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Generalization of the density-matrix method to a nonorthogonal basis

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We present a generalization of the Li, Nunes, and Vanderbilt density-matrix method to the case of a nonorthogonal set of basis functions. A representation of the real-space density matrix is chosen in such a way that only the overlap matrix, and not its inverse, appears in the energy functional. The generalized energy functional is shown to be variational with respect to the elements of the density matrix, which typically remains well localized.

Recently, the search for so-called order-N methods (for which the computational effort scales only linearly with system size N) has led to the development of a number of real-space approaches to the solution of the electronic structure problem.[1–4] These are based either on the use of a localized, Wannier-like representation of the occupied subspace,[3,4] or on the locality of the real-space density matrix.[1,2] In the latter case, an energy functional is defined such that the variational degrees of freedom are the matrix elements of the density matrix in a real-space-localized set of orthonormal orbitals. However, in many situations it is more convenient to work with a nonorthogonal basis (e.g., linear combination of atomic orbitals calculations using Gaussian orbitals). For that reason, it becomes desirable to extend the density-matrix based approaches to those cases.

In this paper, we show how the approach proposed by Li, Nunes, and Vanderbilt (LNV) (Ref. 1) can be extended to a nonorthogonal basis. This is done by introducing a quantity $\bar{\rho} = S^{-1}\rho S^{-1}$ (where S is the overlap matrix $S_{ij} = \langle \phi_i \mid \phi_j \rangle$, and $\rho = \langle \phi_i \mid \hat{\rho} \mid \phi_j \rangle$ is the density matrix) as an alternative representation for the density operator, which is shown to have similar localization properties as ρ. Using $\bar{\rho}$, we write a generalized expression for the total energy in which the inverse overlap matrix S^{-1} does not appear explicitly; moreover, the generalized-density-matrix (GDM) functional is shown to be variational with respect to $\bar{\rho}$.

First, we briefly review the LNV approach as applied to an orthonormal basis.[1] For simplicity we consider a tight-binding description of a system formed by replicating a unit (super)cell containing N atoms with M basis orbitals per site. For the moment we assume that the basis orbitals $\{\phi_i\}$ are orthonormal, i.e., $\langle \phi_i \mid \phi_j \rangle = \delta_{ij}$. For the eigenstates of the Hamiltonian, $\hat{H} \mid \psi_n \rangle = \epsilon_n \mid \psi_n \rangle$, we write

$$\mid \psi_n \rangle = \sum_i c_{ni} \mid \phi_i \rangle \ . \tag{1}$$

The density matrix is defined as

$$\rho_{ij} = \sum_n c^*_{ni} \, c_{nj} \ , \tag{2}$$

where i and j run over all tight-binding basis orbitals in the system and n runs over the occupied eigenstates of H. Recall that ρ is a projection onto the subspace of occupied states, and therefore it obeys the idempotency requirement $\rho^2 = \rho$.

As discussed in Ref. 1, both the standard **k**-space diagonalization of H and the minimization of the grand potential $\Omega = \mathrm{tr}\,[\rho\,(H-\mu)]$ (μ is a chemical potential used to eliminate the particle number constraint $N_e = \mathrm{tr}\,[\rho]$) with respect to ρ amount to an $O(N^3)$ operation. In the latter case this a result of the idempotency constraint.

In order to achieve an $O(N)$ solution to the problem, LNV use the following strategy. First, they take advantage of the fact that the density matrix is local in real space[5–7] (in the sense that $\rho_{ij} \to 0$ as $R_{ij} \to \infty$, where R_{ij} is the distance between basis orbitals ϕ_i and ϕ_j), and introduce a trial density matrix X which is set to zero for $R_{ij} > R_c$ (R_c is chosen large enough to get a good approximation to the true density matrix). Second, no idempotency constraint is explicitly imposed; rather, they make use of the purification transformation proposed by McWeeny:[8]

$$\rho = 3X^2 - 2X^3 \ . \tag{3}$$

This transformation is such that a matrix which is nearly idempotent ($\lambda_X = 1+\delta$ or δ, $|\delta| \ll 1$, where λ_X is an eigenvalue of X) transforms into a matrix which is more nearly idempotent [$\lambda_\rho = 1 - O(\delta^2)$ or $+O(\delta^2)$]. Then, ρ is treated as a physical density matrix (i.e., $\mathrm{tr}[\rho A]$ gives the physical expectation value of operator A) and X as a trial density matrix whose elements constitute the variational degrees of freedom to be determined by minimization of the grand potential,

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$$\Omega = \mathrm{tr}\left[\rho\left(H-\mu\right)\right] = \mathrm{tr}\left[\left(3X^2-2X^3\right)\left(H-\mu\right)\right], \quad (4)$$

with respect to X. As shown in Ref. 1, Ω in Eq. (4) has a variational local minimum (i.e., $\Omega \geq \Omega_{\mathrm{exact}}$) at which ρ is idempotent to second order. Since the number of degrees of freedom per atom is fixed by R_c and no diagonalization or orthonormalization step is performed, the above procedure amounts to an $O(N)$ solution to the problem.

We now extend the LNV energy functional to a nonorthogonal basis $\{\phi_i\}$, with the overlap matrix given by $S_{ij} = \langle\phi_i \mid \phi_j\rangle$. In what follows, we use $X_{ij} = \langle\phi_i \mid \hat{\rho} \mid \phi_j\rangle$ for the trial density matrix in the nonorthogonal basis, to be consistent with the notation introduced above. The eigenstates of $\hat{H}$ are given by Eq. (1) and the coefficients $\{c_{ni}\}$ are determined by solving the secular equation,

$$\sum_j \left(H_{ij} - \epsilon_n S_{ij}\right) c_{nj} = 0 \,, \quad (5)$$

where $H_{ij} = \langle\phi_i \mid \hat{H} \mid \phi_j\rangle$.

Let $\mathbf{C}$ be the matrix defined by $\mathbf{C}_{in} = c_{ni}$ (i.e., $\mathbf{C}$ has the eigenvectors $\{\psi_n\}$ as its columns); it then follows that $\mathbf{C}$ defines a congruence transformation that diagonalizes H, S and X simultaneously:

$$\begin{aligned} \mathbf{C}^\dagger H \mathbf{C} &= \Lambda \,, \\ \mathbf{C}^\dagger S \mathbf{C} &= I \,, \\ \mathbf{C}^\dagger X \mathbf{C} &= X_H \,, \end{aligned} \quad (6)$$

where I is the identity matrix, and $\Lambda_{mn} = \epsilon_n \delta_{mn}$ and $(X_H)_{mn} = \theta(\mu - \epsilon_n)\delta_{mn}$ are, respectively, the matrices of $\hat{H}$ and $\hat{\rho}$ in the basis $\{\psi_n\}$ of the eigenvectors of H [$\theta(x)$ is the theta function]. From Eq. (6), we have

$$S^{-1} = \mathbf{C}\mathbf{C}^\dagger \,. \quad (7)$$

Using Eqs. (6) and (7), and $\rho_H = 3X_H^2 - 2X_H^3$ following Eq. (3), we can now generalize Eq. (4) as follows:

$$\begin{aligned} \Omega &= \mathrm{tr}[\rho_H(\Lambda-\mu)] \\ &= \mathrm{tr}[(3S^{-1}XS^{-1}XS^{-1} - 2S^{-1}XS^{-1}XS^{-1}XS^{-1})H'], \end{aligned} \quad (8)$$

where $H' = H - \mu S$.

As a matter of convenience, we would like to eliminate S^{-1} from the energy expression in favor of S. This can be accomplished by defining the two quantities,

$$\begin{aligned} \bar{X} &= S^{-1}XS^{-1} \,, \\ \bar{\rho} &= 3\bar{X}S\bar{X} - 2\bar{X}S\bar{X}S\bar{X} \,, \end{aligned} \quad (9)$$

as alternative representations[9] for the trial and physical density matrices, respectively. We observe that $\bar{X}$ is a more natural representation of the density operator, in the sense that Eq. (2) still holds, i.e., $\bar{X}_{ij} = \sum_n c_{ni}^* c_{nj}$, whereas $X_{ij} = \sum_n \sum_{kl} S_{ik} c_{nk}^* c_{nl} S_{lj}$. Furthermore, the expectation value of any operator is given by $\langle\hat{A}\rangle = \mathrm{tr}\,[\bar{X}A]$, where $A_{ij} = \langle\phi_i \mid \hat{A} \mid \phi_j\rangle$.

In terms of $\bar{X}$ and $\bar{\rho}$ the particle number becomes

$$N_e = \mathrm{tr}\,[\bar{\rho}S] = \mathrm{tr}\left[\left(3\bar{X}S\bar{X} - 2\bar{X}S\bar{X}S\bar{X}\right)S\right] \,, \quad (10)$$

and the energy functional is written

$$\Omega = \mathrm{tr}\,[\bar{\rho}H'] = \mathrm{tr}\left[\left(3\bar{X}S\bar{X} - 2\bar{X}S\bar{X}S\bar{X}\right)H'\right] \,. \quad (11)$$

To show that Eq. (11) is variational with respect to $\bar{X}$, we note the following. At the solution, the density matrix must obey the idempotency constraint $X_H^2 = X_H$, which in the new representation is expressed as

$$\bar{X}S\bar{X} = \bar{X} \,; \quad (12)$$

furthermore, it must also commute with the Hamiltonian, i.e, $X_H\Lambda = \Lambda X_H$. In terms of $\bar{X}$, we have

$$S\bar{X}H = H\bar{X}S \,. \quad (13)$$

Equations (12) and (13) can easily be obtained by applying the transformation generated by $\mathbf{C}$ to the more familiar expressions in the basis $\{\psi\}$, and then using $X = S\bar{X}S$. From Eqs. (12) and (13), it follows immediately that the variational gradient

$$\begin{aligned} \frac{\delta\Omega}{\delta\bar{X}} &= 3\left(S\bar{X}H' + H'\bar{X}S\right) \\ &\quad -2\left(S\bar{X}S\bar{X}H' + S\bar{X}H'\bar{X}S + H'\bar{X}S\bar{X}S\right) \end{aligned} \quad (14)$$

vanishes at the solution, thus showing that Ω is variational with respect to $\bar{X}$.

We consider now a derivative of the grand potential Ω (at fixed μ) with respect to a parameter λ (e.g., an atomic coordinate):

$$\frac{d\Omega}{d\lambda} = \frac{\partial\Omega}{\partial\bar{X}}\frac{d\bar{X}}{d\lambda} + \frac{\partial\Omega}{\partial H}\frac{dH}{d\lambda} + \frac{\partial\Omega}{\partial S}\frac{dS}{d\lambda} \,. \quad (15)$$

The first term vanishes at the solution, due to the variational nature of Ω, so that this force is given by

$$\frac{d\Omega}{d\lambda} = \mathrm{tr}\left[\bar{\rho}\frac{dH'}{d\lambda}\right] + \mathrm{tr}\left[\bar{X}H'\bar{X}\left(3-4S\bar{X}\right)\frac{dS}{d\lambda}\right] \,. \quad (16)$$

Equations (10), (11), (14), and (16) constitute the central results of this work. Note that the standard LNV scheme is recovered from these equations upon substituting $S_{ij} = \delta_{ij}$.

Before proceeding further, let us comment on the real-space-localization properties of S and S^{-1}. We are interested in the case where the basis orbitals are localized in real space, and therefore S is also localized. It can be shown that S^{-1} is then exponentially localized,[10,11] with a decay length that depends on the spread of the eigenvalues of S. If S is an ill-conditioned matrix, i.e., $\max(\lambda_S)/\min(\lambda_S) \gg 1$ [$\max(\lambda_S)$ and $\min(\lambda_S)$ are, respectively, the maximum and minimum eigenvalues of S], then S^{-1} has a long decay length.

The advantage of using Eq. (11) is that it eliminates the need to compute S^{-1}. A possible concern, in making use of the current approach, may be that the matrix $\bar{X}$ may decay more slowly with distance than would the density matrix expressed in terms of orthogonal ba-

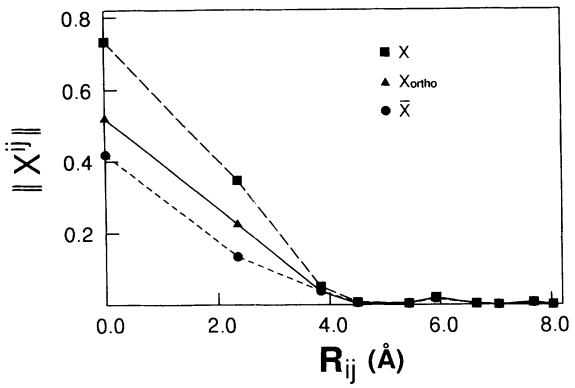

FIG. 1. X, $\bar{X}$, and X_{ortho}, as functions of the distance R_{ij} between two basis orbitals, for the tight-binding model of the text.

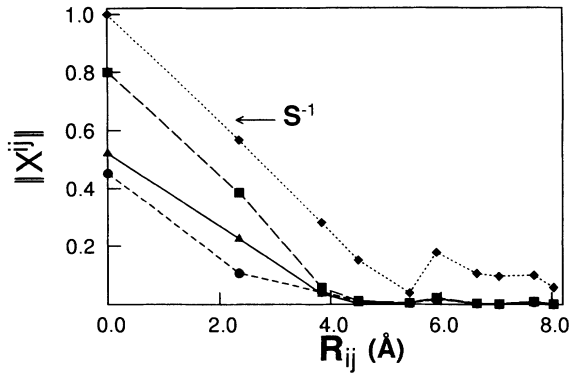

FIG. 2. Same as before for ill-conditioned S ($k = 1.35$); long range behavior of S^{-1} is also shown.

sis orbitals. This may happen when S is ill-conditioned, such that S^{-1} has a longer exponential decay than X.[12] When this is the case, it becomes necessary to increase the cutoff radius R_c to obtain the same level of accuracy. However, as we discuss below, our numerical evidence suggests that X and $\bar{X}$ will, in general, have very similar decay as each other, and very similar to that of X for an orthogonal basis, and therefore the transformation leading from Eq. (4) to Eq. (11) typically preserves the localization properties of Ω. Note also that the presence of S in Eq. (11) [as compared to Eq. (4)] does not affect the linear scaling of the method, since S is as localized as H in a local basis.

Next, we present some numerical tests for a three-dimensional tight-binding (TB) model for silicon, to illustrate the localization properties of X and $\bar{X}$. We use the universal TB model proposed by Harrison in its extension to a nonorthogonal basis.[13] The matrix elements of S in a minimal sp^3 basis are given by $S_{ll'n} = 2kV_{ll'n}(\epsilon_l + \epsilon_{l'})^{-1}$, where l and l' run over s and p orbitals and n indicates the type (σ or π) of interaction. The $V_{ll'n}$'s are the universal TB parameters introduced by Harrison,[13] ϵ_l are atomic on-site energies and k is an adjustable parameter. For the Hamiltonian matrix we have $H_{ll'n} = (1 + k - S_2^2)V_{ll'n}$, where S_2 is the overlap between two sp^3 hybrids $S_2 = (S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma})/4$. Both H and S are restricted to first neighbors only. For simplicity, we set $k = 1$ which is very close to the value 1.042 commonly used for silicon.

In Fig. 1, we show the behavior of X and $\bar{X}$ as functions of the distance R_{ij}, between two orbitals ϕ_i and ϕ_j. Plotted is the norm $||X^{ij}|| = [\sum_{\alpha\beta} |X^{ij}_{\alpha\beta}|^2/N]^{1/2}$, where α and β run over $\{s, p_x, p_y, p_z\}$ and $N = 4$ is the block dimension. Also shown is the behavior of X_{ortho} for orthogonal orbitals, which is obtained by setting $k = 0$ in the TB model. It can be seen that within a distance $R_{ij} = 8.00$ Å, both X and $\bar{X}$ as well as X_{ortho} decay to $\sim 2.0\%$ of their values at the origin.

We have also calculated X and $\bar{X}$ for a basis with an ill conditioned (almost singular) S, by setting $k = 1.35$ (this implies a large overlap between neighboring orbitals). The results are shown in Fig. 2. Also shown is the long range behavior of S^{-1} [S^{-1} has been normalized to its value at the origin, $S^{-1}(0) = 3.96$]. Although S^{-1} has a very long decay length in this case, X and $\bar{X}$ still decay very similarly as X_{ortho}. The point here is to show that, provided that the basis is sufficiently localized, $\bar{X}$ can be as localized as X_{ortho} for an orthonormal basis, even when S^{-1} is ill conditioned. In any case, by using Eq. (11), the convergence of both quantities, $\hat{\rho}$ and S^{-1}, is built into a single quantity $\bar{X}$, and is controlled by a single parameter R_c.

Because of the fact that S is of the same range as H (i.e., $R_S = R_H$), the GDM scheme preserves the $O(N)$ scaling of the original method. Nevertheless, the presence of S in Eq. (11) implies an increase in the scaling prefactor. In the orthonormal case, the time-dominant step involves the calculation of a product $X_{jk}(XH)_{ki}$ of two matrices of range R_c and $R_c + R_H$, out to a radius $R_{ij} \leq R_c$. In the nonorthonormal case, the corresponding dominant operation involves two matrices $(SX)_{jk}(SXH)_{ki}$ of range $R_c + R_H$ and $R_c + 2R_H$, calculated also up to the radius R_c [see Eq. (14)]. In order to estimate the slowdown factor, we determined the ratio of the number of terms that contribute in each case, which was found to be 3.6 using the R_c and R_H of Ref. 1.

In summary, we have presented a generalization of the LNV density-matrix approach to the case of a nonorthogonal basis. An alternative real-space representation of the density operator is introduced, which is argued to have similar localization properties as the conventional density matrix, as suggested by the numerical evidence presented. In this generalized energy functional, only the overlap matrix S appears explicitly (as opposed to S^{-1}). The new functional is shown to retain its variational property and its linear scaling with system size.

We recently became aware of an alternative derivation of the GDM functional proposed by P. Ordejón and collaborators.[14]

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