Rapidly Convergent Bond Order Expansion for Atomistic Simulations

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An $O(N)$ and rapidly convergent method for calculating the bond order potential and forces for the atomistic simulation of covalent systems is described. A derivation of a novel many-atom expansion, which allows the Green's functions not only to handle the symmetry problem correctly but also to retrieve equivalence between the site-diagonal and intersite descriptions for the bond energy, is given. The convergence of the bond orders and bond energies is demonstrated for d-valent transition metals.

Atomistic simulation is regarded as a powerful approach to understanding structural properties and processes of condensed matter. In order to deal with very large, low symmetry and covalently bonded systems, the central problem has been to develop *efficient, real-space,* and *accurate* methods for calculations of binding energy and interatomic forces. Recently, several groups have proposed $O(N)$ methods [1–3], in which the number of arithmetic operations grows linearly with system size N, to bring very large systems within our reach.

It is well known that the Lanczos tight binding recursion method (LTBRM) [4,5] is a real-space, efficient $O(N)$ method, which represents the site-diagonal (SD) Green's functions $G^{I,I}$ in continued fraction form, and also the intersite (IS) Green's functions $G^{I,J}$ directly from the difference, $\frac{1}{2}(G^{I+J,I+J} - G^{I-J,I-J})$, between the continued fractions associated with bonding and antibonding orbitals. The LTBRM maps the problem of the local electronic structure about a given orbital onto the semi-infinite recursion chain model with diagonal (a_n) and subdiagonal (b_n) coefficients. In practice, these are often approximated from some level by repeating constants $(a_\infty$ and $b_\infty)$ for an infinite number of levels, so that the continued fraction is terminated.

However, this approximation at any level causes problems which are serious enough to have discouraged people from applying LTBRM to the calculation of energy and forces for atomistic simulations. The most drastic effects are the following: (i) Disastrously *poor convergence* [6] of the bond energy calculated by the IS approach as a function of exact recursion levels, in contrast with rapid convergence of SD approach; hence (ii) the *breakdown of equivalence* between SD and IS approaches. This failure of the IS approach meant that the bond orders and the Hellmann-Feynman (HF) expression for the forces (see, e.g., [7] and references therein) could not be used; in both approaches there is a "symmetry difficulty" [8] resulting in (iii) the *breakdown of invariance* of energy and forces under a rotation of quantization axis for degenerate atomic orbitals.

The standard remedy for problem (iii) is the so-called *matrix* recursion method (MRM) [8,9], in which the chain coefficients are matrices instead of scalars. However, it is clear from the examples shown in Fig. 1 that even the IS-MRM cannot get rid of the poor convergence, whereas the SD-MRM converges well. Therefore, problem (ii) remains the most important.

The many-atom expansion for the IS Green's function and the bond order, first derived perturbatively [10], was further developed [11] and then proved to be *exact* [12]. But again, the truncated expansion suffered from convergence as poor as that given by the IS-LTBRM. The rotational invariance was preserved, in a somewhat restricted manner, by choosing a local axis along the bond direction, and by introducing two-dimensional auxiliary vector spaces with π and δ bond orbitals [12].

Very recently, the importance of the sum rule which follows from the identity $(E-\hat{H})\hat{G} = 1$ has been pointed out and its power has been demonstrated for simple s-valent equivalent-site systems [13,14]: It was shown within the fourth moment approximation that the bond order expansion could give the same bond energy as that given by the SD method, by choosing the terminator (b_∞) so as to satisfy the sum rule. But, the previously derived many-atom expansion has been (iv) unable to fulfill the
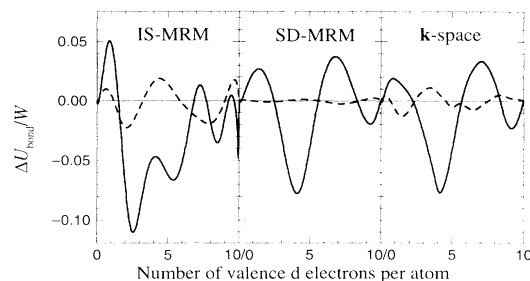

FIG. 1. TB bond energy differences for bcc, hcp, and fcc structures (solid and dashed lines for bcc-fcc and hcp-fcc, respectively). W is nominal bandwidth of the canonical d-band model (see, e.g., Refs. [6,7]). From left to right the three panels show the results by the IS-MRM (retaining exact moments to the sixth moment), by the SD-MRM (to the fifth moment), and by the k-space method (exact), respectively.

sum rule for *all* energies E, for *any* system and at *any* level of approximation. In this Letter, I derive a generalized many-atom expansion for the IS Green's functions, which solves problems (i)–(iv) *simultaneously* for the first time.

Within the two-center orthogonal tight binding (TB) approximation, the covalent bond energy is written in the SD description as $U_{\text{bond}} = \sum_{i,\ell} U^{i\ell}_{\text{bond}}$ with

$$U^{i\ell}_{\text{bond}} = \int^{E_F} 2(E - E^{i\ell})n^{i\ell}(E)dE, \qquad (1)$$

where E_F is the Fermi level, $E^{i\ell}$ is the d_ℓ ($\equiv 2\ell + 1$)-fold degenerate atomic energy level on atom i, and $n^{i\ell}$ is the ℓ-projected local density of states per spin.

In the IS description, the contributions come from individual bonds about the atom as

$$U^{i\ell}_{\text{bond}} = \frac{1}{2}\sum_{m,j,L'}^{(j\neq i)} 2H^{iL,jL'}\Theta^{jL',iL}(E_F), \qquad (2)$$

where $H^{iL,jL'} = \langle \phi^{iL}|\hat{H}|\phi^{jL'}\rangle$ are matrix elements of the TB Hamiltonian $\hat{H}$ and ϕ^{iL} are atomic orbitals with the usual convention L for the angular momentum indices ℓm. The orbital bond order, i.e., the off-diagonal element of the density matrix, is given by

$$\Theta^{jL',iL}(E_F) = -\frac{2\text{Im}}{\pi}\int^{E_F} G^{jL',iL}(E + \text{i}0)dE \qquad (3)$$

with the Green's functions defined as the elements, $G^{jL',iL} = \langle \phi^{jL'}|\hat{G}|\phi^{iL}\rangle$, of the Greenian $\hat{G} = (E - \hat{H})^{-1}$.

The key to improving the convergence in the IS method is to ensure the equivalence of the bond energies found by the SD and IS methods, Eqs. (1) and (2), which can be maintained only if the sum rule

$$(E - E^{i\ell})\bar{G}^{i\ell}(E) - 1 = \frac{1}{d_\ell}\sum_{m,j,L'}^{(j\neq i)} H^{iL,jL'}G^{jL',iL}(E) \qquad (4)$$

with $\bar{G}^{i\ell} = d_\ell^{-1}\sum_m G^{iL,iL}$ is fulfilled for *any arbitrary energy* E. How this can be accomplished is now shown.

Consider an auxiliary Hilbert space **A** spanned by a set of orthonormal vectors $\{e_{iL}\}$, in which the elements have a one-to-one correspondence with the orthonormal atomic orbitals $\{\phi^{iL} \in \mathbf{O}\}$, and define vectors as $e^\lambda_{iL} = \sum_{kL''} e_{kL''}\lambda_{kL'',iL}$ with an arbitrary matrix λ. We then define a normalized vector in the direct product space $\mathbf{O}\otimes\mathbf{A}$ as

$$|w^\lambda_0\} = \sum_{iL} |\phi^{iL}\rangle|e^\lambda_{iL}) \qquad (5)$$

with the condition $\{w^\lambda_0|w^\lambda_0\} = \text{tr}[\Lambda] = 1$, where the elements of matrix Λ are defined by scalar products $\Lambda_{jL',iL} \equiv (e^\lambda_{jL'}|e^\lambda_{iL})$ in **A**. For any linear operator acting on **O**, including the Greenian, we see

$$G^\Lambda_{00} \equiv \{w^\lambda_0|\hat{G}|w^\lambda_0\} = \sum_{iL}\sum_{jL'} G^{jL',iL}\Lambda_{jL',iL}. \qquad (6)$$

We then find for $jL' \neq iL$ the following expression:

$$G^{jL',iL} = \frac{\partial G^\Lambda_{00}}{\partial\Lambda_{jL',iL}}, \qquad (7)$$

which exists if $|\Lambda_{iL,iL}|^2 + |\Lambda_{jL',jL'}|^2 > 0$ [15].

G^Λ_{00} may be written as a continued fraction since the Lanczos method [4] can naturally be carried out in $\mathbf{O}\otimes\mathbf{A}$ to generate the chain coefficients a^Λ_n and b^Λ_n and the orthonormal recursion basis w^λ_n such that

$$\hat{H}|w^\lambda_n\} = |w^\lambda_{n-1}\}b^\Lambda_n + |w^\lambda_n\}a^\Lambda_n + |w^\lambda_{n+1}\}b^\Lambda_{n+1} \qquad (8)$$

with $b^\Lambda_0 \equiv 0$. From Eq. (7) we find the exact expansion

$$G^{jL',iL} = \sum_{n=0}^{\infty} G^\Lambda_{0n}G^\Lambda_{n0}\left[\frac{\partial a^\Lambda_n}{\partial\Lambda_{jL',iL}}\right] \\ + \sum_{n=1}^{\infty} 2G^\Lambda_{0n-1}G^\Lambda_{n0}\left[\frac{\partial b^\Lambda_n}{\partial\Lambda_{jL',iL}}\right], \qquad (9)$$

since $\partial G^\Lambda_{00}/\partial a^\Lambda_n = G^\Lambda_{0n}G^\Lambda_{n0}$ and $\partial G^\Lambda_{00}/\partial b^\Lambda_n = 2G^\Lambda_{0n-1}G^\Lambda_{n0}$ [16], where G^Λ_{0n} are Green's functions along the recursion chain, namely, $G^\Lambda_{0n} = \{w^\lambda_0|\hat{G}|w^\lambda_n\}$.

Equation (9) can be further simplified in terms of the moments μ^Λ_r and interference matrices $\zeta^{jL',iL}_{r+1}$ defined by

$$\mu^\Lambda_r = \{w^\lambda_0|\hat{H}^r|w^\lambda_0\} = \sum_{iL}\sum_{jL'}\langle\phi^{jL'}|\hat{H}^r|\phi^{iL}\rangle\Lambda_{jL',iL} \qquad (10)$$

and

$$\zeta^{jL',iL}_{r+1} = \frac{\partial\mu^\Lambda_r}{\partial\Lambda_{jL',iL}} = \langle\phi^{jL'}|\hat{H}^r|\phi^{iL}\rangle. \qquad (11)$$

It follows that

$$\frac{\partial a^\Lambda_n}{\partial\Lambda_{jL',iL}} = \sum_{r=1}^{2n+1}\frac{\partial a^\Lambda_n}{\partial\mu^\Lambda_r}\zeta^{jL',iL}_{r+1} \qquad (12)$$

and

$$\frac{\partial b^\Lambda_n}{\partial\Lambda_{jL',iL}} = \sum_{r=1}^{2n}\frac{\partial b^\Lambda_n}{\partial\mu^\Lambda_r}\zeta^{jL',iL}_{r+1}. \qquad (13)$$

The expansion Eq. (9) with Eqs. (12) and (13) is valid for a choice $\Lambda_{iL,iL} = \Lambda_{jL',jL'} = \frac{1}{2}$ with all other elements zero for given a pair of orbitals ϕ^{iL} and $\phi^{jL'}$, which leads to the exact many-atom expansion derived previously in Ref. [12], where G^Λ_{0n} were defined in terms of average moments $\mu^\Lambda_r = \frac{1}{2}(\mu^{iL}_r + \mu^{jL'}_r)$.

However, this choice does *not* guarantee that the sum rule is fulfilled and that the rotational invariance is preserved. Instead, the sum rule and rotational invariance are *guaranteed* by the choice $\Lambda = \Lambda^{i\ell}$ with $\Lambda^{i\ell}_{kL'',kL''} = d_\ell^{-1}\delta_{k,i}\delta_{\ell'',\ell}$ with all the off-diagonal elements zero, with

which we obtain the expansion for the IS Green's functions propagating from or to the ℓ-component orbitals at atom i. The recursion chain with this choice corresponds to the rotationally invariant ℓ-projected local density of states on atom i, and thus $G_{0n}^\Lambda = G_{0n}^{i\ell}$, $a_n^\Lambda = a_n^{i\ell}$, and $b_n^\Lambda = b_n^{i\ell}$ are defined in terms of rotationally invariant ℓ-projected moments $\mu_r^\Lambda = \mu_r^{i\ell}$. The right-hand sides of Eqs. (12) and (13) become

$$\alpha_n^{jL',iL} = \sum_{r=1}^{2n+1} \frac{\partial a_n^{i\ell}}{\partial \mu_r^{i\ell}} \zeta_{r+1}^{jL',iL} \qquad (14)$$

and

$$\beta_n^{jL',iL} = \sum_{r=1}^{2n} \frac{\partial b_n^{i\ell}}{\partial \mu_r^{i\ell}} \zeta_{r+1}^{jL',iL}, \qquad (15)$$

where the reference atom is indicated with the underline.

Using the relation

$$\frac{1}{d_\ell} \sum_{m,j,L'}^{(j\neq i)} H^{iL,jL'} \zeta_{r+1}^{jL',iL} = \mu_{r+1}^{i\ell} - E^{i\ell} \mu_r^{i\ell} \qquad (16)$$

and the moments-recursion coefficients relationship [see, e.g., Eqs. (2.10)–(15) in Ref. [11]], we obtain

$$\frac{1}{d_\ell} \sum_{m,j,L'}^{(j\neq i)} H^{iL,jL'} \left\{ \begin{array}{c} \alpha_n^{jL',iL} \\ 2\beta_n^{jL',iL} \end{array} \right\} = \left\{ \begin{array}{c} A_n^{i\ell} \\ B_n^{i\ell} \end{array} \right\} \qquad (17)$$

with $A_n^{i\ell} \equiv (b_{n+1}^{i\ell})^2 - (b_n^{i\ell})^2$ and $B_n^{i\ell} \equiv (a_n^{i\ell} - a_{n-1}^{i\ell})b_n^{i\ell}$. Using this with Eq. (9) simplifies the right-hand side of Eq. (4) as

$$\sum_{n=0}^\infty G_{0n}^{i\ell} G_{n0}^{i\ell} A_n^{i\ell} + \sum_{n=1}^\infty G_{0n-1}^{i\ell} G_{n0}^{i\ell} B_n^{i\ell}. \qquad (18)$$

Using the recursive relation of Green's function along the reference chain,

$$(E - a_n^{i\ell})G_{0n}^{i\ell} - b_n^{i\ell}G_{0n-1}^{i\ell} - b_{n+1}^{i\ell}G_{0n+1}^{i\ell} = \delta_{0,n}, \qquad (19)$$

we see almost all the terms in (18) cancel, leaving only the term $b_1^{i\ell}G_{01}^{i\ell}$. This exactly equals the left-hand side of Eq. (4) from Eq. (19) with $n = 0$. We have, thus, proved that the expansion Eq. (9) with $\Lambda = \Lambda^{i\ell}$ fulfills the sum rule Eq. (4) at any level of approximation for the coefficients a's, b's, α's, and β's as long as the relation Eq. (17) is not violated.

If we wish to make a Mth moment model, which retains exact moments to the Mth order, then we may terminate the continued fraction, $G_{00}^{i\ell}$, by approximating $a_{p+1}^{i\ell} = a_{p+2}^{i\ell} = \cdots = a_\infty^{i\ell}$ and $b_{q+1}^{i\ell} = b_{q+2}^{i\ell} = \cdots = b_\infty^{i\ell}$ with $p = [(M-1)/2]$ and $q = [M/2]$ ($[x]$ is the greatest integer which does not exceed x). Then, the series (18) is truncated because $A_n^{i\ell} = 0$ for $n > q$ and $B_n^{i\ell} = 0$ for $n > p+1$. The simplest way to truncate Eq. (9) with the constraints given by Eq. (17) is to approximate the last two coefficients with *truncators*:

$$\left\{ \begin{array}{c} \alpha_q^{jL',iL} \\ 2\beta_{p+1}^{jL',iL} \end{array} \right\} = \left\{ \begin{array}{c} (b_\infty^{i\ell})^2 - (b_q^{i\ell})^2 \\ (a_\infty^{i\ell} - a_p^{i\ell})b_{p+1}^{i\ell} \end{array} \right\} H^{jL',iL}/(b_1^{i\ell})^2. \qquad (20)$$

With this approximation, the bond order expansion is truncated as

$$\Theta^{jL',iL}(E_F) = -2 \left[\sum_{n=0}^q \chi_{0n,n0}^{i\ell}(E_F)\alpha_n^{jL',iL} \right.$$
$$\left. + \sum_{n=1}^{p+1} \chi_{0n-1,n0}^{i\ell}(E_F)2\beta_n^{jL',iL} \right], \qquad (21)$$

where the response functions are defined by

$$\chi_{0n,n'0}^{i\ell}(E_F) = \frac{\mathrm{Im}}{\pi} \int^{E_F} G_{0n}^{i\ell}(E + \mathrm{i}0)G_{n'0}^{i\ell}(E + \mathrm{i}0)dE. \qquad (22)$$

In the Mth moment model, the bond energy given by the IS description, Eq. (2), simplifies to a new, rapidly convergent moment expansion for the bond energy, namely,

$$U_{\mathrm{bond}}^{i\ell} = -2d_\ell \left[\sum_{n=0}^q \chi_{0n,n0}^{i\ell} A_n^{i\ell} + \sum_{n=1}^{p+1} \chi_{0n-1,n0}^{i\ell} B_n^{i\ell} \right]. \qquad (23)$$

This is equivalent to that given by the SD description, Eq. (1), for any order M. Note that the bond order contributes to the total bond energy and the HF forces in a symmetric form, i.e., $\frac{1}{2}(\Theta^{jL',iL} + \Theta^{jL',iL})$.

Figure 2 shows the bond energy which is given by the present model for $M = 4$, 6, and 18. The bond orders in the fcc structure for the same number of exact moments are displayed in Fig. 3. The convergence of the energy and bond orders is impressively rapid.

For a low-order moment model in the present scheme, however, there remains a finite, but small discrepancy between the HF and numerical forces. For example, the HF and numerical forces acting between two neighboring atoms in a half-filled s-valent infinite linear chain agree within errors of $3\times10^{-3}\%$ and $6\times10^{-4}\%$ in the fourth and sixth moment models, respectively, with no discernible discrepancy in the eighth moment model. For the "surface" atom of a semi-infinite linear chain, the discrepancy between the forces is slightly worse, being 0.9%
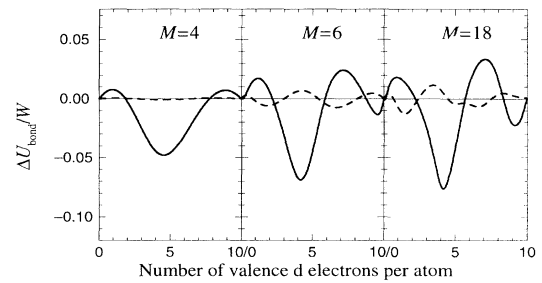

FIG. 2. Convergence of TB bond energy differences with the present fourth, sixth, and eighteenth moment models.
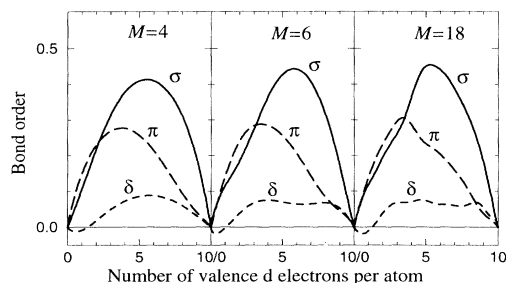
FIG. 3. Convergence of σ, π, and δ bond orders between the nearest neighbors in d-bonded fcc lattice.

in the sixth moment model. However, if we include the strongly distance-dependent repulsive forces, such a small discrepancy will lead to a very small error in the relaxed atomic positions.

Computations can be performed fast. The integrations to evaluate the response functions, Eq. (22), and also the number of electrons are carried out using semianalytical expressions [17]. $\mu_r^{i\ell}$ and $\zeta_{r+1}^{jL',iL}$ can be obtained efficiently from scalar products among power vectors $|\hat{H}^n \phi^{iL}\rangle$ for each orbital. Moreover, computations may be highly parallelized as the power vectors can be generated independently for individual atoms. Local charge neutrality (LCN) [7] is achieved easily by shifting atomic energy levels, at each step of simulation, by $\Delta E^{i\ell} = -\eta(\sum_\ell d_\ell \chi_{00,00}^{i\ell})^{-1} \Delta N^i$ with appropriate damping factor η, where ΔN^i is the number of electrons to be added in order to achieve LCN at atom i.

In conclusion, an efficient, $O(N)$, real-space and rapidly convergent method for calculating the bond order potentials and forces for the atomistic simulation of covalent systems, such as transition metals and semiconductors and their compounds, is now available by having solved several longstanding problems with the ISLTBRM and the recently derived bond order expansion.

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[15] Instead of giving a lengthy proof, I point out if $\Lambda_{I,I} = \Lambda_{J,J} = 0$ (thus $\Lambda_{J,I} = 0$), we see from the Cauchy-Schwarz inequality that an infinitesimal variation in $\Lambda_{J,I}$ causes $\frac{1}{2}(|\delta\Lambda_{I,I}|^2 + |\delta\Lambda_{J,J}|^2) \geq |\delta\Lambda_{I,I}||\delta\Lambda_{J,J}| \geq |\delta\Lambda_{J,I}|^2 > 0$, and therefore $\delta\Lambda_{J,I}$ cannot be treated as an independent variable to derive Eq. (7).

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