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Direct minimization technique for metals in density functional theory

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We present a scheme to solve the Kohn-Sham equations of density functional theory using orthonormal wave functions and an independent pseudo-Hamiltonian matrix. Our ansatz is based on a direct minimization of the electronic free energy with conjugate-gradient techniques. In contrast to previous approaches, continuous changes in the occupation numbers and subspace rotations are naturally included and allow therefore for exponential convergence. The algorithm is demonstrated for Mo bulk and surfaces.

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Density functional theory (DFT) has become the work horse of modern *ab initio* electronic-structure theory and is nowadays being routinely applied to a huge variety of systems. Correspondingly, a large number of computer codes are available to solve the underlying Kohn-Sham equations. Their algorithms differ by complexity, computational demands in terms of (main) memory or CPU time, speed of convergence, robustness, and may have been optimized for, or even restricted to, certain material classes. The general strategy is to linearize the problem and then to either iterate the interdependent fundamental quantities such as the density, the effective potential, and the wave functions to self-consistency[1,2] or to follow the energy gradients to the minimum in parameter space. The most efficient wave-function-based algorithms available today rely on efficient mixing schemes of densities[2] or a direct minimization of the ground-state energy.[3–7] For semiconductors, the latter strategy yields generally applicable preconditioned conjugate-gradient algorithms with an extremely fast and stable convergence when only the coefficients of occupied wave functions are varied. For metals, also the occupation numbers and unitary transformations of the wave functions need to be taken into account. Attempts to generalize direct minimization to metals have so far not succeeded in achieving a performance comparable to semiconductor schemes.[5,7] Here, we present a formulation of DFT in terms of orthonormal wave functions and an independent pseudo-Hamiltonian matrix, which is well suited for this task.

In Kohn-Sham density functional theory, the electronic energy is given in terms of orthonormal wave functions ψ_n, which reproduce the exact electron density,

$$\rho(\mathbf{r}) = \sum_n f_n |\psi_n(\mathbf{r})|^2, \tag{1}$$

with occupation numbers $0 \le f_n \le 1$. The global index n includes state and spin indices; for periodic systems, additional **k** indices and weights appear. The total electronic energy is given by

$$E[f_n,\psi_n] = \sum_n f_n \langle \psi_n | -\frac{1}{2}\nabla^2 + \hat{V}^{\text{ext}} | \psi_n \rangle + \frac{1}{2}\int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{\text{xc}}[\rho]. \tag{2}$$

The external potential $\hat{V}^{\text{ext}}$ accounts for the electron-ion interactions and may include nonlocal pseudopotentials. All electron-electron interactions beyond the classical Hartree energy [the 2nd term in Eq. (2)] are rolled up in the exchange-correlation functional E^{xc} for which reasonable approximations such as the local-density approximation or generalized-gradient approximations are available.

For a given set of occupation numbers f_n, the ground state is the global minimum of E. Imposing normalization via Lagrange multipliers ε_n gives rise to the Kohn-Sham equations,

$$\hat{H}|\psi_n\rangle = \epsilon_n |\psi_n\rangle, \tag{3}$$

where $\hat{H}$ denotes the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 + \hat{V}^{\text{ext}} + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V^{\text{xc}}[\rho], \tag{4}$$

with the exchange-correlation potential

$$V^{\text{xc}}(\mathbf{r}) = \frac{\delta E^{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}. \tag{5}$$

In order to improve the convergence with respect to computational parameters such as the Brillouin-zone sampling, it is common practice to employ finite-temperature occupation numbers,

$$f_n = \{1 + \exp[(\epsilon_n - \mu)/kT]\}^{-1}, \tag{6}$$

with an electronic temperature T; k denotes the Boltzmann constant. The chemical potential μ (or Fermi energy at $T=0$) is chosen such that the occupations sum up to the total number of electrons N. With this finite-temperature expression, it is not the total energy E but the free energy,

$$F[f_n,\psi_n] = E[f_n,\psi_n] - TS[f_n], \tag{7}$$

which becomes minimal at the self-consistent solution,[4] where the entropy S is

$$S[f_n] = -k\sum_n f_n \ln f_n + (1-f_n)\ln(1-f_n). \tag{8}$$

Smearing schemes other than Fermi distribution may also be used but require altered expressions for the entropy. Introducing Lagrange multipliers $\lambda_{nn'}$ and μ to enforce orthonormality and electron number conservation, the functional to be made stationary becomes

$$L[f_n,\psi_n] = F[f_n,\psi_n] - \sum_{nn'} \lambda_{nn'}(\langle\psi_n|\psi_{n'}\rangle - \delta_{nn'}) - \mu\left(\sum_n f_n - N\right). \tag{9}$$

The gradient of L with respect to $\langle\psi_n|$ is given by

$$\frac{\delta L}{\delta\langle\psi_n|} = f_n H|\psi_n\rangle - \sum_{n'} \lambda_{nn'}|\psi_{n'}\rangle. \tag{10}$$

Multiplying from left with $\langle\psi_{n''}|$ yields the Lagrange multipliers $\lambda_{nn'} = f_n\langle\psi_n'|H|\psi_n\rangle$. Noting that

$$\frac{\partial(TS)}{\partial f_n} = -kT\ln\frac{f_n}{1-f_n} = (\epsilon_n - \mu), \tag{11}$$

the gradient with respect to the occupations reads as

$$\frac{\partial L}{\partial f_n} = \langle\psi_n|H|\psi_n\rangle - \epsilon_n. \tag{12}$$

A direct minimization of the free energy is hampered by two things. First, the occupations may attain a boundary minimum at $f=1$ or $f=0$, where the gradient does not vanish. This can be overcome by minimizing with respect to the energies ϵ_n,[7,8] noting that

$$\frac{\partial f_n}{\partial(\epsilon_n - \mu)} = -f_n(1-f_n)/kT. \tag{13}$$

Second, L is *not* invariant against unitary transformations,

$$|\psi_n\rangle \to \sum_n U_{mn}|\psi_m\rangle, \tag{14}$$

among states with different occupations, even if the gradients [Eqs. (10) and (12)] vanish. In other words, L may become stationary outside the desired minimum of F against individual variations in the orbitals. Therefore, global variations in terms of unitary transformations must be included.[4,5] Ismail-Beigi and Arias[5] suggested to express the unitary transformations as $\mathbf{U}=e^{i\mathbf{B}}$ and vary the Hermitean matrix $\mathbf{B}$. In their algorithm, however, the occupations are not treated as variational parameters but rather updated at regular intervals. On the other hand, in the algorithms of Grumbach *et al.*[8] and Kresse and Furthmüller[7] (both are closely related), the unitary rotation does not originate from a free parameter but is rather computed from the current wave functions. All three schemes were found to be dramatically less efficient for metals than for semiconductors.[5,7] In the present Rapid Communication, we propose an approach which guarantees a consistent treatment of occupations and subspace rotation.

The key idea is to combine U_{mn} and ϵ_n into a pseudo-Hamiltonian matrix,

$$\eta_{mm'} = \sum_n U_{mn}\epsilon_n U^\dagger_{nm'}. \tag{15}$$

At the minimum, η becomes identical to the Hamiltonian in the subspace of the wave functions. In general, however, we treat η as independent. We then define

$$\tilde{L}[\psi_m,\eta_{mm'}] := L\left[\sum_m U_{mn}[\eta]|\psi_m\rangle, f_n[\eta]\right]. \tag{16}$$

We used the notation $[\eta]$ here to emphasize that the unitary transformations and the occupation numbers are functions of η, but we will omit this from now on. In practice, U and ϵ_n are obtained by diagonalizing η. The occupation numbers are then obtained from ϵ_n via Eq. (6). An analogous construction by Marzari *et al.*[3] uses the occupation matrix ($\epsilon_n \to f_n$) instead of the pseudo-Hamiltonian and provides an equally consistent approach. In contrast to us, they then minimize with respect to the occupation matrix for each set of wave functions, which renders their scheme much more costly.

The gradients of $\tilde{L}$ with respect to its parameters are

$$\frac{\delta\tilde{L}}{\delta\langle\psi_m|} = \sum_n U^\dagger_{nm}\left(f_n\hat{H}|\tilde{\psi}_n\rangle - \sum_{n'}\lambda_{nn'}|\tilde{\psi}_{n'}\rangle\right), \tag{17}$$

where $|\tilde{\psi}_n\rangle = \Sigma_m U_{mn}|\psi_m\rangle$ and

$$\begin{aligned}\frac{\partial\tilde{L}}{\partial\eta_{mm'}} &= \sum_n \frac{\partial\tilde{L}}{\partial f_n}\frac{\partial f_n}{\partial(\epsilon_n-\mu)}\frac{\partial(\epsilon_n-\mu)}{\partial\eta_{mm'}} \\ &\quad + \sum_{nm''}\frac{\delta\tilde{L}}{\partial U_{m''n'}}\frac{\partial U_{m''n'}}{\partial\eta_{mm'}} + \frac{\delta\tilde{L}}{\partial U^\dagger_{n'm''}}\frac{\partial U^\dagger_{n'm''}}{\partial\eta_{mm'}} \\ &= -\frac{1}{kT}\sum_n(\langle\tilde{\psi}_n|\hat{H}|\tilde{\psi}_n\rangle - \epsilon_n)f_n(1-f_n) \\ &\quad \times\left(U^\dagger_{nm}U_{m'n} - \frac{\partial\mu}{\partial\eta_{mm'}}\right) \\ &\quad + \sum_{n\neq n'}\frac{f_{n'}-f_n}{\epsilon_{n'}-\epsilon_n}\langle\tilde{\psi}_{n'}|\hat{H}|\tilde{\psi}_n\rangle U^\dagger_{n'm}U_{m'n}.\end{aligned} \tag{18}$$

$\partial\mu/\partial\eta_{mm'}$ may be obtained from the condition

$$\frac{\partial}{\partial\eta_{mm'}}\sum_n f_n = 0 \Rightarrow \frac{\partial\mu}{\partial\eta_{mm'}} = \frac{\sum_n f_n(1-f_n)U^\dagger_{nm}U_{m'n}}{\sum_n f_n(1-f_n)}. \tag{19}$$

However, as we will see later, these single terms are never needed.

$\tilde{L}$ is invariant under a unitary transformation $\tilde{U}$ when ψ_m and η_m are transformed simultaneously according to

$$\psi_m \to \sum_p \tilde{U}_{pm}\psi_p, \tag{20}$$

$$\eta_{mm'} \to \sum_{pp'}\tilde{U}^\dagger_{mp}\eta_{pp'}\tilde{U}_{p'm'}. \tag{21}$$

The equations can be drastically simplified if we choose the above transformation such that η becomes diagonal at any point. With this gauge, we have $U_{mn}=\delta_{mn}$, $|\tilde{\psi}_n\rangle = |\psi_n\rangle$, and the gradients simplify to

$$|g_n^{\psi}\rangle := \frac{\delta\tilde{L}}{\delta\langle\psi_n|} = f_n\left(1 - \sum_{n'} |\psi_{n'}\rangle\langle\psi_{n'}|\right)H|\psi_n\rangle, \tag{22}$$

$$g_{nn'}^{\eta} := \frac{\partial\tilde{L}}{\partial\eta_{nn'}} = -\frac{\delta_{nn'}}{kT}(\langle\psi_n|\hat{H}|\psi_n\rangle - \epsilon_n)f_n(1-f_n) + \delta_{nn'}\frac{\partial\mu}{\partial\eta_{nn'}}\frac{\partial F}{\partial\mu} + \frac{f_{n'}-f_n}{\epsilon_{n'}-\epsilon_n}\langle\psi_n|\hat{H}|\psi_{n'}\rangle(1-\delta_{nn'}), \tag{23}$$

where

$$\frac{\partial F}{\partial\mu} = \frac{1}{kT}\sum_n (\langle\psi_n|\hat{H}|\psi_n\rangle - \epsilon_n)f_n(1-f_n) \tag{24}$$

contains the free-energy density at the Fermi level. The three terms in Eq. (23) clarify the role of variations in the pseudo-Hamiltonian: the diagonal elements give rise to changes in the occupation numbers (first term) and changes in the electron chemical potential (second term). Nondiagonal elements induce the subspace rotations (third term).

Algorithm. In order to improve the conditioning of the problem,[3] we do not minimize along the gradients but rather employ a preconditioned primary search direction,

$$|\Delta\psi_n\rangle := -\hat{K}\left(\hat{H}|\psi_n\rangle - \sum_{n'} |\psi_{n'}\rangle\langle\psi_{n'}|\hat{H}|\psi_n\rangle\right), \tag{25}$$

$$\Delta\eta_{nn'} := \kappa(\langle\psi_n|\hat{H}|\psi_{n'}\rangle - \epsilon_n\delta_{nn'}), \tag{26}$$

with a preconditioner $\hat{K}$ for the wave functions and a scalar preconditioner κ for the pseudo-Hamiltonian. The actual search direction for step i according to the preconditioned conjugate-gradient scheme is[1,4,5,7]

$$|X_{\psi}^{(i)}\rangle := |\Delta\psi^{(i)}\rangle + \gamma|X^{(i-1)}\rangle, \tag{27}$$

$$X_{\eta}^{(i)} := \Delta\eta^{(i)} + \gamma X_{\eta}^{(i-1)}, \tag{28}$$

where

$$\gamma = \frac{\mathrm{Re}\ \mathrm{tr}\{\langle g^{(i)}|\Delta^{(i)}\rangle\}}{\mathrm{Re}\ \mathrm{tr}\{\langle g^{(i-1)}|\Delta^{(i-1)}\rangle\}}. \tag{29}$$

$|X_{\psi}\rangle$ is then orthogonalized to the current wave functions in order to maintain orthonormality to first order. Along the search direction, a quadratic line minimization is performed in the line coordinate ξ using the free energy, with its gradient at $\xi=0$,

$$\left.\frac{\partial F}{\partial\xi}\right|_{\xi=0} = 2\ \mathrm{Re}\ \mathrm{tr}\{\langle g|X\rangle\} \tag{30}$$

and one additional trial energy at $\xi=\xi_{\mathrm{trial}}$.[5] From the line minimum ξ_{min}, η and ψ are updated according to

$$\psi^{(i+1)} = \psi^{(i)} + \xi_{\mathrm{min}}X_{\psi}^{(i)}, \tag{31}$$

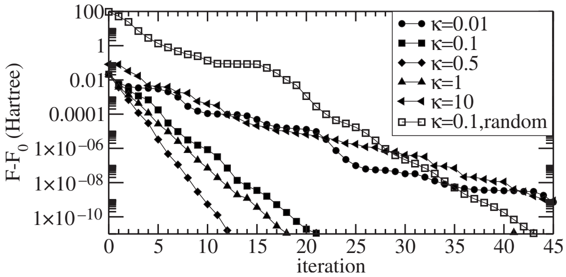

FIG. 1. Convergence of the free energy for a two-atom bcc Mo cell for different values of κ (see text). Initial guess: linear combination of atomic orbitals (lcao) (full symbols) or random numbers (empty symbols).

$$\eta^{(i+1)} = \eta^{(i)} + \xi_{\mathrm{min}}X_{\eta}^{(i)}, \tag{32}$$

followed by a synchronous unitary rotation according to Eqs. (20) and (21) with $\tilde{U}=U^{(i+1)}$ in order to restore the diagonality of η. Note that this rotation must also be applied to the search direction $X^{(i)}$ for consistency in the next conjugate-gradient step. To eliminate the second-order errors, the wave functions are explicitly orthonormalized using the Gram-Schmidt scheme. Finally, μ is determined from the updated ϵ_n. The same procedure is of course applied at the trial point ξ_{trial}. Equations (25)–(32) are iterated until the change in the free energy falls short of the desired accuracy.

In this context, we note that the contribution of the μ shift [second term in Eq. (23)] to the free-energy gradient can be factored into $(\partial F/\partial\mu)(\partial\mu/\partial\xi)$. In analogy to Eq. (19), the total electron chemical-potential shift along the search direction is obtained from

$$\frac{\partial\mu}{\partial\xi} = \frac{\sum_n f_n(1-f_n)(X_{\eta})_{nn}}{\sum_n f_n(1-f_n)}. \tag{33}$$

We have implemented this algorithm into the SPHInX library.[9] For the wave-function preconditioner $\hat{K}$, we use a standard prescription.[1,7] For κ, we employ an initial value of 0.1 and possibly adjust the value during the calculation as described below. In the early stages of the convergence, significant deviations from a quadratic behavior may occur along the search directions. The most dramatic changes are associated with nonlinear changes in the occupations. Fortunately, these can be easily detected by monitoring the change in the electron chemical potential. If the actual change deviates from Eq. (33) by more than 10%, we gradually reduce the step length in the η direction until we stay in the linear regime. It also proved advantageous to restart the conjugate-gradient search with $\gamma=0$ if the convergence appears to stagnate.

In Fig. 1, we demonstrate the performance of our algorithm for bcc Mo (simple-cubic cell with 2 atoms, 4×4×4 **k**-point mesh, and $kT=0.1$ eV). When starting from a lcao (full symbols),[10] the convergence is rapid and obviously exponential, as is expected for a consistent implementation of the conjugate-gradient scheme. Even for the worst possible starting point, namely, random numbers (open symbols), the algorithm succeeds, although the initial convergence is slower. The preconditioner parameter κ influences the convergence rate; in this case a value of 0.5 proved optimal. Our convergence rate (10 orders of magnitude in 12 steps) may be contrasted to the prescription of Ismail-Beigi and Arias.[5] For the same system, they achieve ~6 orders of magnitude in 200 steps, and the convergence rate visibly deviates from an exponential behavior.

We have studied a variety of different systems and have found a very stable and fast convergence in all cases. For most systems the optimal κ lies between 0.05 and 0.5. For large calculations, we automatically adjust κ. For this, we consider the quadratic line minimum from two energies (at $\xi=0$, ξ_t) and one gradient (at $\xi=0$),

$$F_{\min} = - \frac{\left.\frac{\partial F}{\partial \xi}\right|_{\xi=0} \cdot \xi_t^2}{2\left(F(\xi_t) - F(\xi=0) - \left.\frac{\partial F}{\partial \xi}\right|_{\xi=0} \cdot \xi_t\right)}. \tag{34}$$

For $\xi_t=\xi_{\min}$, we note that $\partial F_{\min}/\partial\kappa$ depends on

$$\left.\frac{\partial^2 F}{\partial \xi\, \partial\, \kappa}\right|_{\xi=0} = 2 \operatorname{Re} \operatorname{tr}\{\langle g^{\eta,(i)} | \tilde{\Delta}^{\eta,(i)} \rangle\} \tag{35}$$

and

$$\frac{\partial F(\xi_{\min})}{\partial \kappa} = 2 \operatorname{Re} \operatorname{tr}\{\langle g^{\eta,(i+1)} | \tilde{\Delta}^{\eta,(i)} \rangle\}. \tag{36}$$

$\tilde{\Delta}^{\eta}=\partial\Delta^{\eta}/\partial\kappa$ denotes the unpreconditioned search direction. If the dependence of $F_{\min}$ on κ is significant (compared to, e.g., $\partial F/\partial\xi$), κ is changed in steps of ±10%, +50/−33%, or +100/−50%.

A big advantage of line minimization is the continuous transformation of the electronic state. Charge sloshing, which arises for discontinuous density-mixing methods if the long-range screening is insufficiently accounted for,[11] should not occur: since the screening is effectuated by essentially the same density fluctuations with opposite sign, locating the equilibrium long-range density distribution is basically a line minimization problem. To verify this, we performed a calculation for a bcc Mo (111) 20 layer slab system. Figure 2 illustrates that the convergence is indeed extremely stable and reasonably fast. In contrast to Ref. 7, we find that the present formulation of a direct method is competitive with the density-mixing scheme (squares in Fig. 2).

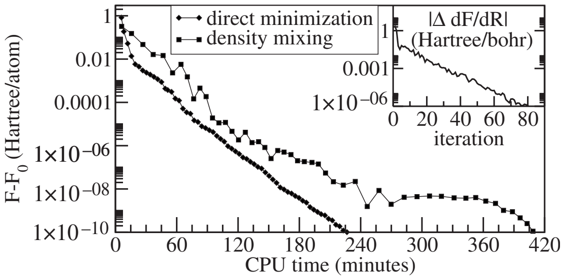

FIG. 2. Convergence of the free energy for a 20-layer bcc Mo (111) slab. The inset shows the exponential convergence of forces for the direct minimization.

We like to emphasize that the exponential convergence behavior is not limited to the free energy but applies to other properties as well. The inset in Fig. 2 illustrates this for atomic (Hellmann-Feynman) forces by showing the deviation from the converged force (averaged over atoms) at each iteration. However, the convergence exponent for forces is found to be smaller than that of the free energy by a factor of 2. This factor matches perfectly the theoretically expected difference in convergence speed between variational (affected by errors only in second order) and nonvariational properties (first order).

In summary, we have presented a formulation of density functional theory in terms of orthonormal wave functions and a pseudo-Hamiltonian matrix which is well suited for direct minimization of the free energy. Changes in the occupation numbers and subspace rotations are generated from the same parameter set, which leads to a fast and stable convergence. Our results highlight that, for the conjugate-gradient minimization, all relevant independent parameters must be treated consistently. Using our approach, the excellent convergence of direct minimization is no longer restricted to semiconductors but can be achieved also for metallic systems. In contrast to preconditioned density-mixing schemes, which rely in part on appropriate models for screening (e.g., Kerker preconditioning),[11] no part of our algorithm relies on the physics of the system, which makes it ideally suited for cases where conventional screening models fail.

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