Linear-scaling moment-based electronic structure calculation

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The kernel polynomial method and the bond-order potential are two well-known methods to construct interatomic potentials by means of Chebyshev polynomials. This Brief Report derives an approach which generalizes these two methods in that it can employ arbitrary orthogonal polynomials. In addition, this approach systematically extends the widely used second-moment approximations, such as the Friedel rectangular model and the Finnis-Sinclair potential. Some well-known orthogonal polynomials are chosen to investigate this approach. The first-kind and the second-kind Chebyshev polynomials as well as the Legendre polynomials can reproduce the bond energy well with a few moments. Hermite polynomials are also able to reproduce the bond energy well for the simple cubic lattice with a few moments.

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The tight-binding (TB) method[1–3] has been widely applied in materials simulations. However, due to its $O(N^3)$ limitation, it is very expensive to carry out large-scale calculations. Therefore, it is ideal to have linear-scaling approach. Among many $O(N)$ approaches,[4–16] the kernel polynomial method (KPM) (Refs. 4–6) and the bond-order potential (BOP) (Refs. 9–11) are two well-known methods. The closely related KPM and BOP can be derived from a semi-infinite linear chain and an infinite linear chain, respectively. Eventually, they are constructed using different kinds of Chebyshev polynomials.[17] In this Brief Report, we demonstrate that any arbitrary type of orthogonal polynomials can be employed to construct the interatomic potential through moments. Therefore, it generalizes the KPM and the BOP. The Finnis-Sinclair potential[18] or its closely related embedded-atom method[19,20] is the most widely used potential in molecular dynamics. The Finnis-Sinclair potential is derived from a second-moment approximation.[3,18] The approach in this Brief Report is able to extend this second-moment approximation by systematically including higher moments. Similarly, it can also systematically extend the well-known Friedel rectangular model.[21] Finally the simple square and cubic lattices will be taken as examples to investigate this approach. The first-kind and the second-kind Chebyshev polynomials as well as the Legendre and Hermite polynomials will be chosen for the investigation.

For simplicity, this Brief Report will focus on the description of s electrons; however, the proposed approach can be conveniently extended to include other types of electrons. Within the TB method,[22–24] the elements of the Hamiltonian matrix can be expressed as $H_{ij} = \langle i | \hat{H} | j \rangle$. The atom-centered orbitals $|i\rangle$ are assumed to be orthogonal, where i is the atom index. The diagonal elements of the Hamiltonian matrix are the on-site energies H_{ii}. For simple description, H_{ii} will be taken to be 0 as the reference energy. Then the bond energy associated with each atom i can be expressed as

$$U_i = 2 \int_{-\infty}^{\epsilon_F} \epsilon n_i(\epsilon) d\epsilon, \qquad (1)$$

where $n_i(\epsilon)$ is the local density of states and ϵ_F is the Fermi energy. The nth moment of $|i\rangle$ is defined as[2]

$$\mu_i^{(n)} = \int_{-\infty}^{\infty} \epsilon^n n_i(\epsilon) d\epsilon. \qquad (2)$$

Orthogonal polynomials $P_m(\epsilon)$ satisfy[25]

$$\int_{\epsilon_l}^{\epsilon_u} w(\epsilon) P_m(\epsilon) P_n(\epsilon) d\epsilon = \begin{cases} 0 & m \neq n \\ I_m & m = n. \end{cases} \qquad (3)$$

Here $[\epsilon_l, \epsilon_u]$ is the support interval. I_m is a function of m and $w(\epsilon)$ is the weight function which satisfies

$$\int_{\epsilon_l}^{\epsilon_u} w(\epsilon) d\epsilon = 1. \qquad (4)$$

Supposing that the density of states has been shifted and scaled in order to be bounded within $[\epsilon_l, \epsilon_u]$,[5,11] $n_i(\epsilon)$ can be expanded in terms of $P_m(\epsilon)$

$$n_i(\epsilon) = w(\epsilon) \sum_{m=0} \sigma_m P_m(\epsilon), \qquad (5)$$

where σ_m are the expansion coefficients and they can be obtained by taking advantage of Eq. (3), namely,

$$\sigma_m = \frac{1}{I_m} \int_{\epsilon_l}^{\epsilon_u} P_m(\epsilon) n_i(\epsilon) d\epsilon. \qquad (6)$$

$P_m(\epsilon)$ can be expressed in terms of their coefficients p_{mn} (Ref. 25)

$$P_m(\epsilon) = \sum_{n=0}^{m} p_{mn} \epsilon^n. \qquad (7)$$

Substituting Eq. (7) into Eq. (6) and using the moment definition in Eq. (2), we have

$$\sigma_m = \frac{1}{I_m} \sum_{n=0}^{m} p_{mn} \mu^{(n)}. \qquad (8)$$

Combining Eqs. (5) and (8), an analytic form of $n_i(\epsilon)$ can be expressed as

TABLE I. Properties of the four types of $P_m(\epsilon)$ (Ref. 25). Here σ is the standard deviation of the Gaussian function.

		$[\epsilon_l, \epsilon_u]$	$w(\epsilon)$	A_m	B_m	C_m	I_m
First	Chebyshev	$[-1,1]$	$\frac{1}{\pi\sqrt{1-\epsilon^2}}$	$1/2$	0	$1/2$	$\frac{1}{2}(1+\delta_{m0})$
Second	Chebyshev	$[-1,1]$	$\frac{2}{\pi}\sqrt{1-\varepsilon^2}$	$1/2$	0	$1/2$	1
	Legendre	$[-1,1]$	$\frac{1}{2}$	$\frac{m+1}{2m+1}$	0	$\frac{m}{2m+1}$	$\frac{1}{2m+1}$
	Hermite	$[-\infty,\infty]$	$\frac{1}{\sqrt{2}\pi\sigma}e^{(-\epsilon^2/2\sigma^2)}$	σ^2	0	m	$m!/\sigma^{2m}$

$$n_i(\epsilon) = \frac{w(\epsilon)}{I_m} \sum_{m=0}^{n_{\max}} \sum_{n=0}^{m} p_{mn}\mu^{(n)}P_m(\epsilon), \qquad (9)$$

where $n_{\max}$ is the maximum number of moments used in the calculation.

Substituting Eq. (5) into Eq. (1), we have

$$U_i = 2\int_{\epsilon_l}^{\epsilon_F} w(\epsilon)\sum_{m=0} \sigma_m P_m(\epsilon)\epsilon d\epsilon = 2\sum_{m=0}\sigma_m \int_{\epsilon_l}^{\epsilon_F} w(\epsilon)\epsilon P_m(\epsilon)d\epsilon. \qquad (10)$$

It is known that a three-term recurrence relation always holds for $P_m(\epsilon)$

$$\epsilon P_m(\epsilon) = A_m P_{m+1}(\epsilon) + B_m P_m(\epsilon) + C_m P_{m-1}(\epsilon), \qquad (11)$$

where A_m, B_m, and C_m are coefficients depending on the type of $P_m(\epsilon)$. Substituting Eq. (11) into Eq. (10), we have

$$U_i = 2\sum_{m=0}\sigma_m \times \int_{\epsilon_l}^{\epsilon_F} w(\epsilon)[A_m P_{m+1}(\epsilon) + B_m P_m(\epsilon)$$
$$+ C_m P_{m-1}(\epsilon)]d\epsilon. \qquad (12)$$

Defining $\hat{\chi}_m(\epsilon_F)$ as

$$\hat{\chi}_m(\epsilon_F) = \int_{\epsilon_l}^{\epsilon_F} w(\epsilon)P_{m-1}(\epsilon)d\epsilon \qquad (13)$$

then Eq. (12) can be rewritten as

$$U_i = 2\sum_{m=0}^{n_{\max}}\sigma_m \times [A_m\hat{\chi}_{m+2}(\epsilon_F) + B_m\hat{\chi}_{m+1}(\epsilon_F) + C_m\hat{\chi}_m(\epsilon_F)]. \qquad (14)$$

The Rodrigues' formula[25] can lead to

$$w(\epsilon)P_{m-1}(\epsilon) = \frac{1}{c_{m-1}}\frac{d^{m-1}}{d\epsilon^{m-1}}\{w(\epsilon)[g(\epsilon)]^{m-1}\}, \qquad (15)$$

where $g(\epsilon)$ is a polynomial and c_m is a number related to m. These two quantities depend on the type of $P_m(\epsilon)$. Integrating both sides of Eq. (15), we have

$$\int w(\epsilon)P_{m-1}(\epsilon)d\epsilon = \int \frac{1}{c_{m-1}}\frac{d^{m-1}}{d\epsilon^{m-1}}\{w(\epsilon)[g(\epsilon)]^{m-1}\}d\epsilon$$
$$= \frac{1}{c_{m-1}}\frac{d^{m-2}}{d\epsilon^{m-2}}\{w(\epsilon)[g(\epsilon)]^{m-1}\}. \qquad (16)$$

The right hand of Eq. (16) can be computed for $m\geq 2$. $\hat{\chi}_1(\epsilon_F)$

can be calculated directly from Eq. (13) by integrating the weight function. Therefore, an analytic form of $\hat{\chi}_m(\epsilon_F)$ can always be obtained for arbitrary $P_m(\epsilon)$. As a result, an analytic form of the bond energy in Eq. (14) can be obtained.

Following Eq. (5), the number of electrons in terms of band filling is given by

$$N_i = 2\int^{\epsilon_F} n_i(\epsilon)d\epsilon = 2\int^{\epsilon_F} w(\epsilon)\sum_{m=0}\sigma_m P_m(\epsilon)d\epsilon$$
$$= 2\sum_{m=0}\sigma_m\hat{\chi}_{m+1}(\epsilon_F). \qquad (17)$$

Equation (17) determines ϵ_F and then Eq. (14) will be used to calculate the bond energy. This procedure analytically calculates the bond energy.

The bond order and the force can be derived in a similar procedure to that in Ref. 11. The bond order Θ_{ij} will be

$$\Theta_{ij} = 4\sum_{m=1}^{n_{\max}}\sum_{n=0}^{m}[A_m\hat{\chi}_{m+2}(\epsilon_F) + B_m\hat{\chi}_{m+1}(\epsilon_F)$$
$$+ C_m\hat{\chi}_m(\epsilon_F)]p_{mn}n\xi_{ij}^{(n-1)}, \qquad (18)$$

where ξ_{ij} is the interference path.[11] The force expression will be

$$F_k = -\nabla_k\sum_i U_i = -\sum_{i,j}\Theta_{ij}\nabla_k H_{ji}. \qquad (19)$$

This force expression follows the local charge neutrality approximation[9,26] within the tight-binding bond model.[22] So far we have established an approach to construct linear-scaling moment-based potential through orthogonal polyno-

TABLE II. $\hat{\chi}_m(\epsilon_F)$ for different type of $P_m(\epsilon)$. Here $\phi_F = \cos^{-1}(\epsilon_F)$ and erf represents the error function (Ref. 25).

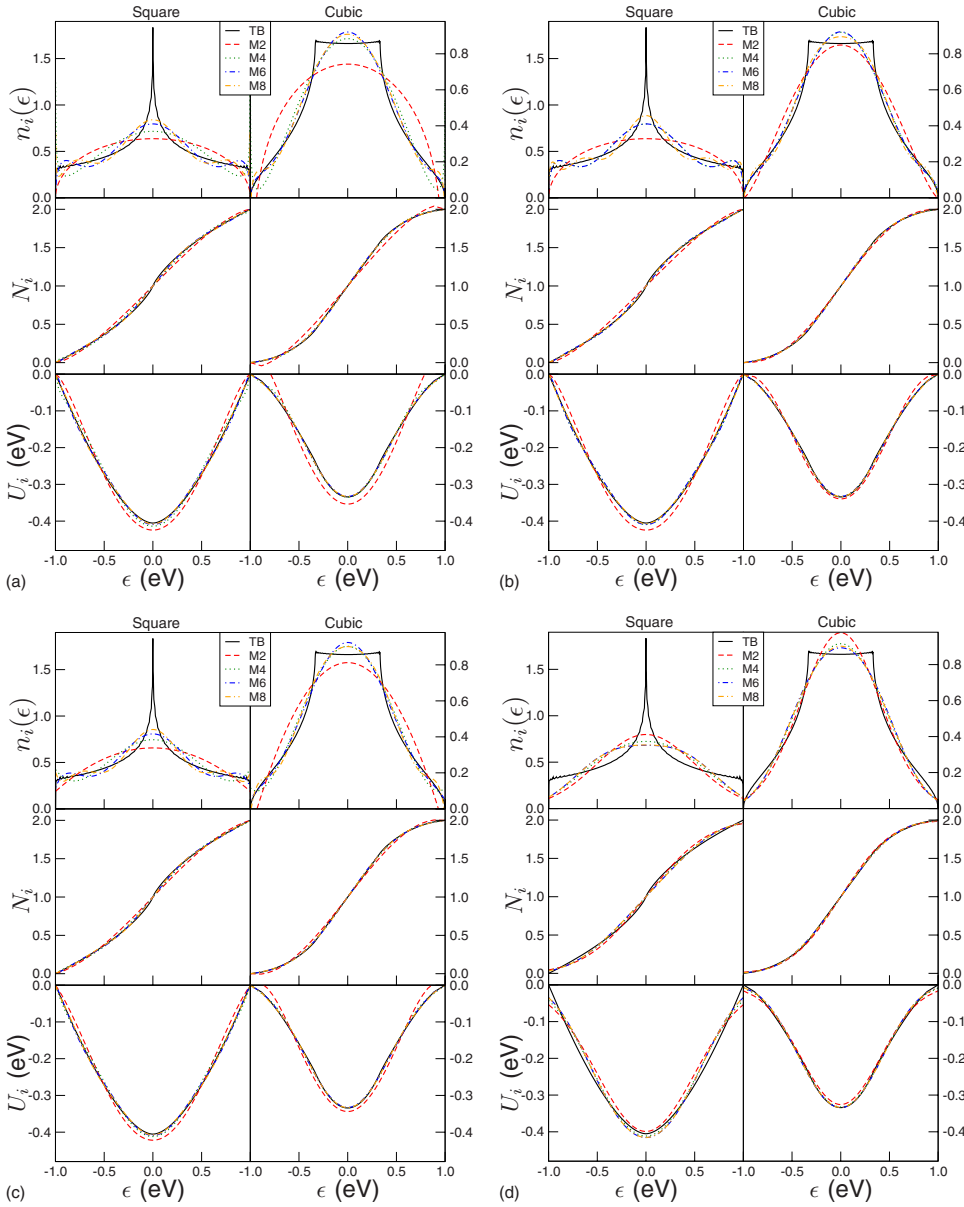|		$m=0$	$m=1$	$m\geq 2$
First	Chebyshev[a]	$-\frac{\sin(\phi_F)}{\pi}$	$1-\frac{\phi_F}{\pi}$	$-\frac{\sin(m-1)\phi_F}{\pi(m-1)}$
Second	Chebyshev[b]	0	$1-\frac{\phi_F}{\pi}$	$-\frac{\sin(m-1)\phi_F}{(m-1)\pi}$
			$+\frac{2}{\pi}\sin 2\phi_F$	$+\frac{\sin(m+1)\phi_F}{(m+1)\pi}$
	Legendre	0	$\frac{1}{2}(\epsilon_F+1)$	$\frac{P_m(\epsilon_F)-P_{m-2}(\epsilon_F)}{2(2m-1)}$
	Hermite	0	$\frac{1}{2}[\text{erf}(\frac{\epsilon_F}{\sqrt{2}\sigma})+1]$	$-P_{m-2}(\epsilon_F)w(\epsilon_F)$

[a]Reference 17.
[b]Reference 11.

FIG. 1. (Color online) Results of the LMPO approach using different types of orthogonal polynomials: (a) first-kind Chebyshev, (b) second-kind Chebyshev, (c) Legendre, (d) Hermite. In each figure, the left-hand panels are the results for the simple square lattice and the right-hand panels are for the simple cubic lattice. The upper panels are the density of states, the middle panels show the number of electrons as a function of band filling, and the lower panels display the bond energy as a function of band filling. The legend is labeled in the following way for the LMPO approach: M plus the maximum number of moments.

mials (LMPO). The mathematical format for the density of states in Eq. (9), the number of electrons in Eq. (17), the bond energy in Eq. (14), the bond order in Eq. (18), and the force in Eq. (19) are the same for arbitrary type of $P_m(\epsilon)$. While applying different type of $P_m(\epsilon)$, only the quantities depending on $P_m(\epsilon)$ need to be replaced. In addition, it can be seen that the KPM and the analytic BOP are two particular cases of this approach by choosing the first-kind and the second-kind Chebyshev polynomials, respectively. Next the first-kind and the second-kind Chebyshev polynomials as well as the Legendre and the Hermite polynomials will be implemented in the LMPO. Their properties are listed in Table I.

The weight functions in Table I are normalized so that they satisfy Eq. (4). It can be noticed that the weight functions have been used in some well-known second-moment approximations. For example, the weight function of the Legendre polynomials was used in the Friedel rectangular model[21] to explain the trend of the binding energy and the

bulk modulus across the nonmagnetic transition-metal series.[2] The weight function of the Hermite polynomials, which is a Gaussian form, was used to construct Finnis-Sinclair potentials.[1,18,27] The LMPO has extended these second-moment approximations by systematically including higher moments.

For different $P_m(\epsilon)$, $\hat{\chi}_m(\epsilon_F)$ can be derived, and the results are summarized in Table II. The simple square and cubic lattices will be taken to investigate the LMPO. Their density of states is set to be bounded within $[-1,1]$ for simple illustration. Therefore, their eigenvalues from the TB method are[1]

$$E(\mathbf{k}) = \begin{cases} -1/2(\cos k_x + \cos k_y) & \text{square} \\ -1/3(\cos k_x + \cos k_y + \cos k_z) & \text{cubic,} \end{cases} \quad (20)$$

where k_x, k_y, and k_z are the k points in the $\mathbf{k}$ space. $n_i(\epsilon)$, N_i, and U_i can be obtained from these eigenvalues.[28] On the other hand, these quantities can be calculated through the LMPO.

As is well known, the involvement of a few moments can reproduce the main pattern of the density of states, such as the center of the gravity, the mean-square width, how skewed the band is and whether the density of states is unimodal or bimodal.[1,2] The main pattern of the density of states is reproduced using a few moments in Figs. 1(a)–1(c); however, it shows that oscillations appear in the density of states between the LMPO and the TB method. These oscillations actually are intrinsic properties for orthogonal polynomial expansions, namely, the Gibbs oscillations.[5] It is observed that with six moments included, the number of electrons and the bond energy are very close to the TB results. Therefore, we suggest accepting a reasonable degree of Gibbs oscillations in the density of states and consequently the computational time can be gained significantly with only a few moments involved to calculate the bond energy. We would like to call the density of states calculated by the LMPO as moment-conserving pseudodensity of states. The first-kind Chebyshev, the second-kind Chebyshev and the Legendre polynomials have finite support intervals as seen from Table I. When applying polynomials that have finite support intervals, the band range can be obtained by means of Lanczos algorithm.[6,29] Here the band range is known and taken as m $[-1, 1]$. It shows that the polynomials that have finite support intervals perform well with only a few moments involved.

The Hermite polynomials have an infinite support interval, which means the band range is not required. The second moment of the Gaussian function is σ^2. In this Brief Report, σ^2 will be taken as the $\mu^{(2)}$ of the simple square or cubic lattice. The results in Fig. 1(d) indicate that a few moments can reproduce the bond energy for the simple cubic. Due to the strong singularity in the density of states of the simple square, the Hermite polynomials perform better for the simple cubic than for the simple square. The convergence for simple square may be improved by optimizing σ, which will be investigated in future research.

In summary, the LMPO can employ arbitrary type of orthogonal polynomials to construct interatomic potentials, and thus it generalizes the well-known KPM and BOP. Moreover, the LMPO extends the well-known Friedel rectangular model and the Finnis-Sinclair potential. Therefore, the LMPO should prove invaluable in constructing interatomic potentials for atomistic simulations. The simple square and cubic lattices were taken to examine the popular orthogonal polynomials. The first-kind Chebyshev, the second-kind Chebyshev, and the Legendre polynomials perform well with a few moments involved. The Hermite polynomials also perform well with a few moments for the simple cubic lattice. Other types of orthogonal polynomials can be conveniently applied in the LMPO which will be carried on for future work.

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