

ELECTRONIC STRUCTURE CALCULATIONS IN PLANE-WAVE CODES WITHOUT DIAGONALIZATION

LAURENT O. JAY*, HANCHUL KIM †, YOUSEF SAAD ‡, AND
JAMES R. CHELIKOWSKY §

Abstract. We present an algorithm to reduce the computational complexity for plane-wave codes used in electronic structure calculations. Our proposed algorithm avoids the diagonalization of large Hermitian matrices arising in such problems. The computational time for the diagonalization procedure typically grows as the cube of the number of atoms, or the number of eigenvalues required. To reduce this computational demand, we approximate directly in a certain subspace the occupation operator corresponding to the eigenvectors associated with the occupied states, without actually computing these eigenvectors. A smoothed Chebyshev-Jackson expansion of the Heaviside function of the Hamiltonian matrix is used to represent the occupation operator. This procedure requires only matrix-vector products and is intrinsically parallelizable.

Key words. Chebyshev polynomials, eigenvalue problem, electronic structure calculations, Jackson approximation.

AMS subject classifications. 65F15, 90C06

1. Introduction. Quantum-mechanical calculations have been proven to be accurate and successful in predicting the electronic and structural properties of real materials [1]. Among various quantum-mechanical methods, *ab initio* pseudopotential plane-wave method [2, 3, 4] based on the local density functional theory [5, 6] has been the most popular choice owing to easy implementation and to the systematic control of computational errors. However, the computational demands of this method prohibits its application to systems containing more than a few hundreds of atoms. The leading contributions to the computational load are (i) the matrix-vector multiplications which scales as $N^2 \log N$ (for plane-wave methods) and (ii) the orthogonalization of wavefunctions which scales as N^3 , where N is the number of atoms or eigenvalues to be determined.

There have been many efforts to devise linear-scaling (*or* order- N) algorithms. These include the density-matrix method [7, 8, 9], the orbital method [10, 11, 12, 13], and the Fermi-operator method [14, 15]. Most of the proposed order- N methods are based on a tight-binding approach and many of them do not involve fully self-consistent calculations [14, 15, 16, 17, 18, 19, 20, 21]. Typically, order- N type algorithms sacrifice some accuracy relative to standard methods in an attempt to achieve linear-scaling. Here, we center on developing an algorithm which eliminates any N^3 operations from the *ab initio* plane-wave calculations without any loss in the accuracy, *e.g.*, we wish to retain a fully self-consistent solution.

Our algorithm utilizes the Fermi operator expansion (FOE) method developed by Goedecker and Teter [15]. The FOE is a candidate linear-scaling algorithm if used with real-space-localized basis functions. Another important feature of the FOE

*Department of Mathematics, 14 MacLean Hall, The University of Iowa, Iowa City, IA 52242-1419, USA (na.1jay@na-net.ornl.gov)

†Division of Engineering and Applied Sciences, Harvard University, Gordon McKay Laboratory, 9 Oxford Street, Cambridge, MA 02138, USA (hanchul@cmt.harvard.edu)

‡Department of Computer Science and Engineering, University of Minnesota, 4-192 EE/CS Bldg., 200 Union Street S.E., Minneapolis, MN 55455-0159, USA (saad@cs.umn.edu)

§Department of Chemical Engineering and Materials Science, University of Minnesota, 151 Amundson Hall, 421 Washington Avenue SE, Minneapolis, MN 55455, USA (jrc@msi.umn.edu)

is the intrinsically parallel character of the algorithm. We propose the application of FOE to *ab initio* electronic structure calculations using a plane-wave basis with pseudopotentials.

In §2, we briefly describe the Fermi operator. The Chebyshev–Jackson polynomial expansion of the Fermi operator is formulated in §3. The detailed formulation of the electronic charge density and the occupation operator are given in §4 and §5, respectively. In §6, we schematically present the algorithm of the computation. Finally, the numerical examples are described in §7.

2. Fermi operator. The Fermi operator is defined by

$$\hat{F} \equiv f_{E_F}(\hat{H}),$$

where f_{E_F} is the Fermi-Dirac distribution function:

$$f_{E_F}(\hat{H}) = \lim_{T \rightarrow 0} \frac{1}{1 + \exp((\hat{H} - E_F)/T)}.$$

The chemical potential is E_F and \hat{H} is the Hamiltonian operator. Physically, T can be interpreted as the temperature. Here we consider the limit of zero temperature, *i.e.*, the Fermi-Dirac distribution function is treated as a Heaviside function. Within this definition, the eigenvalue of the Fermi operator for each eigenvector ψ_i of \hat{H} is the occupation number of the eigenstate

$$\begin{aligned} \hat{F}\psi_i &= f_{E_F}(\varepsilon_i)\psi_i \\ &= \begin{cases} \psi_i & \text{if occupied } (\varepsilon_i < E_F), \\ 0 & \text{otherwise } (\varepsilon_i > E_F). \end{cases} \end{aligned}$$

Each state ψ_i is occupied below the Fermi level; each state above is empty.

Many interesting physical quantities can be expressed in terms of the Fermi operator. For example, the band energy E_{band} , the total number of electrons N_{el} , and the Fourier component of the electronic charge density $\varrho(G)$ (where the charge density is given by $\varrho(r) = \sum_G \varrho(G) \exp(iG \cdot r)$) can be written as follows:

$$\begin{aligned} E_{band} &= \text{Tr}(\hat{H}\hat{F}), \\ N_{el} &= 2 \text{Tr}(\hat{F}), \\ \varrho(G) &= 2 \sum_{G'} \langle G' | \hat{F} | G' - G \rangle \end{aligned}$$

where $\text{Tr}(\cdot)$ is the trace.

3. Chebyshev–Jackson polynomial approximation. For a function defined by $h : [-1, 1] \mapsto \mathbf{R}$, its *Chebyshev expansion of order M* can be expressed as

$$h(x) \approx \frac{\mu_0}{2} + \sum_{m=1}^M \mu_m T_m(x)$$

where the coefficients μ_m are given by

$$\mu_m = \frac{2}{\pi} \int_{-1}^1 \frac{h(t)T_m(t)}{\sqrt{1-t^2}} dt$$

and the functions $T_m(x) = \cos(m \arccos(x))$ are the *Chebyshev polynomials of the first kind*. For the *Heaviside function* (Fig. 1)

$$H_\gamma(x) = \begin{cases} 1 & \text{if } x \in [-1, \gamma], \\ 0 & \text{else,} \end{cases}$$

the Chebyshev coefficients are fairly easy to compute. Using the definition for Cheby-

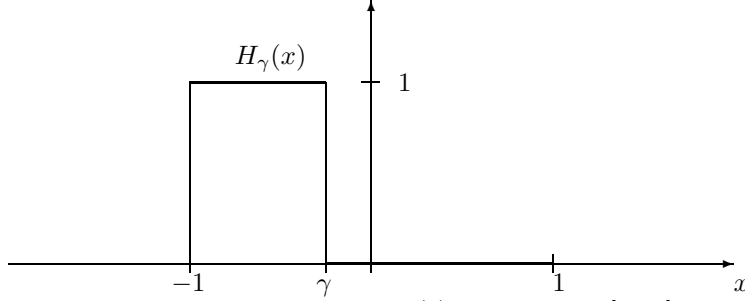


FIG. 1. The Heaviside function $H_\gamma(x)$ on the interval $[-1, 1]$

shev polynomials and the change of variable $t = \cos(u)$ we obtain

$$(1) \quad \mu_m(\gamma) = \frac{2}{\pi} \int_{-\pi}^{\arccos(\gamma)} \cos(mu) du = \begin{cases} 2 \left(1 - \frac{\arccos(\gamma)}{\pi}\right) & \text{for } m = 0, \\ -\frac{2 \sin(m \arccos(\gamma))}{m\pi} & \text{for } m \geq 1. \end{cases}$$

As is well known, least-square, high degree polynomial expansions of the Heaviside function show Gibbs oscillations around points of discontinuity owing to the truncation of the expansion at finite order M . To overcome this phenomenon the series can be smoothed by using appropriate damping factors. A smoothed expansion is given by the *Jackson approximation* [22, 23, 24]

$$h(x) \approx \frac{\mu_0}{2} + \sum_{m=1}^M g_{m,M} \mu_m T_m(x)$$

where

$$(2) \quad g_{m,M} = \sum_{i=0}^{M-m} a_{i,M} a_{m+i,M}, \quad a_{i,M} = \frac{U_i(\lambda_{\max,M})}{\sqrt{\sum_{n=0}^M U_n^2(\lambda_{\max,M})}}$$

with

$$(3) \quad \lambda_{\max,M} = \cos(\alpha_M), \quad \alpha_M = \frac{\pi}{M+2}$$

and the $U_n(x)$ are *Chebyshev polynomials of the second kind*

$$(4) \quad U_n(x) = \frac{T'_{n+1}(x)}{n+1} = \frac{\sin((n+1) \arccos(x))}{\sin(\arccos(x))}.$$

A direct calculation shows that

$$a_{i,M} = \frac{\sin((i+1)\alpha_M)}{\sqrt{\sum_{n=0}^M \sin^2((n+1)\alpha_M)}}.$$

A closed expression for the Jackson damping factors $g_{m,M}$ is as follows.

LEMMA 3.1. *The coefficients $g_{m,M}$ in (2) for $m = 1, \dots, M$ satisfy*

$$(5) \quad g_{m,M} = \frac{\left(1 - \frac{m}{M+2}\right) \sin(\alpha_M) \cos(m\alpha_M) + \left(\frac{1}{M+2}\right) \cos(\alpha_M) \sin(m\alpha_M)}{\sin(\alpha_M)}$$

where α_M is given in (3). The proof is given in the Appendix.

Figure 2 illustrates how the Jackson damping factor works for the Heaviside function in Fig. 1 with different degrees of the polynomial expansion. The Jackson damping factor is indispensable for an accurate approximation of the Heaviside function.

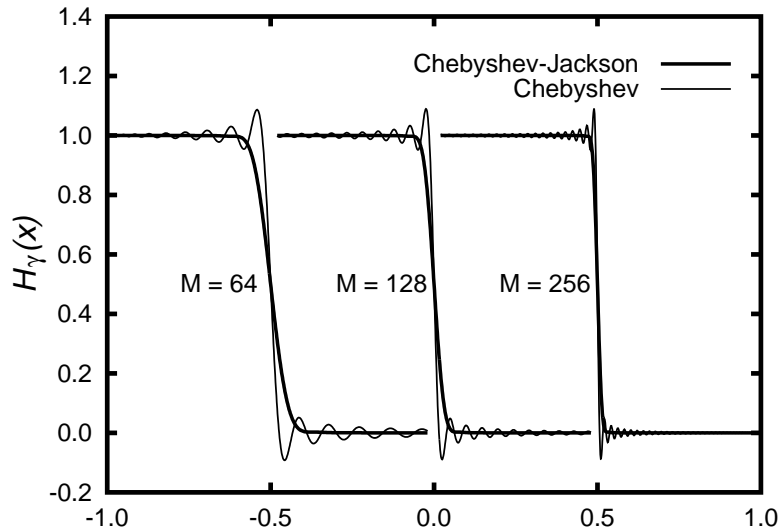


FIG. 2. Approximation of the Heaviside function with (thick line) and without (thin line) the Jackson damping factor for three different degrees M of the Chebyshev polynomial. Note that we use different γ 's for different M 's for the purpose of illustration: $\gamma = -0.5, 0.0$, and 0.5 for $M = 64, 128$, and 256 , respectively.

4. Computation of the charge density. For a given k -point in reciprocal (Fourier) space, the *occupation operator* \hat{O}^k corresponding to the eigenvectors ψ_n^k of the Hamiltonian matrix \hat{H}^k associated with the occupied states is given component-wise by

$$(6) \quad \hat{O}_{GG'}^k = 2 \sum_n \theta_n^k \psi_n^k(G) \psi_n^{k*}(G')$$

where k is the wave vector, the factor 2 comes from the spin degeneracy and θ_n^k is the *occupation number* of the state ψ_n^k

$$\theta_n^k \equiv f_{E_F}(\varepsilon_n^k) = \begin{cases} 1 & \text{if } \psi_n^k \text{ is occupied,} \\ 0 & \text{if } \psi_n^k \text{ is unoccupied.} \end{cases}$$

The *occupation operator* \hat{O} is given by the direct sum of the k -point dependent occupation operators \hat{O}^k , and is equal to twice of the Fermi operator:

$$(7) \quad \hat{O} = \bigoplus_k \hat{O}^k \quad (= 2\hat{F}).$$

The *density matrix* is

$$\rho(r, r') = \sum_k \sum_{GG'} e^{i(k+G)\cdot r} \hat{O}_{GG'}^k e^{-i(k+G')\cdot r'}$$

and the *charge density* is simply expressed by

$$\rho(r) \equiv \rho(r, r) = \sum_k \sum_{GG'} e^{i(G-G')\cdot r} \hat{O}_{GG'}^k .$$

In reciprocal space the charge density is given as follows

$$(8) \quad \varrho(G) = \frac{1}{L} \sum_r e^{-iG\cdot r} \rho(r) = \sum_k \sum_{G'G''} \hat{O}_{G'G''}^k \frac{1}{L} \sum_r e^{i(G'-G''-G)\cdot r} = \sum_k \sum_{G'} \hat{O}_{G',G'-G}^k$$

where L is the number of grid points in the unit-cell and the following property is used

$$\frac{1}{L} \sum_r e^{iG\cdot r} = \delta_{G,0}$$

where δ denotes the Kronecker symbol. There is no need to apply Fourier transformations when computing the charge density from the occupation operator as is done in conventional plane-wave codes.

5. Computation of the occupation operator. The usual way to obtain the occupation operator (7) is to compute the eigenvectors of each k -th occupation operator \hat{O}^k (6) by resorting to a partial diagonalization of each Hamiltonian matrix \hat{H}^k . One drawback of such a procedure is its computational cost which grows cubically with the number of occupied eigenstates. Since the size of the Hamiltonian matrices \hat{H}^k are proportional to the number N of atoms, this approach is often limited to a few hundred atoms. To reduce the amount of computation, it has been proposed for Gaussian basis functions to find directly the density matrix by minimization techniques [14, 15]. For a plane-wave basis set, we propose an alternative approach by directly approximating the occupation operator using a Chebyshev–Jackson expansion of the Heaviside function of the Hamiltonian matrices.

We assume for the moment that the Fermi level E_F and the extremal eigenvalues λ_{\min}^k and λ_{\max}^k of the Hamiltonian matrices \hat{H}^k are given. We can then approximate the k -th occupation operator as follows

$$(9) \quad \hat{O}^k \approx \hat{O}_{\gamma^k(E_F)}^k := \mu_0(\gamma^k(E_F))I + 2 \sum_{m=1}^{M^k} g_{m,M^k} \mu_m(\gamma^k(E_F)) T_m(A^k)$$

where

$$A^k = c^k I + d^k \hat{H}^k, \quad \gamma^k(E_F) = c^k + d^k E_F, \quad c^k = -\frac{\lambda_{\max}^k + \lambda_{\min}^k}{\lambda_{\max}^k - \lambda_{\min}^k}, \quad d^k = \frac{2}{\lambda_{\max}^k - \lambda_{\min}^k}.$$

The parameters c^k and d^k are chosen to rescale the eigenvalues interval $[\lambda_{\min}^k, \lambda_{\max}^k]$ to $[-1, 1]$. Since the operator \hat{O}^k can be seen as a multiple (by a factor 2) of the Heaviside function of the Hamiltonian matrix \hat{H}^k , the coefficients $\mu_m(\gamma^k(E_F))$ are those given in (1).

We denote the subspace spanned by the occupied eigenvectors as Ψ^k . Ψ^k is invariant by application of the k -th occupation operator \hat{O}^k . This suggests restricting the Chebyshev–Jackson expansion to a certain subspace V^k which accurately approximates Ψ^k . We use the following recursions to build the Chebyshev series $T_m(A^k)V^k$. We start from $T_0(A^k)V^k = V^k$ and $T_1(A^k)V^k = A^kV^k$, we successively form

$$(10) \quad T_m(A^k)V^k = 2A^kT_{m-1}(A^k)V^k - T_{m-2}(A^k)V^k \quad \text{for } m = 2, \dots, M^k.$$

Since each column of $T_m(A^k)V^k$ is independent, this recursion requires only matrix-vector products which can be fully parallelized. We approximate the occupation operator \hat{O} on the subspace $V = \bigoplus_k V^k$ by

$$(11) \quad \hat{O}V \approx \bigoplus_k \hat{O}_{\gamma^k(E_F)}^k V^k.$$

In our current implementation of this algorithm, we compute the smallest and the largest eigenvalues λ_{\min}^k and λ_{\max}^k of \hat{H}^k using an iterative Lanczos method. Since they are the only eigenvalues which are computed by this procedure, this requires only a few matrix-vector multiplications. To determine the Fermi level E_F , we assume that each V^k is represented by an orthogonal matrix, *i.e.*, $V^{kT}V^k = I_{\dim(V^k)}$. Since $\text{Tr}(\hat{O}) = \sum_k \text{Tr}(\hat{O}^k) = N_{el}$, we compute E_F from the nonlinear scalar equation

$$(12) \quad \phi(E_F) := \sum_k \text{Tr} \left(V^{kT} \hat{O}_{\gamma^k(E_F)}^k V^k \right) - N_{el} = 0$$

by means of Newton iteration

$$(13) \quad E_{F,i+1} := E_{F,i} - \frac{\phi(E_{F,i})}{\phi'(E_{F,i})}.$$

$\phi(E_F)$ and its derivative with respect to E_F are given by

$$(14a) \quad \phi(E_F) = \sum_k \mu_0(\gamma^k(E_F)) \dim(V^k) + 2 \sum_k \sum_{m=1}^{M^k} g_{m,M^k} \mu_m(\gamma^k(E_F)) \text{Tr} \left(V^{kT} T_m(A^k) V^k \right) - N_{el},$$

$$(14b) \quad \phi'(E_F) = \sum_k d^k \mu'_0(\gamma^k(E_F)) \dim(V^k) + 2 \sum_k \sum_{m=1}^{M^k} g_{m,M^k} d^k \mu'_m(\gamma^k(E_F)) \text{Tr} \left(V^{kT} T_m(A^k) V^k \right).$$

Differentiating the coefficients $\mu_m(\gamma)$ in (1) with respect to γ we get

$$(15) \quad \mu'_m(\gamma) = \frac{2T_m(\gamma)}{\pi\sqrt{1-\gamma^2}} \quad \text{for } m = 0, \dots, M,$$

where $T_m(\gamma)$ is the m th Chebyshev polynomial of the first kind.

6. Algorithms. The computation of the occupation matrix \hat{O} is performed as follows.

ALGORITHM 6.1. *Computation of the occupation matrix.*

0. For all k -points do:
 1. Compute the smallest and the largest eigenvalues λ_{\min}^k and λ_{\max}^k of \hat{H}^k .
 2. Select a subspace V^k .
 3. Select a degree M^k for the Chebyshev–Jackson expansion (9).
 4. Compute $T_m(A^k)V^k$ by the recursion (10) and store for each k .
 5. Compute the Jackson coefficients g_{m,M^k} (5).
6. Obtain an estimate to the Fermi level E_F .
7. For all k -points compute the Chebyshev coefficients $\mu_m(\gamma^k(E_F))$ (1).
8. Compute $\phi(E_F)$ by (14a).
9. If $|\phi(E_F)| \leq TOL$ where TOL is a given tolerance Then
 10. Form the approximation (11) to the occupation operator using (9). Stop.
- Else
 11. For all k -points compute the Chebyshev coefficients $\mu'_m(\gamma^k(E_F))$ (15).
 12. Compute $\phi'(E_F)$ by (14b).
 13. Apply a Newton correction (13) for E_F . Repeat from 7.

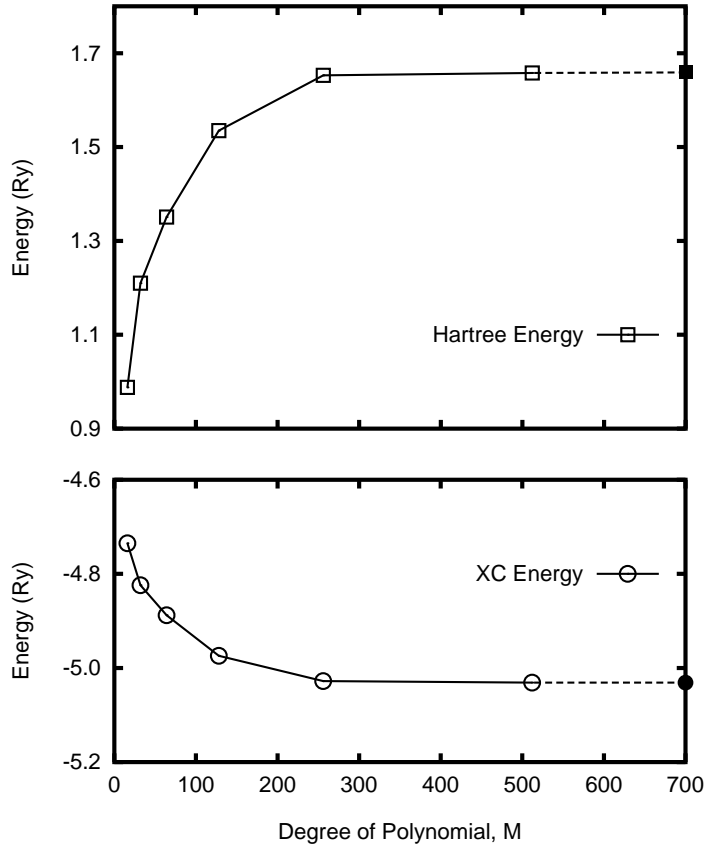


FIG. 3. Convergence of the Hartree and exchange-correlation energies with respect to the degree M of the Chebyshev polynomial for a crystalline silicon. Solid symbols denote the corresponding energies obtained by the iterative diagonalization scheme.

The *self consistent iteration* procedure is as follows.

ALGORITHM 6.2. *Self consistent iteration.*

0. Obtain the initial charge density $\rho(r)$ by superposing the atomic charge densities.
1. Obtain the potentials V_{xc} , V_{ion} , and the initial V_H .
2. Compute the occupation matrix using Algorithm 6.1.
3. Compute the charge density $\rho(F)$ in reciprocal space from (8).
4. Compute the new potentials V_H and V_{tot} .
5. ‘Mix’ the potentials with a Broyden-type quasi-Newton approach.
6. If self-consistency test satisfied Then stop. Else repeat from 2.

7. Numerical results. We have applied the current algorithm to crystalline silicon. To investigate convergence with respect to the degree of the polynomial expansion, we have calculated the Hartree and the exchange-correlation energy of the bulk silicon (diamond structure: two atoms per cell). The kinetic energy cutoff of 9 Ry is used and a single k -point (Γ) is sampled to perform the Brillouin zone integrations. The results are plotted in Fig. 3. The energies converge to the correct values (obtained using iterative diagonalization) when a sufficiently large degree is used in the Chebyshev expansion. The plots indicate that one should use at least $M \simeq 250$ to ensure these energies are converged. Unfortunately, a polynomial expansion with a large value for M produces a large prefactor for the remaining operations. It is conceivable that different polynomial expansions which might result in faster convergence with respect to the degree of expansion are required.

For the purpose of assessing the scaling property of this scheme, we have done self-consistent calculations varying the system size from 2 to 64 atoms. We used a kinetic energy cutoff of 6.25 Ry and Γ -point sampling. The CPU times are plotted in Fig. 4 with fits to $N^2 \log N$. Our results show that the N^3 scaling operations due to orthogonalization are avoided in the current scheme. Fig. 4 confirms that the

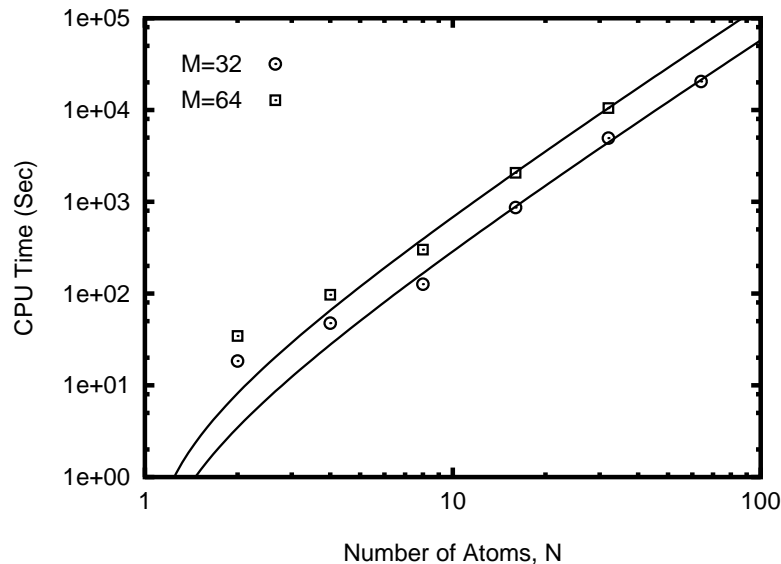


FIG. 4. *Scaling behavior of the CPU time to achieve the self-consistency with respect to the number N of atoms in the simulation cell: Symbols denote the calculations performed and the lines are fits to the functional form $N^2 \log N$.*

proposed algorithm scales as $\mathcal{O}(N^2 \log N)$. This scaling results from the matrix–vector multiplication to calculate the Chebyshev polynomial.

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Appendix. Jackson damping factor.

Proof. [Lemma 3.1] From (2)-(3)-(4) we get

$$g_{m,M} = \frac{1}{\left(\sum_{i=0}^M \sin^2((i+1)\alpha_M)\right)} \cdot \sum_{i=0}^{M-m} \sin((i+1)\alpha_M) \sin((m+i+1)\alpha_M).$$

Let us compute

$$\begin{aligned} (16) \sum_{i=0}^{M-m} \sin((i+1)\alpha_M) \sin((m+i+1)\alpha_M) &= \sum_{j=0}^{M-m+1} \sin(j\alpha_M) \sin((m+j)\alpha_M) \\ &= \frac{1}{2} \sum_{j=0}^{M-m+1} \left(\cos(m\alpha_M) - \cos((2j+m)\alpha_M) \right) \\ &= \frac{1}{2} \left((M-m+2) \cos(m\alpha_M) - \sum_{j=0}^{M-m+1} \cos((2j+m)\alpha_M) \right). \end{aligned}$$

The last sum is given by

$$\begin{aligned} \sum_{j=0}^{M-m+1} \cos((2j+m)\alpha_M) &= \mathbf{Re} \left(\left(\frac{e^{im\alpha_M} - e^{i(2M-m+4)\alpha_M}}{1 - e^{i2\alpha_M}} \right) \cdot \left(\frac{1 - e^{-i2\alpha_M}}{1 - e^{-i2\alpha_M}} \right) \right) \\ &= \frac{1}{2(1 - \cos(2\alpha_M))} \left(\cos(m\alpha_M) + \cos((2M-m+2)\alpha_M) \right. \\ &\quad \left. - \cos((m-2)\alpha_M) - \cos((2M-m+4)\alpha_M) \right) \\ &= \frac{1}{2(1 - \cos(2\alpha_M))} \left(2 \cos((M+1)\alpha_M) \cos((M-m+1)\alpha_M) \right. \\ &\quad \left. - 2 \cos((M+1)\alpha_M) \cos((M-m+3)\alpha_M) \right) \\ &= \frac{\cos((M+1)\alpha_M)}{1 - \cos(2\alpha_M)} 2 \sin(\alpha_M) \sin((M-m+2)\alpha_M) \\ &= \frac{\cos((M+1)\alpha_M) \sin((M-m+2)\alpha_M)}{\sin(\alpha_M)}. \end{aligned}$$

Hence, for $m = 0$ in (16) we get

$$\sum_{i=0}^M \sin^2((i+1)\alpha_M) = \frac{M+2}{2}$$

leading to

$$g_{m,M} = \frac{1}{M+2} \left((M-m+2) \cos(m\alpha_M) - \frac{\cos((M+1)\alpha_M) \sin((M-m+2)\alpha_M)}{\sin(\alpha_M)} \right)$$

which simplifies to (5). \square

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