1}\langle\varphi_i|-\tfrac{1}{2}\nabla^2|\varphi_j\rangle \\ &+\int d\mathbf{r}\, V^{\text{ext}}(\mathbf{r})n(\mathbf{r})+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &+E^{\text{sc}}[n]+\tfrac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} \ . \end{aligned} \tag{22}$$

Then, for orthonormal $\{\varphi_i\}$, one obtains

$$\frac{\delta E}{\delta\varphi_i^*(\mathbf{r})}=H\varphi_i(\mathbf{r})-\sum_m\langle\varphi_m|H|\varphi_i\rangle\varphi_m(\mathbf{r}) \ . \tag{23}$$

Initially orthonormal orbitals become nonorthonormal after a CG step. Although in principle irrelevant, it is numerically convenient to reorthonormalize the $\{\varphi_i\}$ at any step. This will ensure that the S matrix remains nonsingular and allows the use of Eq. (23). The orthonormalization procedure leaves the value of E unchanged and therefore does not affect the final results. Obviously the orthonormalization can be done in many different ways. In our numerical implementation of the CG scheme we have used the Gram-Schmidt procedure. Equation (23) defines the "gradient" $g^{(n)}$ from which one obtains the conjugate direction $h^{(n)}$ using Eq. (18). A one-dimensional minimization of the functional E along $h^{(n)}$ allows us to compute $\lambda^{(n)}$ and to accomplish the CG step defined in Eq. (16). In order to keep things simple in the one-dimensional minimization we proceed as in non-self-consistent calculations and instead of E we minimize $\tilde{E}$ given by

$$\tilde{E}(\lambda^{(n)})=\sum_{ij}\langle\varphi_i^{(n+1)}|\tilde{H}|\varphi_j^{(n+1)}\rangle S_{ij}^{-1^{(n+1)}} \ , \tag{24}$$

where $\varphi_i^{(n+1)}=\varphi_i^{(n)}+\lambda^{(n)}h_i^{(n)}$ and $\tilde{H}=\tilde{H}[\{\varphi_i^{(n)}\}]$; in other words V^H and μ^{xc} are not varied as $\lambda^{(n)}$ is changed but are instead determined by the density corresponding to $\{\varphi_i^{(n)}\}$. This approximation becomes progressively better as the minimum is approached. However, there might be cases where one has to take into account self-consistency in the line minimizations. This was not the case for the examples considered in Sec. IV.

The computation of $\tilde{E}(\lambda^{(n)})$ requires the evaluation of the following matrices: $\langle\varphi|H|\varphi\rangle$, $\langle\varphi|H|h\rangle$, $\langle h|H|h\rangle$, $\langle\varphi|h\rangle$, and $\langle h|h\rangle$. $O(NM'\log_2 M')$ operations are required to compute $H\varphi$ and Hh, when using a local pseudopotential. $O(N^2M)$ operations are required to compute each one of the above matrices, whereas $O(N^3)$ operations are required for each inversion of the matrix S. In addition $O(N^2M)$ operations have to be performed to reorthonormalize the wave functions at the end of every CG step. Putting all the operation counts together, taking into account the symmetry properties of the matrices, and retaining only the most time-consuming terms we obtain $2NM'\log_2 M'+4N^2M$. We see that in the size range where the multiplication of H with the wave functions dominates, the approximate cost of the CG step is the same as the DI step and twice the SD or the MSD step. In the asymptotic regime dominated by the N^2M operations, the CG step is slightly more econonomical than the DI step ($4N^2M$ versus $\frac{11}{2}N^2M$), but may be significantly more costly (up to a factor of 8) then the simpler SD or MSD step. In such situations, SD methods may be comparable or even more convenient than the more sophisticated approaches based on CG or DI methods. The above considerations hold for a local pseudopotential scheme. When nonlocal pseudopotentials are used, operations of the kind N^2M are also required to compute $H\varphi$, as explained in the Appendix. In this case, the SD step is still more economical than the CG or DI step but the difference in cost is greatly reduced and is more than counterbalanced by the better efficiency of the latter method.

IV. NUMERICAL TESTS AND CONCLUSIONS

We have performed a number of test calculations in order to study the numerical efficiency of the various methods for large-scale electronic structure calculations introduced in the preceding sections. Few simple structures consisting of Si and C atoms were used as test systems. In all cases we used nonlocal norm-conserving pseudopotentials[18] and adopted the parametrization of Ref. 19 for exchange-correlation effects. The size of the test systems was not too large and always in the range where the computationally most relevant operations are products of the kind $H\varphi$.

The first system considered was crystalline silicon, as described by a periodically repeated simple cubic supercell with eight atoms arranged in perfect diamond lattice positions. The value of the experimentally observed lattice constant ($a = 10.26$ a.u.) was taken as the unit-cell dimension. The above structure is referred to as ordered. A different structure, referred to as disordered, was obtained by randomly displacing the atoms from their diamond lattice sites. Small displacements having maximum amplitude of 0.2 a.u. were used. We performed plane-wave calculations for both ordered and disordered Si structures with an energy cutoff of 7 Ry. The Brillouin-zone integrals were approximated either by the point $\mathbf{k}=(0,0,0)$ or by the point $\mathbf{k}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ (Baldereschi point[20]). The initial trial wave functions, used in all calculations, were obtained by filling the lowest-energy states resulting, from a diagonalization of a small Hamiltonian matrix constructed by assuming a uniform valence charge density and an energy cutoff of 2 Ry for the wave functions.

We measure the efficiency of the different schemes for electronic structure calculations by the number of steps necessary to achieve convergence in the total energy. The results obtained for both ordered and disordered Si structures are given in Fig. 1, which shows the variation of the total energy with the number of steps for the various schemes. The total number of steps that were necessary to achieve convergence in the different cases are reported in Table I. MSD, DI, and CG have comparable efficiencies for the ordered structure. The search for the minimum appears to be considerably more difficult in the disordered case, where all the methods require a larger number of steps to converge. In this case the convergence of SD and MSD slows down by almost an order of magnitude, whereas DI and CG still retain a satisfactory rate of convergence; the latter being, however, significantly faster. MSD is almost as efficient as CG or DI in the case of the ordered structure, but fails badly in the case of the disordered system, due to the presence of numerical instability even when the same time step Δ of SD is used.

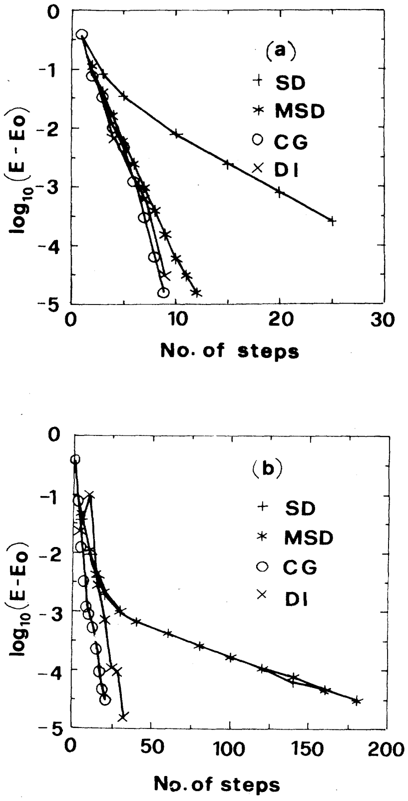

FIG. 1. The rate of convergence of the total energy E in SD, MSD, CG, and DI methods for (a) an ordered [$\mathbf{k}=(0,0,0)$] Si system and (b) a disordered [$\mathbf{k}=(0,0,0)$] Si system. E_0 indicates the converged ground-state energy.

TABLE I. Comparison of several tested methods in number of steps for the silicon system. Convergence in seven significant figures is assumed. If not given otherwise, the time step $\Delta = 0.16$ for the SD and MSD methods. For the DI method, the number of self-consistency cycles, I_{sc} is given in parentheses.

	SD	MSD	DI	CG
ordered Si [$\mathbf{k}=(0,0,0)$]	42	13[a]	10(3)	11
disordered Si [$\mathbf{k}=(0,0,0)$]	251	222[b]	39(9)	23
disordered Si [$\mathbf{k}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$]	73	203[b]	26(6)	16

[a] Time step $\Delta = 0.63$.

[b] The calculation was discontinued when convergence in only six significant digits was achieved, because at this point signs of numerical instability were beginning to appear.

In order to study the efficiency of the various schemes in a different situation, we have applied them to graphite. Owing to its quasi-two-dimensional structure, in ordinary electronic structure calculations, a larger number of iterations $I_{\rm sc}$ than in the case of Si is required to achieve convergence for graphite. We have represented the experimental graphitic structure with a periodically repeated orthorhombic supercell containing eight atoms and having dimensions $a=4.65$, $b=8.05$, and $c=12.00$ a.u. The eight atoms are arranged in two planes containing four atoms each and having the appropriate stacking. We use an energy cutoff of 18 Ry. As in the case of Si, we approximated the Brillouin-zone integrals either by $\mathbf{k}=(0,0,0)$ or by $\mathbf{k}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The initial trial wave functions were obtained by diagonalizing a Hamiltonian matrix corresponding to an energy cutoff of 15 Ry and a uniform charge density. The results are summarized in Table II. As in the case of ordered Si, DI and CG have comparable efficiencies. Instead SD faces serious difficulties and MSD, which we have not included in the table, shows the same signs of numerical instability as in the disordered Si case.

Notice that in order to obtain the results given in Tables I and II for the DI method, it has been necessary to be careful in deciding the convergence schedule; namely (i) an efficient mixing algorithm[3] has been used and (ii) the degree of convergence of each Davidson iterative process has been tuned:[6] as a general rule we found it convenient to stop the DI scheme when the difference between two sucessive estimates of the eigenvalues is less than one-hundredth of the mean square deviation between the input and output potentials of the previous iteration.

From the above and other calculations not reported here, the CG scheme seems to be the more robust and the less sensitive to a poor choice of the initial trial wave functions; namely wave functions whose projection onto the ground state is rather small. In summary, we can draw the following conclusions. We have compared a number of methods for ground-state electronic structure calculations based on direct minimization of the energy functional and nonstandard diagonalization techniques. All of them exploit the fact that only the lowest N occupied KS orbitals are necessary for finding the ground-state energy within DFT. Since with plane-wave basis sets usually $N \ll M$, all the above methods largely reduce the calculations. In particular, we have introduced a new computational tool by conveniently adapting the well-known CG minimization method to the problem of electronic structure calculations.

TABLE II. Comparison of several tested methods in number of steps for graphite. Convergence in seven significant figures is assumed. For the DI method, the number of self-consistency cycles $I_{\rm sc}$ is given in parentheses.

	SD	DI	CG
$\mathbf{k}=(0,0,0)$	213[a]	22(5)	26
$\mathbf{k}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	40[a]	25(7)	21
	+135[b]		

[a] Time step $\Delta=0.083$.

[b] Time step $\Delta=0.030$.

When the convergence rate is measured in terms of the number of steps needed to achieve convergence, the CG scheme is definitely better than any SD technique and it compares well with the more traditional DI approach, even though in this case the gain with the CG method may not be as substantial. However, an important advantage of the CG method compared to both SD and DI is the absence in the CG scheme of any convergence controlling parameter (such as the mixing parameter in DI or the time step Δ in SD). In general, the convenience of the CG scheme is more pronounced in difficult low-symmetry situations. When the number of operations per time step is also taken into account, the better efficiency of CG compared to SD methods may be in part compensated by the lower number of operations required in the simpler SD step, particularly for very large systems when using local pseudopotentials. We feel, however, that in most situations the CG approach should be significantly superior to any SD-based approach.

Given the efficiency and the robustness of the CG method, one may think of using it to calculate the Hellman-Feynman forces needed in a MD scheme for the ions. This would provide a means to search for the global minimum via dynamical simulated annealing. However, we have found that such a formulation is significantly less convenient than the generalized Lagrangian formulation of Ref. 7.

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APPENDIX: NONLOCAL PSEUDOPOTENTIALS

The usual expression for the total pseudopotential of the crystal can be written as $V_{\rm ps}(\mathbf{r})=\sum_I v_{\rm ps}(\mathbf{r}-\mathbf{R}_I)$, where the ionic pseudopotential is usually taken as

$$v_{\rm ps}(\mathbf{r})=\sum_{l=1}^{\infty} v_l(\mathbf{r})\hat{\mathbf{P}}_l \ , \tag{A1}$$

where $\hat{\mathbf{P}}_l$ is the projector onto the lth angular momentum. The infinite sum in Eq. (A1) is evaluated by assuming that $v_l(r)=v^*(r)$ for $l \geq \bar{l}$. A natural choice which has been followed here and in Ref. 11 is to take $v^*(r)=v_{\bar{l}}(r)$. This allows one to rearrange (A1) in the form

$$v_{\rm ps}(\mathbf{r})=v_{\bar{l}}(\mathbf{r})+\Delta_{nl}(\mathbf{r})=v_{\bar{l}}(\mathbf{r})+\sum_{l=1}^{\bar{l}-1} v_l(\mathbf{r})\hat{\mathbf{P}}_l \ , \tag{A2}$$

where $\Delta v_l(\mathbf{r})=v_l(\mathbf{r})-v_{\bar{l}}(\mathbf{r})$.

The first term $v_{\bar{l}}(\mathbf{r})$ in Eq. (A2) is purely local and can be treated as described earlier. The nonlocal contribution comes from the second term in Eq. (A2), when summed over all the atoms in the system: this is most conveniently written in Fourier space as

$$\Delta V_{nl}(\mathbf{q},\mathbf{q}') = \sum_I \sum_{l=0}^{\bar{l}-1} \exp(-i\mathbf{q}\cdot\mathbf{R}_I)\Delta v_l(\mathbf{q},\mathbf{q}') \times \exp(i\mathbf{q}'\cdot\mathbf{R}_I) \ , \tag{A3}$$

where

$$\Delta v_l(\mathbf{q},\mathbf{q}') = \frac{4\pi}{\Omega}(2l+1)P_l(\hat{\mathbf{q}}\cdot\hat{\mathbf{q}}') \times \int_0^\infty dr\, r^2 \Delta v_l(r) j_l(qr) j_l(q'r) \ . \tag{A4}$$

In Eq. (A4) P_l and j_l are Legendre polynomials and spherical Bessel functions, respectively. $\hat{\mathbf{q}}$ and $\hat{\mathbf{q}}'$ are unit vectors in directions $\mathbf{q}$ and $\mathbf{q}'$, respectively, and Ω is the unit-cell volume. A straightforward application of the matrix to the wave function in Fourier space requires NM^2 operations and substantial storage.

In order to reduce the number of operations required it is very useful to rewrite Eq. (A4) in a separable form

$$\Delta v_l(\mathbf{q},\mathbf{q}') = \sum_i W_i(\mathbf{q})W_i^*(\mathbf{q}') \ . \tag{A5}$$

This can be achieved by making use of the addition theorem for spherical harmonics

$$P_l(\hat{\mathbf{q}}\cdot\hat{\mathbf{q}}') = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}(\hat{\mathbf{q}})Y_{lm}^*(\hat{\mathbf{q}}') \ , \tag{A6}$$

and by approximating the radial integral

$$\int_0^\infty dr\, r^2 \Delta v_l(r) j_l(qr) j_l(q'r) \approx \sum_i w_i j_l(qr_i) j_l(q'r_i) \ , \tag{A7}$$

where r_i and w_i are nodes and weights of an appropriate Gauss integration scheme. In our application, $\Delta v_l(r)$ has a Gaussian behavior, and it is therefore convenient to use a Gauss-Hermite integration formula. The number of integration points N_{GH} depends on the cutoff $G_{\max}$: we found that a number of integration points N_{GH} equal to 6 and 8, for Si and C, respectively, provided a very accurate approximation to the integral in Eq. (A4). The use of this approximation leads to a total number of operations $(L)N_{GH}N_INM$ where N_I is the total number of atoms and $L=\sum_{l=0}^{\bar{l}-1}(2l+1)$. Clearly, this approach becomes useful only for $(L)N_{GH}N_I < M$.

In the same spirit the use of potentials of the form proposed by Kleinman and Bylander[21] (KB) has recently been suggested,[22] these being separable by construction. The count of operations is in this case equal to ours with $N_{GH}=1$. The saving is therefore substantial, and thus the KB pseudopotential is to be used in all the cases where it is safe to do so.

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[1] See, for instance, *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] D. G. Anderson, J. Assoc. Comput. Mach. **12**, 547 (1965).

[4] E. R. Davidson, in *Methods in Computational Molecular Physics*, edited by G. H. F. Diercksen and S. Wilson Vol. 113 of *NATO Advanced Study Institute, Series C* (Plenum, New York, 1983), p. 95.

[5] D. M. Wood and A. Zunger, J. Phys. A **18**, 1343 (1985).

[6] S. Baroni and M. Marinelli (unpublished).

[7] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[8] S. Kirkpatrick, G. D. Gelatt, Jr., and M. P. Vecchi, Science **220**, 671 (1983).

[9] See, for instance, D. Hohl, R. O. Jones, R. Car, and M. Parrinello, Chem. Phys. Lett. **139**, 540 (1987); R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988); P. Ballone, W. Andreoni, R. Car, and M. Parrinello, *ibid.* **60**, 271 (1988); D. Hohl, R. O. Jones, R. Car, and M. Parrinello, J. Chem. Phys. **89**, 6823 (1988).

[10] Even at fixed ions, several local minima may be introduced by allowing the basis functions to depend nonlinearly on a set of variational parameters; see, for instance, M. Sprik and M. L. Klein, J. Chem. Phys. **89**, 1592 (1988).

[11] M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, and D. M. Vanderbilt, Phys. Rev. Lett. **56**, 2656 (1986).

[12] A. Williams and J. Soler, Bull. Am. Phys. Soc. **32**, 562 (1987).

[13] R. Car, M. Parrinello, and W. Andreoni, in *Proceedings of the First NEC Symposium of Fundamental Approaches to New Material Phases,* edited by S. Sugano and S. Ohnishi (Springer, Berlin, 1987), p. 134.

[14] W. M. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986), p. 301; L. A. Hageman and D. M. Young, *Applied Iterative Methods, Computer Science and Applied Mathematics* (Academic, New York, 1981), p. 138.

[15] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[16] M. C. Payne, N. Needels, and J. D. Joannopoulos, Phys. Rev. B **37**, 8138 (1988).

[17] J. L. Martins and M. L. Cohen, Phys. Rev. B **37**, 6134 (1988).

[18] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[19] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[20] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973).

[21] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[22] D. C. Allan and M. P. Teter, Phys. Rev. Lett. **59**, 1136 (1987).