

Density-matrix electronic-structure method with linear system-size scaling

X.-P. Li, R. W. Nunes, and David Vanderbilt

Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849

(Received 27 July 1992)

We introduce a method for the solution of the electronic-structure problem in the independent-electron approximation. The method is based upon a variational solution for the density matrix, which is truncated to zero beyond a real-space radius R_c , and becomes exact as $R_c \rightarrow \infty$. Most importantly, the computer time scales only linearly with system size. The method is tested in the context of tight-binding models in one and three dimensions.

Most current methods for solution of the electronic-structure problem suffer from poor scaling with system size. Even the solution of the independent-electron problem, which is required for Kohn-Sham density-functional theory (DFT),¹ scales as $O(N^3)$ for large systems (here, N is the number of atoms in a cluster or supercell). This is true for iterative as well as standard eigensolution methods, and reflects the need to keep the occupied wave functions orthonormal. Just to check orthonormality requires $(N_{\text{bands}})^2 \times N_{\text{basis}}$ operations, and both N_{bands} and N_{basis} scale linearly with N . Current large-scale DFT calculations are rapidly approaching the point where this $O(N^3)$ scaling is the time-limiting consideration. It is already the limiting consideration in tight-binding total-energy (TBTE) methods, which have been very successfully applied to covalently bonded systems:²⁻⁵ such calculations are limited in practice to systems containing up to one or two hundred atoms.

Recently, several workers have begun exploring methods that in principle provide $O(N)$ scaling. One approach is to represent the occupied subspace using Kohn-Sham orbitals that are forced to be localized.^{6,7} Another possibility is to use methods, such as the recursion method,^{8,9} that focus on solving for the electron Green function instead of the wave functions. A related possibility is to solve directly for the density matrix, which can be represented in terms of an energy integral of the Green function. Although methods for direct solution of the density matrix have been available for some time,¹⁰⁻¹³ existing methods do not have $O(N)$ scaling, nor have they been formulated in such a way as to be applicable to extended periodic systems.

In this paper, we introduce a variational method for solving for the electron density matrix. The method takes advantage of the locality of the density matrix in real space to achieve $O(N)$ scaling. Only a single approximation is involved; it is controlled by a parameter R_c , the real-space radius used to truncate off-diagonal elements of the density matrix, and the method becomes exact as $R_c \rightarrow \infty$. The solution of the variational problem involves only an *unconstrained* minimization, which may be performed using conjugate gradients or other standard techniques. The method is ideally suited for incorporation into iterative schemes such as molecular-dynamics simulations. We demonstrate the method by applying it

in the context of tight-binding methods, in particular to a TBTE description of crystalline Si. For this system, we find $R_c = 6.0 \text{ \AA}$ gives good accuracy ($\sim 2\%$) for electronic and structural properties. Moreover, we estimate that the "break-even" system size at which this method becomes computationally superior to standard TBTE is below 100 atoms.

Consider, for definiteness, a tight-binding description of a system formed by replicating a unit (super)cell containing N atoms with M basis orbitals per site. (Self-consistent screening is omitted for now, and spin labels are suppressed.) The density matrix is defined as

$$\rho_{ij} = \sum_n \psi_{n,i}^* \psi_{n,j}, \quad (1)$$

where i and j run over all tight-binding basis orbitals in the system, and n labels occupied eigenstates of the Hamiltonian,

$$\sum_j H_{ij} \psi_{n,j} = \epsilon_n \psi_{n,i}. \quad (2)$$

The standard solution is to transform Eq. (2) to k space and diagonalize the $(NM) \times (NM)$ Hamiltonian matrix on a dense mesh of k points; one can then obtain ρ via Eq. (1). Alternatively, one may try to solve directly for ρ . In either case, the particle number and electronic energy of the system are given by

$$N_e = \text{tr}[\rho] = \sum_i \rho_{ii} \quad (3)$$

and

$$E = \text{tr}[\rho H] = \sum_{ij} \rho_{ij} H_{ji}. \quad (4)$$

Finally, recall that because ρ is a projection operator onto the space of occupied states, it must satisfy the idempotency constraint

$$\rho^2 = \rho. \quad (5)$$

Now we would like to take advantage of the fact that the density matrix is local in real space, in the sense that $\rho_{ij} \rightarrow 0$ as $R_{ij} \rightarrow \infty$ (here, R_{ij} is the distance between basis orbitals i and j). The decay is power law in metals (R^{-d} in d dimensions), and exponential in insulators; in the latter case, the decay length is related to that of the Wan-

nier functions.¹⁴ Therefore we are motivated to develop a method in which the central approximation is to set $\rho_{ij}=0$ for $R_{ij}>R_c$, where R_c is chosen large enough to get a good approximation to the true ρ . By translational symmetry, $\rho_{ij}=\rho_{i'j'}$ (where both indices on the right have been translated by a common lattice vector). Thus, the unique elements of ρ are enumerated by letting i run over the NM orbitals in a single unit cell, for each i, j runs over a number LM of orbitals on the L sites contained within a sphere of radius R_c centered on site i . Consequently, the number of degrees of freedom is just $N \times L \times M^2$, or $O(N)$.

Thus, it is tempting to imagine that one could just minimize Eq. (4) with respect to the nonzero elements ρ_{ij} using steepest descents or other standard methods, subject to the constraint of fixed N_e , Eq. (3). Actually, it would be more convenient to work at fixed chemical potential (Fermi level) μ , and minimize the grand potential

$$\Omega = E - \mu N_e = \text{tr}[\rho(H - \mu)], \quad (6)$$

thereby eliminating the constraint on N_e . If this worked, it would provide a very simple $O(N)$ solution. However, the idempotency constraint (5) must not be forgotten. If Eq. (6) is minimized without constraint, eigenvalues λ_ρ of ρ corresponding to states below the Fermi level ("occupied states") will tend to $+\infty$, while those lying above μ ("unoccupied states") will tend to $-\infty$. On the contrary, idempotency requires that the eigenvalues λ_ρ should all be either 1 or 0 (for occupied or unoccupied states respectively). Unfortunately, just to compute the eigenvalues of ρ is again an $O(N^3)$ operation, so nothing has been gained as yet.

We observe, however, that it would be sufficient to constrain the λ_ρ to lie on the interval $[0,1]$. Then the minimization procedure would naturally drive $\lambda_\rho \rightarrow 1$ and $\lambda_\rho \rightarrow 0$ for occupied and unoccupied states, respectively. However, at first sight it is not at all obvious how this constraint can be imposed in such a way as to fulfill the potential for $O(N)$ scaling.

The key to our approach is the following trick for imposing the constraint $\lambda_\rho \in [0,1]$. We make use of the "purification transformation" discussed by McWeeny:¹⁰ If ρ is a trial density matrix which is nearly idempotent, then

$$\tilde{\rho} = 3\rho^2 - 2\rho^3 \quad (7)$$

is a *purified* version which is more nearly idempotent. The function $f(x) = 3x^2 - 2x^3$ is sketched in Fig. 1. Note that an idempotent matrix is invariant under this transformation ($\tilde{\rho} = \rho$ if $\rho^2 = \rho$), which is reflected in the fact that $f(0) = 0$ and $f(1) = 1$. Moreover, a matrix which is nearly idempotent ($\lambda_\rho = 1 + \delta$ or δ , $|\delta| \ll 1$) transforms into a matrix which is more nearly idempotent [$\lambda_{\tilde{\rho}} = 1 - O(\delta^2)$ or $+O(\delta^2)$], because f is stationary at 1 and 0. Most importantly, because f is concave down at 1 and up at 0, the eigenvalues $\lambda_{\tilde{\rho}}$ are constrained to lie in the interval $[0,1]$, as long as the λ_ρ remain clustered around 1 and 0. (In fact, this will be true as long as $\lambda_\rho \in [-0.5, 1.5]$.)

This observation suggests the following approach: we

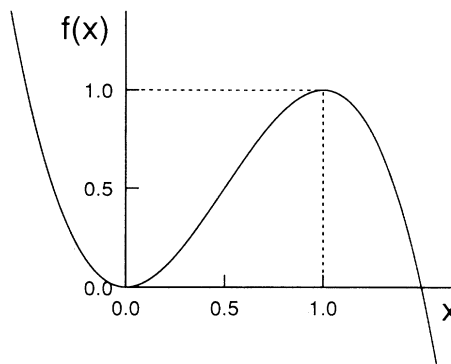


FIG. 1. The function $f(x) = 3x^2 - 2x^3$.

think of $\tilde{\rho}$ in Eq. (7) as the *physical* density matrix (i.e., $\text{tr}[\tilde{\rho}A]$ gives the physical expectation value of operator A), whereas ρ is a *trial* density matrix whose elements constitute our variational degrees of freedom. That is, we minimize

$$\Omega = \text{tr}[\rho(H - \mu)] = \text{tr}[(3\rho^2 - 2\rho^3)(H - \mu)] \quad (8)$$

with respect to ρ , taking $\rho_{ij} = 0$ for $R_{ij} > R_c$. *No constraint is explicitly imposed.* We seek a local minimum of Ω at which the eigenvalues of ρ and $\tilde{\rho}$ corresponding to occupied and unoccupied states are clustered around 1 and 0, respectively. The minimization is accomplished by starting with an initial guess for ρ (typically $\rho_{ij} = \frac{1}{2}\delta_{ij}$), and then iteratively calculating the gradient

$$\frac{\delta\Omega}{\delta\rho} = 3(\rho H' + H'\rho) - 2(\rho^2 H' + \rho H'\rho + H'\rho^2), \quad (9)$$

where $H' = H - \mu$, for use in steepest descents, conjugate gradients, or some other minimization algorithm. This constitutes our approach. We make the following remarks about our method.

(1) The minimum is *not* a global minimum: there are *runaway solutions* corresponding to $\rho \rightarrow +\infty$ for states above μ , and $\rho \rightarrow -\infty$ for states below μ . However, if we start from $\tilde{\rho} = \rho = \frac{1}{2}$, we may hope that the system evolves under minimization to the desired metastable local minimum, and does not find its way onto the runaway solutions. Our experiences to date indicates that this is the case in practice.

(2) Assuming (1) is true, we have $\lambda_{\tilde{\rho}} \in [0,1]$ as desired, so $\Omega \geq \Omega_{\text{exact}}$, i.e., we obtain a *variational upper bound* to the exact energy.

(3) The method becomes exact, i.e., $\Omega \rightarrow \Omega_{\text{exact}}$, as $R_c \rightarrow \infty$.

(4) First-order errors in ρ (i.e., first-order deviations of λ_ρ from 0 or 1) result in *second-order errors* in $\tilde{\rho}$ and Ω . Thus $\Omega - \Omega_{\text{exact}} \propto (\delta\rho)^2$.

(5) The method should work best for insulators, for which ρ will be relatively short ranged.

(6) The method requires no integral over an energy contour, unlike recursion methods.^{8,9}

(7) The time-dominant step in the method is the multiplication of banded matrices, e.g., obtaining ρ^2 from ρ . However, in practice it turns out that quantities such as

ρ^2 need only be calculated up to a radius $R_c + R_H$ (the latter being the range of the Hamiltonian). The overall computer time scales as $N \times L^2 \times M^3$, assuming that the number of iterations required to obtain convergence is independent of system size.

Items (2)–(4) above express the fact that the method is a variational one. This has several useful consequences. For example, it implies that forces may be calculated by a Hellmann-Feynman expression. In general, a derivative of the grand potential Ω with respect to a parameter λ (e.g., an atomic coordinate) at fixed μ can be written

$$\frac{d\Omega}{d\lambda} = \frac{\partial\Omega}{\partial\rho} \frac{d\rho}{d\lambda} + \frac{\partial\Omega}{\partial H} \frac{dH}{d\lambda}, \quad (10)$$

but the first term vanishes at the variational solution, so that this “force” is given by

$$\frac{d\Omega}{d\lambda} = \text{tr} \left[\tilde{\rho} \frac{dH}{d\lambda} \right]. \quad (11)$$

The variational nature of our scheme should also make it particularly easy to implement as part of iterative structural-relaxation or molecular-dynamics calculations. Molecular dynamics could be implemented either following the Car-Parrinello fictitious Lagrangian method,¹⁵ treating the ρ_{ij} as classical electron degrees of freedom, or simply by converging the conjugate-gradients solution adequately at each time step.

We first apply the method to a one-dimensional (1D) tight-binding chain at half filling. We choose R_c such that only on-site and nearest-neighbor elements appear in the trial ρ . The energy Ω was found to be minimized at $\rho_{ii} = 0.5$ and $\rho_{i,i+1} = \frac{1}{2}\sqrt{3}$. The variational energy is $\Omega = -1/\sqrt{3} = -0.577$, which differs by only 9% from the exact value $-2/\pi = -0.637$. The accuracy is remarkably good, considering that the system is metallic, and the most extreme truncation of ρ has been adopted. In Fig. 2, ρ and $\tilde{\rho}$ are plotted in k space, where they are diagonal, and compared with ρ_{exact} . It is clear that the spectrum of $\tilde{\rho}$ is bounded to the interval $[0,1]$, while that of ρ is not, and that $\tilde{\rho}$ is a better approximation to the true density matrix than is ρ .

We have also studied a corresponding model of a 1D insulator by letting the on-site energy alternate between

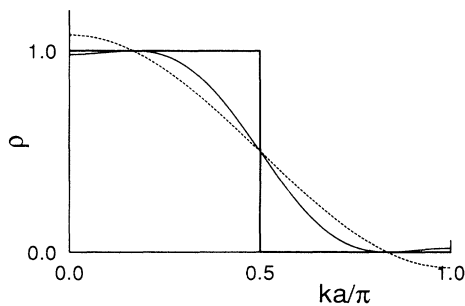


FIG. 2. Density matrix in k space for one-dimensional tight-binding metal at half filling. Heavy solid line, exact density matrix; dashed line, trial density matrix ρ ; light solid line, physical density matrix $\tilde{\rho}$.

TABLE I. Ratio of minimized energy to exact energy for the one-dimensional tight-binding insulator model for R_c containing up to nearest and up to second-nearest neighbors.

t/Δ	E/E_{exact} (nearest neighbor)	E/E_{exact} (second-nearest neighbor)
0.5	0.985	0.999
1.0	0.950	0.988
1.5	0.929	0.974
2.0	0.918	0.961
2.5	0.912	0.951
3.0	0.909	0.943

$-\Delta$ and Δ on consecutive sites. The model is characterized by a dimensionless parameter $|t/\Delta|$, where t is the nearest-neighbor hopping parameter (we take $\mu=0$). We solved this model using up to nearest-neighbor, and up to second-nearest-neighbor, matrix elements in ρ . The accuracy of the computed electronic energy is presented in Table I. Naturally, the accuracy is better than for the metallic model, and better for the second-nearest-neighbor than for the nearest-neighbor approximation.

We now turn to a discussion of the application of the method to the case of a TBTE description of Si using a minimal sp^3 basis.^{2,5} the chemical potential was fixed at 0.5 eV above the valence-band maximum.¹⁶ The minimization was accomplished using the conjugate-gradients scheme. We have calculated a variety of electronic and structural properties of bulk Si as a function of R_c using our method, and compared them to an “exact” calculation carried out by conventional diagonalization of the Hamiltonian on a dense mesh of k points.

The results are shown in Fig. 3, where the percentage error is plotted on a log scale vs the radius R_c used to truncate ρ . Each plotted point represents the addition of a complete shell of neighbors. It can be seen that the electron number N_e converges extremely rapidly to the correct value of four electrons per site. The cohesive energy converges less rapidly, but is already within $\sim 10\%$ at the second-nearest-neighbor shell ($R_c = 4.0 \text{ \AA}$, $L = 17$)

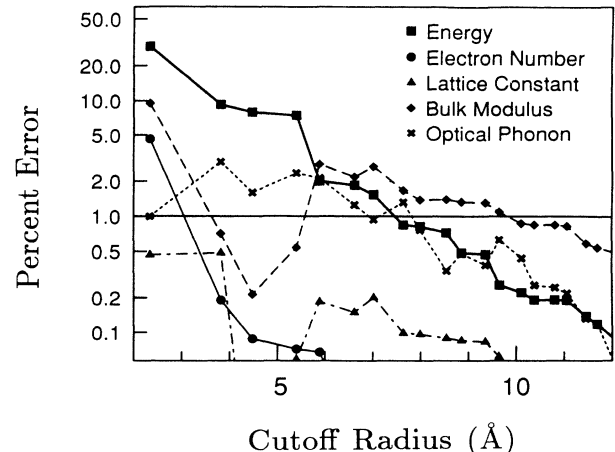


FIG. 3. Fractional errors introduced by current method, on a log scale, vs the cutoff radius R_c , for the TBTE model of Si.

and $\sim 2\%$ at the fifth-nearest-neighbor shell ($R_c = 6.0 \text{ \AA}$, $L = 47$). Generally, all the properties are converged to within $\sim 2\%$ by the time the fifth-nearest-neighbor shell is included; since this is probably better than the intrinsic accuracy of the TBTE method, we judge this to be a good approximation. (The accuracy of the approximation improves noticeably when the fifth-nearest-neighbor shell is included. Inspection of the exact density matrix also reveals a large amplitude for fifth-nearest neighbors, which correspond to third-nearest neighbors along the zig-zag chains running in the $\langle 110 \rangle$ directions. This is consistent with previous indications of the importance of interactions along these chains for screening¹⁷ and phonon^{17,18} properties.)

As explained above, the computer time for the present scheme scales as $N \times L^2 \times M^3$. We have timed the present code (using $L = 47$) against a standard diagonalization at a single k point for large supercells. We assume that ten iterations through Eq. (9) are needed to get adequate convergence (this is quite conservative in the context of molecular dynamics, where extrapolation from previous time steps can be used to get a good starting guess). We find that the break-even point at which this method becomes more efficient than the conventional one occurs at only $N \simeq 90$ atoms. Thus, we expect our method to find immediate use in such calculations.

We have recently become aware of the development of a very closely related method by Daw,¹⁹ who has derived an iterative scheme for calculating the density matrix based on the idea of evolving the density matrix in temperature from $T = \infty$ to $T = 0$. In the case where the density matrix is not truncated to finite range, Daw's method precisely corresponds to a steepest-descent implementation of our method. However, the two methods are not identical when truncation beyond R_c is included; in particular, Daw's approach is not variational in this case. For this reason, we believe our method to be preferable.

While we have not included self-consistent screening above, it can easily be added. For example, one can re-

verse Eq. (8) according to

$$\Omega^{\text{eff}} = \Omega + \frac{1}{2} \sum_{ijkl} U_{ij,kl} \tilde{\rho}_{ij} \tilde{\rho}_{kl} . \quad (12)$$

Then Eq. (9) is still valid if one replaces H in $H' = H - \mu$ by

$$H_{ij}^{\text{eff}} = H_{ij} + \sum_{kl} U_{ji,kl} \tilde{\rho}_{kl} . \quad (13)$$

For the simple case of an on-site Hubbard U , as used in some TBTE approaches,⁴ this procedure certainly introduces no special problems. Likewise, exchange-correlation terms, being local in real space, are easily included. On the other hand, if the full long-range Coulomb interaction is kept, evaluation of Eq. (13) appears to entail $O(N^2)$ operations; however, it is possible that $O(N)$ scaling could be restored by using fast-Fourier-transform or related techniques to handle the long-range tail. In fact, we are currently exploring the feasibility of extending the present method to perform DFT calculations using a real-space mesh or localized-orbital basis.

In summary, we have proposed a method for solution of the electronic-structure problem which is based on a direct solution for the density matrix. The approach is variational, and becomes exact in the limit that the real-space radius used to truncate off-diagonal elements of the density matrix is increased. The method scales only linearly with the system size, and should lend itself to efficient implementation on parallel computer architectures. We expect the method to find immediate use in TBTE calculations, and prospects for application of this scheme to *ab initio* DFT calculations are currently under investigation.

This work was supported by NSF Grant No. NMR-91-15342. R. W. Nunes acknowledges the support from the CNPq-Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil. We wish to thank S. Baroni and M. Daw for useful discussions.

¹W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

²D. J. Chadi, Phys. Rev. B **19**, 2074 (79); **41**, 10 595 (1990).

³D. Tomañek and M. A. Schluter, Phys. Rev. B **36**, 1208 (1987).

⁴O. Alerhand, J. D. Joannopoulos, and E. J. Mele, Phys. Rev. B **39**, 12 622 (1989).

⁵C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **39**, 8586 (1989); **45**, 12 227 (1992).

⁶G. Galli and M. Parrinello, Bull. Am. Phys. Soc. **36**, 835 (1991).

⁷W. Yang, Phys. Rev. Lett. **66**, 1438 (1991).

⁸R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1975).

⁹S. Baroni and P. Giannozzi, Europhys. Lett. **17**, 547 (1992).

¹⁰R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

¹¹B. Kirtman and C. de Melo, J. Chem. Phys. **75**, 4592 (1981).

¹²C. E. Dykstra, *Ab Initio Calculation of the Structures and*

Properties of Molecules (Elsevier, New York, 1988), Chap. 9.

¹³K.-P. Bohnen and S. C. Ying, Phys. Rev. B **22**, 1806 (1980).

¹⁴W. Kohn, Phys. Rev. **115**, 809 (1959); Phys. Rev. B **7**, 4388 (1973).

¹⁵R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

¹⁶The results are found to be quite insensitive to the position of the chemical potential as long as it is deep in the gap, as expected for a semiconductor. More generally, the chemical potential can be adjusted iteratively to obtain the desired electron number N_e ; our tests indicate that this procedure converges rapidly.

¹⁷E. O. Kane, Phys. Rev. B **31**, 5199 (1985); **31**, 7865 (1985).

¹⁸R. Tubino, L. Piseri, and G. Zerbi, J. Chem. Phys. **56**, 1022 (1972).

¹⁹M. Daw (private communication).