

Unconstrained minimization approach for electronic computations that scales linearly with system size

Pablo Ordejón

Department of Physics, University of Illinois, Urbana, Illinois 61801

David A. Drabold

Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701-2979

Matthew P. Grumbach and Richard M. Martin

Department of Physics, University of Illinois, Urbana, Illinois 61801

(Received 8 March 1993)

We present a method for the calculation of total energies and forces that scales linearly with the number of atoms in the system. The key points are (i) an unconstrained conjugate gradient minimization of the electronic energy that avoids the need of explicit orthonormalization, and (ii) description of the electrons in terms of localized wave functions, truncated beyond a radius R_c . The method is variational, giving an upper bound to the exact total energy, and is exact as $R_c \rightarrow \infty$. We test the method for a model tight-binding Hamiltonian, and in full *ab initio* molecular-dynamics calculations.

One of the important undertakings of current theoretical work is to produce efficient means of computing reliable properties in molecular and condensed matter systems. Despite the important advances that have been made recently using Car-Parrinello molecular dynamics methods,¹ minimization techniques,² and efficient basis sets,^{3,4} these widely used methods are limited because the computational time required scales as N^3 , where N is the number of electrons of each spin. This superlinear dependence upon N is a consequence of the Pauli exclusion principle for the electrons expressed in terms of *global* orthonormalization conditions.

Recasting the electronic calculations in an “order N ” form which scales linearly with N has important conceptual and practical consequences. If the full calculation for a large system can be carried out in a time of “order N ,” then the properties of a small region of the large system could be calculated in a time independent of the size of the system. The latter is known to be possible⁵ (except for effects of long range electrostatic potentials which can be handled separately) and can be formulated in terms of Green’s functions, as in the recursion method⁶ or in a density matrix formulation.⁷ Such quantum “order N ” methods will have exactly the same scaling as classical empirical potential methods. Furthermore the independence of different regions allows them to be readily adapted to parallel computation. The practical consequence would be to enable calculations on large systems of great interest in fields such as material science and biology, which are beyond current capabilities.

It is the purpose of this paper to introduce a new “order N ” approach which is immediately applicable to tight-binding methods. Our approach can also be applied to self-consistent plane wave calculations using the methods proposed by Galli and Parrinello,⁸ and is very similar to an approach developed independently by Mauri, Galli,

and Car.⁹ We propose an energy functional which, when freely minimized with no constraints, converges to the exact ground state energy for the electrons and we give conditions under which the desired solution is the global minimum. A key feature of this work is that in the course of minimizing the energy functional, we avoid the orthogonalization step. “Order N ” scaling is achieved by describing the ground state in terms of localized orbitals. We illustrate the method using an orthonormal empirical tight-binding model for silicon, and an *ab initio* molecular dynamics (MD) calculation³ for a 64-atom cell of Si and the Si₃ molecule.

A system with N noninteracting electrons of each spin can be described by N states $\{|\psi_i\rangle\}$ ($i = 1, \dots, N$). The band energy of the system is the trace of the Hamiltonian operator \hat{H} :

$$E = 2 \text{Tr}(\hat{H}) = 2 \sum_{i,j=1}^N S_{ij}^{-1} H_{ji}, \quad (1)$$

where $S_{ij} = \langle \psi_i | \psi_j \rangle$, $H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle$, and the factor of 2 is for spin. The “standard” minimization procedure^{1,2} to find the ground state is to minimize the energy (1) subject to the orthonormalization condition $S_{ij} = \langle \psi_i | \psi_j \rangle = \delta_{ij}$. By explicitly requiring this condition, current methods avoid instabilities; however, this step requires effort proportional to N^2 for ψ ’s expressed in a localized basis and N^3 in a plane wave basis. Ways to improve this scaling have been proposed, but not fully implemented in Refs. 8 and 10.

In our approach we propose a method for unconstrained minimization so that orthonormalization is never explicitly imposed. The approach is suggested by the well-known Lagrange method where one defines the functional

$$\tilde{E} = 2 \left(\sum_{i=1}^N H_{ii} - \sum_{i,j=1}^N \Lambda_{ij} (S_{ij} - \delta_{ij}) \right). \quad (2)$$

In the usual approach, the Lagrange multipliers Λ_{ij} are considered independent variables; minimization of the energy with respect to Λ_{ij} leads to $\delta\tilde{E}/\delta\Lambda_{ij} = 0$, i.e., $S_{ij} = \delta_{ij}$ and $\Lambda_{ij} = H_{ji}$, which is the well-known solution.^{1,2} Our approach is instead to define $\Lambda_{ij} = \langle \psi_j | \hat{H} | \psi_i \rangle$ even for ψ 's which are not at the correct solution. This leads to a functional

$$\tilde{E} = 2 \left(\sum_{i=1}^N H_{ii} - \sum_{i,j=1}^N H_{ji} (S_{ij} - \delta_{ij}) \right) \quad (3)$$

which is defined for all functions ψ_i , $i = 1, \dots, N$, which need not be normalized nor orthonormal. It is apparent that, for a given state defined by the set $\{|\psi_i\rangle\}$, the “modified energy” \tilde{E} will only take the same value of the true band energy E if it is an orthonormal set, in which case the second term in Eq. (3) will vanish. For all other cases it can be shown that $\tilde{E} \geq E$ provided that the Hamiltonian \hat{H} is negative definite (i.e., all the eigenvalues are negative), and therefore the *unconstrained global minimum* of the function \tilde{E} coincides with the minimum of E subject to the orthonormality constraints. We must note that \tilde{E} only has a global minimum in the correct position if all the eigenvalues are negative. If a finite basis set is used, the spectrum of the Hamiltonian is finite and has an upper bound. The energy origin can then be shifted so that all the eigenvalues of \hat{H} can be made negative. In practice, however, the functional \tilde{E} has a *local* minimum provided that the occupied eigenvalues are negative,¹¹ and the energy shift is unnecessary in most cases (as in our example calculations), and, when necessary, can be reduced to force the occupied eigenvalues to be negative. The scheme can therefore also be used if the range of eigenvalues is unrestricted or very wide (as in plane waves). The advantage of this formulation is that no explicit orthogonalization is required, since the constraint term in Eq. (3) forces the wave functions toward orthonormality. We can therefore solve the problem by means of an unconstrained minimization of the function \tilde{E} , for example with a standard conjugate gradient (CG) procedure.

One way of understanding Eq. (3) is that it is the first term in an expansion of $S^{-1} = [\mathbb{1} - (\mathbb{1} - S)]^{-1} = \mathbb{1} + (\mathbb{1} - S) + (\mathbb{1} - S)^2 + \dots$ in Eq. (1), as was shown by Mauri, Galli, and Car.⁹ Thus there exist higher order generalizations of Eq. (3) and stable algorithms can be defined for all approximations which terminate in $(\mathbb{1} - S)^n$, where n is odd.^{9,11} Since S^{-1} is closely related to the density matrix, this expansion is also related to the work of Li, Nunes, and Vanderbilt⁷ and Daw.⁷

In order to fully exploit the present formulation and obtain an “order N ” scaling, we will use the fact that the set of states $|\psi_i\rangle$ that defines the ground state of the system is not unique, since any unitary transformation of these states has the same total energy. In particular, we can describe the ground state by means of orthonormal localized wave functions (LWF's) centered at different

positions. Since, similarly to the Wannier functions, the LWF's decay rapidly with distance (with a power-law in the case of metals and exponentially in insulators¹²), we can, as an approximation, truncate the LWF's beyond a certain cutoff radius R_c from the center. In that case, the number of operations necessary to evaluate the energy \tilde{E} in Eq. (3) is proportional to N , since for each localized orbital ψ_i only the matrix elements H_{ji} and S_{ij} with orbitals ψ_j inside the radius R_c must be calculated (a number that is independent of the system size). The “order N ” scaling is preserved regardless of the type of basis set $\{|\phi_\mu\rangle\}$ utilized to expand the LWF's:

$$|\psi_i\rangle = \sum_{\mu=1}^M C_{i\mu} |\phi_\mu\rangle. \quad (4)$$

If plane wave bases are used, the Hamiltonian and overlap matrix elements and the charge density can be calculated in a small mesh around each LWF as proposed by Galli and Parrinello,⁸ which, using fast Fourier transform algorithms, requires an effort proportional to N . If a localized basis set (e.g., atomic orbitals) is used, each of the LWF's is expanded only in terms of those basis orbitals inside the localization radius R_c , so that for each $|\psi_i\rangle$ there is a limited number of $|\phi_\mu\rangle$ for which $C_{i\mu} \neq 0$. The cost of calculation of each LWF is therefore independent of the size of the system, as is the calculation of each of the nonzero Hamiltonian and overlap matrix elements

$$H_{ij} = \sum_{\mu,\nu} C_{i\mu}^* C_{j\nu} H_{\mu\nu}, \quad (5)$$

$$S_{ij} = \sum_{\mu,\nu} C_{i\mu}^* C_{j\nu} S_{\mu\nu}, \quad (6)$$

where $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$ and $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$ are the Hamiltonian and overlap matrices in the localized orbitals basis.

Expressing Eq. (3) for the energy \tilde{E} as a function of the coefficients $C_{i\mu}$ by means of Eqs. (5) and (6), the problem reduces to an unconstrained minimization of \tilde{E} with respect to $C_{i\mu}$. We have used a conjugate gradient scheme² to perform the minimization. The calculation of the gradients $\partial\tilde{E}/\partial C_{i\mu}^*$ is straightforward, and also scales linearly with N . During the minimization, for each step a direction of search is determined by the conjugate gradient. An *exact* line minimization is then performed in that direction: since \tilde{E} is a quartic form of the coefficients $C_{i\mu}$ (if the Hamiltonian is not self-consistent, or if it is held fixed during the line minimization), the exact minimum in the line can be found calculating \tilde{E} in five different points. This eliminates the need for choosing a “time” step, and assures a quick convergence towards the global minimum.

The method that we have described shows similarities with that proposed by Wang and Teter,¹³ who also use unconstrained localized orbitals expanded as a linear combination of atomic orbitals within the localization range, and perform a CG minimization to find the LWF's. There are, however, two salient differences between the two schemes: (i) They use normalized LWF's and a penalty function to enforce approximate orthogonality. This penalty function is different from the second

term of our Eq. (2) in that it contains a single adjustable parameter λ instead of our Lagrange matrix Λ_{ij} , and is built to minimize the overlap between neighbor functions, whereas our functional has no free parameters and simultaneously achieves normality and orthogonality. The parameter λ must be chosen properly, since the results depend critically on its value. (ii) Wang and Teter restrict the LWF's to the orbitals of the two atoms forming each bond, and as a consequence they must reparametrize the tight-binding interactions in order to obtain close agreement with exact diagonalization results. We do not need to do that, since our energy functional gives an accurate variational approximation to the exact energy when the localization range is large enough (typically two shells of neighbors for silicon). Obviously, our approach requires a larger computational effort, but eliminates any parametrization.

In order to demonstrate the “order N ” scaling of our method, we have calculated the band energy for silicon supercells in the diamond structure with different numbers of atoms. We have used an orthonormal tight-binding model with first-neighbor interactions.¹⁴ In the calculation, the Brillouin-zone (BZ) sampling has been limited to the Γ point. The localized wave functions have been centered at the bonds, and the initial guess for the coefficients $C_{i\mu}$ consisted of bonds between first neighbors (symmetric combinations of the two hybrid orbitals of the atoms forming the bond). In Fig. 1 we show the scaling of CPU time with the number of atoms in the supercell for two different values of R_c , corresponding to LWF's confined to $n = 26$ and $n = 38$ atoms, respectively. We observe that, in both cases, the CPU time increases linearly with the number of atoms in the supercell. Obviously, the CPU time increases with the number of atoms included in each LWF. For comparison, we also include the CPU time for exact diagonalization, which shows clearly the N^3 behavior mentioned before.

The error in the cohesive energy due to the truncation of the LWF's beyond R_c was, for the 216-atom supercell, $\Delta E = 0.11$ eV/atom for $n = 26$ and $\Delta E = 0.08$ eV/atom for $n = 38$. A detailed analysis of the truncation errors in other properties relevant in MD calculations, as forces

and phonon frequencies, is underway and will be published elsewhere.¹¹

We have tested our functional in local orbital, *ab initio* molecular dynamics as formulated by Sankey and Niklewski.³ The main approximations of this formulation are (1) four confined pseudoatomic orbitals (one s and three p 's) per atom; (2) nonlocal, norm-conserving pseudopotentials,¹⁵ and (3) the non-self-consistent Harris functional version of density functional theory.¹⁶ These approximations have been thoroughly tested in a variety of materials, particularly in Si, to which we will restrict our discussion for the rest of this paper. We have used a confinement radius of $5a_B$ for the pseudoatomic orbitals, producing third-neighbor interactions for the diamond structure (29 interacting atoms for each silicon). For our present purposes, we note that using the Harris functional keeps the Hamiltonian fixed, so that, from a formal point of view, this is a very precise analog of empirical tight binding.

We have performed a MD simulation on a 64-atom cell of c -Si. We restrict the BZ sampling to the Γ point. In Fig. 2 we show the convergence to the (exact) electronic energy starting from different sets of initial guesses. The broken lines represent the first MD step of the simulation, for two different choices of the initial guess (i.e., the $C_{i\mu}$ coefficients chosen to start the CG minimization): the dotted line corresponds to a normalized random set of $C_{i\mu}$, whereas the dashed line corresponds to bonds between first neighbors. The robustness of the method is demonstrated by the fact that even a random initial guess needs less than 50 iterations to reach the exact energy with an error of less than $1 \mu\text{eV}/\text{atom}$. However, the use of bonds is more appealing, since the number of iterations necessary to achieve the same accuracy is smaller and it naturally leads to localized wave functions. The solid lines in Fig. 2 represent typical MD steps, in which the initial coefficients $C_{i\mu}$ were simply the solution of the last MD step. These results were obtained without imposing any localization range to the wave functions. If the wave functions are forced to be localized, the curves are very similar to those shown in Fig. 2, but the energy obviously converges to a value higher than the exact en-

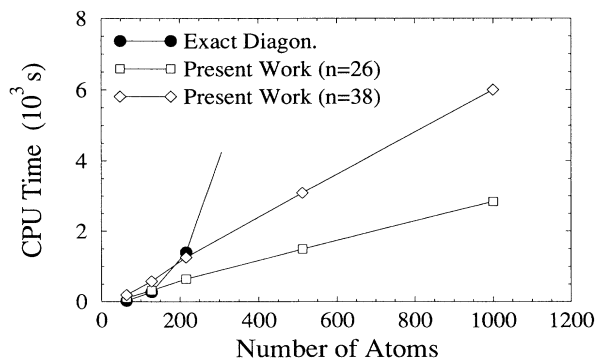


FIG. 1. CPU time (for an IBM RS/6000 model 540) vs number of atoms in the supercell for c -Si, using an empirical tight-binding Hamiltonian. We show the results for exact diagonalization and for our “order N ” scheme with localized wave functions confined to $n = 26$ and $n = 38$ atoms.

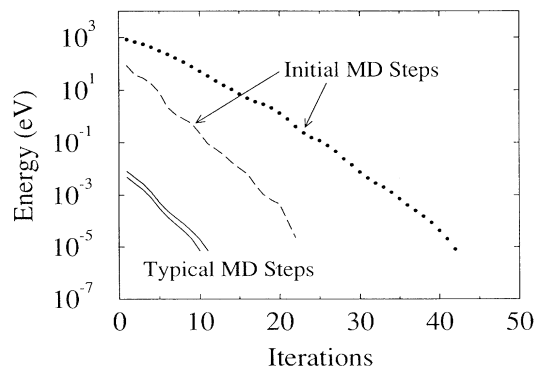


FIG. 2. Energy (relative to the exact value) vs CG iterations for the 64-atom Si cell. Discontinuous lines: initial MD step, with random initial guess (dotted line) and bonds guess (dashed line). Solid lines: typical MD steps, with the solution of the last ionic positions as the input.

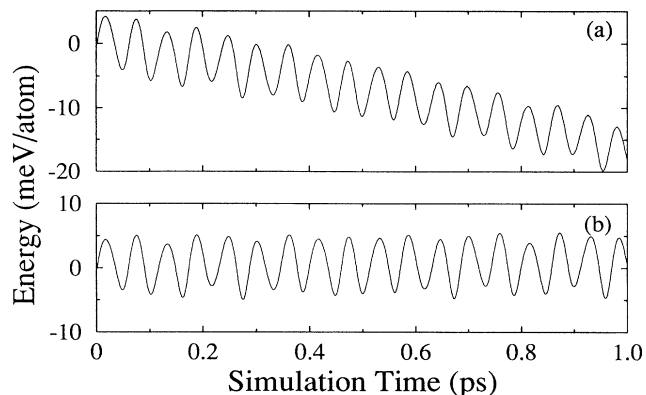


FIG. 3. Deviation from the conservation of the total energy (electronic plus nuclear kinetic) per atom of the Si trimer in a MD run of 1 ps for two different CG relative tolerances: (a) $\tau = 10^{-6}$, (b) $\tau = 10^{-8}$.

ergy, which is more accurate for larger R_c . In that case, the random initial guess is slower to converge than in the nonlocalized calculation, taking some hundreds of iterations.

To demonstrate the quality of the results that the functional can offer in thermal simulations, we have performed a MD simulation of the vibrations of the Si_3 molecule at 150 K during 1 ps, using a time step of 2.0 fs. In this small system the wave functions are not localized, and the results must be the same as those of exact diagonalization. In Fig. 3 we show the deviations as a function

of the simulation time of the conservation of the total energy (electronic energy plus nuclear kinetic energy) for two different values of the CG *relative* tolerance τ (i.e., the ratio of the allowed energy error to the energy value for each atomic configuration). It is possible to conserve the system energy to a very high degree of precision with a sufficiently small CG tolerance. We have calculated the vibrational spectrum with $\tau = 10^{-8}$, and the results are indistinguishable from those obtained from a similar calculation implemented with exact diagonalization. Of course, searches for equilibrium atomic configurations do not require such rigorous convergence in the band energy, and require many fewer CG iterations.

While the present method does not explicitly produce eigenvalues, we note that existing techniques allow the computation of selected eigenvalues or density of states in an “order N ” fashion.^{17,18} This makes it easy to compute the optical gap, for example. These methods can be used as a complement to the present technique.

In conclusion, we have presented a method for solving the electronic structure problem which scales linearly with system size. We have tested it on an orthogonal tight-binding model of Si. The unconstrained minimization approach has been shown to be useful in density functional, LDA MD simulations.

We acknowledge useful conversations with Dr. G. Galli and F. Mauri. This work was supported by NSF Grant No. DMR-89-20538. One of us (P.O.) acknowledges funding from DGICyT (MEC, Spain).

¹ R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

² M. C. Payne *et al.*, *Rev. Mod. Phys.* **64**, 1045 (1992), and references therein.

³ O. F. Sankey and D. J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989).

⁴ C. H. Xu *et al.*, *J. Phys. Condens. Matter* **4**, 6047 (1992).

⁵ V. Heine, R. Haydock, and M. Kelly, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1980); N. Chetty and R. M. Martin, *Phys. Rev. B* **45**, 6074 (1992)

⁶ R. Haydock, V. Heine, and M. J. Kelly, *J. Phys. C* **5**, 2845 (1972); Recent developments using related methods include the “order N ” approaches of S. Baroni and P. Giannozzi, *Europhys. Lett.* **17**, 547 (1992) and W. Zhong, D. Tomanek, and G. F. Bertsch, *Solid State Commun.* **86**, 607 (1993).

⁷ X.-P. Li, R. W. Nunes, and D. Vanderbilt, *Phys. Rev. B* **47**, 10 891 (1993); M. Daw, *ibid.* **47**, 10 895 (1993).

⁸ G. Galli and M. Parrinello, *Phys. Rev. Lett.* **69**, 3547 (1992).

⁹ F. Mauri, G. Galli, and R. Car, *Phys. Rev. B* **47**, 9973 (1993).

¹⁰ T. A. Arias, M. C. Payne, and J. D. Joannopoulos, *Phys. Rev. Lett.* **69**, 1077 (1992).

¹¹ P. Ordejón, D. A. Drabold, M. Grumbach, and R. M. Martin (unpublished).

¹² W. Kohn, *Phys. Rev.* **115**, 809 (1959).

¹³ L. Wang and M. P. Teter, *Phys. Rev. B* **46**, 12 798 (1992).

¹⁴ D. J. Chadi, *Phys. Rev.* **29**, 785 (1984).

¹⁵ G. B. Bachelet, D. R. Hamann, and M. Schluter, *Phys. Rev. B* **26**, 4199 (1982).

¹⁶ J. Harris, *Phys. Rev. B* **31**, 1770 (1985).

¹⁷ D. A. Drabold and O. F. Sankey, *Phys. Rev. Lett.* **70**, 3631 (1993).

¹⁸ G. H. Golub and C. F. Van Loan, *Matrix Computations* (Johns Hopkins University Press, Baltimore, 1983).