An efficient algorithm for electronic-structure calculations

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We show how to adapt the quasi-Newton method to the electronic-structure calculations using systematic basis sets. Our implementation requires less iterations than the conjugate gradient method, while the computational cost per iteration is much lower. The memory usage is also quite modest, thanks to the efficient representation of the approximate Hessian.

KEYWORDS: density-functional theory, quasi-Newton method, BFGS update, finite-element method, Born-Oppenheimer dynamics

§1. Introduction

The importance of the first-principles electronic-structure calculations based on the density-functional theory is increasing year by year. Since the optimization of the ground-state wavefunctions is the most time-consuming part of these calculations, it is crucial to use an efficient algorithm for this purpose. However, the number of degrees of freedom is so large for systematic basis sets like plane-waves, finite-differences, and finite-elements, that the memory usage of the algorithm being used is severely restricted. Currently, the conjugate gradient method seems to be most widely used because of its efficiency and modest memory usage, while the direct inversion in the iterative subspace (DIIS) is also sometimes used.

On the other hand, the quasi-Newton methods have rarely been used for electronic optimization in combination with systematic basis sets, although their efficiency is well known to the best of our knowledge, the application of the quasi-Newton methods in this context has been limited to atomic orbitals or one-dimensional problems. This is presumably because they require significantly more storage for the elements of the (approximate) Hessian matrix. If an all-band update is used, the dimension of the Hessian ($\mathcal{H}$) is given by $\mathcal{N} = N_\alpha N_\sigma$, where $N_\alpha$ is the number of orbitals and $N_\sigma$ is the number of basis functions. Therefore, the storage requirement for $\mathcal{H} (\mathcal{N} \times \mathcal{N})$ will be $\mathcal{N}^2$ in a naive implementation, which is prohibitive for large-scale simulations where $\mathcal{N}$ can exceed $10^7$. A more practical implementation of the quasi-Newton method is also
found in the literature, in which only the previous steps are relevant. Since two update vectors of size $N$ are required per step, the memory usage amounts to $2mN$ elements, where $m$ is usually less than 10. However, this can be further reduced to $mN$ if the initial Hessian is a multiple of the unit matrix. In this article, we present the implementation of the quasi-Newton method using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) formula along this line. As explained in the next section, we make a number of modifications to adapt the algorithm to the electronic-structure calculations. The most important one is the compression of the update vectors by an order of magnitude, which makes this algorithm attractive even for very large systems.

§2. Methods

2.1 Electronic-structure calculations

First of all, we explain the basic problems in the electronic-structure calculations within the density-functional theory. Only real wavefunctions at the Γ-point of the Brillouin zone are considered for notational simplicity, but generalization to complex wavefunctions is straightforward.

The total energy functional for an ionic configuration $R$ is given by

$$E_{\text{total}}[\Psi, R] = \sum_i \int \psi_i(r) \left[ -\nabla^2 + V_{\text{ps}}[R] \right] \psi_i(r) \, dr + E_{\text{Hxc}}[n(r)] + E_{\text{ion}}[R], \quad (2.1)$$

where

$$\Psi = (\psi_1(r) \ \psi_2(r) \ \ldots \ \psi_{N_B}(r))^T, \quad (2.2)$$
$$n(r) = \sum_i |\psi_i(r)|^2, \quad (2.3)$$

and $E_{\text{Hxc}}$ is the sum of the Hartree and exchange-correlation energy, which is a nonlinear and nonlocal functional of the electron density $n(r)$. In practice, each $\psi_i(r)$ is discretized by a basis set expansion, which makes $\Psi$ a huge vector with $N (= N_B N_G)$ elements.

In the conventional approach, the ground-state energy $E_G$ and wavefunctions $\Psi_G$ for the given $R$ are obtained by minimization of $E_{\text{total}}[\Psi, R]$ with respect to the wavefunctions $\Psi$ under the orthonormality constraints:

$$\int \psi_i(r) \psi_j(r) \, dr = \delta_{ij}. \quad (2.4)$$

$\Psi_G$ calculated in this way is then used to study various properties of the system.

In our implementation, on the other hand, the above constraints are eliminated by modifying the total energy functional according to Refs. [17, 33, 35], in which orthonormality of the wavefunctions is satisfied either implicitly or automatically. Moreover, all the orbitals are updated simultaneously and self-consistency of $E_{\text{Hxc}}$ is taken into account in the evaluation of its gradient. Then, if the modified total energy functional for the given $R$ is denoted by $E[\Psi]$, $E_G$ and $\Psi_G$ are obtained by minimization of $E[\Psi]$ with respect to $\Psi$ without any constraints. Thanks to this reformulation, we can easily implement the quasi-Newton method which is one of the most
efficient algorithms for the unconstrained optimization of nonlinear functions. Furthermore, the use of nonorthogonal basis functions is much easier in this case. The above ground-state calculations are usually performed for a series of slowly varying $R$, each of which is called an ionic step.

2.2 BFGS with full Hessian

We illustrate the conventional quasi-Newton method using the BFGS formula, which will serve as a prototype for the implementation in reduced space. For simplicity, we assume the new total energy (eq. (2.7)) is always lower than the previous value.

Choose $\mathcal{H}_0$ and $\Psi_0$.

Calculate $E_0 = E[\Psi_0]$ and $g_0 = \nabla E[\Psi_0]$.

Set $k=0$.

Do while ($|g_k| \geq \epsilon$)

\begin{align*}
p_k &= -\mathcal{H}^{-1}_k g_k \quad \text{(2.5)} \\
\Psi_{k+1} &= \Psi_k + p_k \quad \text{(2.6)} \\
E_{k+1} &= E[\Psi_{k+1}] \quad \text{(2.7)} \\
g_{k+1} &= \nabla E[\Psi_{k+1}] \quad \text{(2.8)} \\
\Delta \Psi_k &= \Psi_{k+1} - \Psi_k \quad \text{(2.9)} \\
\Delta g_k &= g_{k+1} - g_k \quad \text{(2.10)} \\
\mathcal{H}_{k+1} &= \mathcal{H}_k - \frac{\mathcal{H}_k \Delta \Psi_k \Delta \Psi_k^T \mathcal{H}_k}{\Delta \Psi_k^T \mathcal{H}_k \Delta \Psi_k} + \frac{\Delta g_k \Delta g_k^T}{\Delta \Psi_k^T \Delta g_k} \quad \text{(2.11)} \\
& \quad \quad k = k + 1 \quad \text{(2.12)}
\end{align*}

End do

While this algorithm is simple and efficient in terms of the convergence rate, its memory usage and computational effort scale as $O(N^2)$ and $O(N^3)$ respectively, which are prohibitive. Although the latter can be reduced to $O(N^2)$, if the updating formula for the inverse Hessian ($\mathcal{H}^{-1}$) is used, this is still far from practical. The purpose of this article is to present the improved algorithm in which both scale as $O(N)$ with modest prefactors.

2.3 QR-decomposition

At this point, we give a brief introduction to the QR-decomposition, which plays an important role in the algorithm presented in the next section. Let us assume $B(N \times r)$ is a set of linearly independent vectors:

\begin{equation}
B = (p_1 \ p_2 \ \cdots \ p_r),
\end{equation}

(2.13)
where $1 \leq r \ll N$. Then the QR-decomposition of $B$ is given by

$$B = Z T,$$

where $Z(N \times r)$ is a set of orthonormal vectors spanning the same subspace as $B$, i.e.

$$Z^T Z = I,$$

and $T(r \times r)$ is an invertible upper-triangular matrix. In practice, this decomposition is obtained by applying the addition procedure given below repeatedly, which is (mathematically) equivalent to constructing an orthonormal basis from the left ($p_1$) to the right ($p_r$) by the Gram-Schmidt scheme. Note, however, that only $B$ and $T$ are considered explicitly in the following.\[31, 32]\)

Here we show how to update the above QR-decomposition when $B$ is slightly modified. In the first case where a vector $g$ is added to $B$, i.e.

$$B_{+} = (p_1 \ p_2 \ \cdots \ p_r \ g) = (B \ g),$$

the new decomposition is given by

$$B_{+} = Z_{+} T_{+},$$

where

$$T_{+}((r + 1) \times (r + 1)) = \begin{pmatrix} T & \mathbf{u} \\ 0 & \rho \end{pmatrix},$$

$$\mathbf{u} = Z^T g = (T^T)^{-1}(B^T g),$$

and

$$\rho = \sqrt{|g|^2 - |\mathbf{u}|^2}.$$

If $\rho \neq 0$, $T_{+}$ is also an invertible upper-triangular matrix.

Next, we consider the case of dropping the leftmost vector $p_1$ from $B$, i.e.

$$B_{-} = (p_2 \ p_3 \ \cdots \ p_r).$$

The corresponding decomposition is given by

$$B_{-} = Z_{-} T_{-},$$

where $T_{-}$ satisfies

$$T_{-}^T T_{-} = B_{-}^T B_{-}.$$  

Obviously, the right-hand side of eq. \[2.23\] is included in $B^T B$, which is easily calculated from

$$B^T B = T^T T.$$

Therefore, $T_{-}$ is obtained by the Cholesky decomposition of a small matrix at negligible cost. A more refined approach is introduced in Ref. \[32\], but the above procedure seems to be sufficient for our present purpose.
2.4 BFGS with reduced Hessian and limited memory

Here we present the state-of-the-art implementation of the quasi-Newton method, which is obtained by modifying the conventional algorithm (§2.2) under two assumptions: (i) \( H_0 = \sigma I \) \((\sigma > 0)\), and (ii) At most \( m \) previous steps are stored.

In order to fully exploit these conditions, it is more convenient to use a compact representation for the Hessian:

\[
H = Z^T \mathcal{H} Z, \tag{2.25}
\]

where \( Z (N \times r) \) is the current (orthonormal) basis, \( H (r \times r) \) is the reduced Hessian, and \( 1 \leq r \leq m + 1 \ll N \). While \( Z \) and \( \mathcal{H} \) also appear in the following algorithm, they are not explicitly calculated. The reduced vectors are defined in a similar way; the reduced gradient \( u \), for instance, is given by \( u = Z^T g \), where \( g = \nabla E \). The correspondence between the full/reduced vectors is shown in Table I.

1. Initialization:
   Set \( k = 0 \) and \( r = 1 \), where \( k \) and \( r \) denote the loop index and the rank of the reduced space, respectively.
   Choose the initial wavefunction \( (\Psi_0) \), the approximate curvature \( (\sigma) \), the convergence criterion \( (\epsilon) \), and the maximum rank of the reduced space \( (m) \).
   Calculate the total energy
   \[
   E_0 = E [\Psi_0] \tag{2.26}
   \]
   and its gradient
   \[
   g_0 = \nabla E [\Psi_0]. \tag{2.27}
   \]
   IF \((|g_0| < \epsilon)\) THEN quit.
   ELSE \( H_0 = (\sigma) \), \( B_0 = (g_0) \), \( T_0 = (|g_0|) \), and \( v_0 = (|g_0|) \). Moreover, \( Z_0 = (g_0/|g_0|) \) and \( \mathcal{H}_0 = \sigma I \) are implicitly assumed.
   If the Hessian of the previous ionic step is taken over, several modifications are required in this step, which are, however, straightforward.
2. Calculate the new search direction in reduced space:
   \[
   q_k = -H_k^{-1} v_k. \tag{2.28}
   \]
3. Calculate the new search direction:
   \[
   p_k = Z_k q_k = B_k (T_k^{-1} q_k). \tag{2.29}
   \]
4. Update the subspace: \((B_k = Z_k T_k \rightarrow B_k' = Z_k T_k')\), where
   \[
   B_k (N \times r) = (p_{k-r+1} \cdots p_{k-1} g_k) \tag{2.30}
   \]
and

\[ B'_k(N \times r) = (p_{k-r+1} \cdots p_{k-1} p_k). \]  

(2.31)

\( T'_k \) is obtained from \( T_k \) and \( q_k \), whereas \( Z_k \) remains unchanged. \[ 32 \]

5. Set \( \alpha = 1 \) and calculate the gradient of the total energy along \( p_k \) as

\[ E' = \frac{\partial E[\Psi_k + \alpha p_k]}{\partial \alpha} \bigg|_{\alpha=0} = g_k^T p_k = v_k^T q_k. \]  

(2.32)

6. Calculate the new wavefunction:

\[ \Psi_{k+1} = \Psi_k + \alpha p_k. \]  

(2.33)

7. Calculate the new total energy:

\[ E_{k+1} = E[\Psi_{k+1}]. \]  

(2.34)

\[ \text{IF } (E_{k+1} \geq E_k) \text{ THEN estimate the optimal } \alpha \text{ by a parabolic fit with } E_k, E', \text{ and } E_{k+1}, \text{ and go to 6.} \]

8. Calculate the new gradient:

\[ g_{k+1} = \nabla E[\Psi_{k+1}]. \]  

(2.35)

\[ \text{IF } (|g_{k+1}| < \epsilon) \text{ THEN quit.} \]

9. Extend the subspace: \( B''_k(N \times r) = (p_{k-r+1} \cdots p_k g_{k+1}) \)

\[ (2.36) \]

and

\[ B''_k(N \times (r+1)) = (p_{k-r+1} \cdots p_k g_{k+1}). \]  

(2.37)

As explained in \$2.3, \( T''_k \) is obtained from \( T'_k, u_k, \) and \( \rho_{k+1}, \) where

\[ u_k = Z_k^T g_{k+1} = (T_k^T)^{-1}(B'_k^T g_{k+1}) \]  

(2.38)

and

\[ \rho_{k+1} = \sqrt{|g_{k+1}|^2 - |u_k|^2}. \]  

(2.39)

We assume \( \rho_{k+1} \neq 0 \) in the following. Then, the new basis \( Z'_k(N \times (r+1)) \) is given by

\[ Z'_k = (Z_k \ z_{k+1}), \]  

(2.40)

where \( z_{k+1} = (g_{k+1} - Z_k u_k) / \rho_{k+1} \). However, \( z_{k+1} \) is not explicitly calculated.

10. \( r = r + 1 \)

11. Calculate the reduced gradients as

\[ v'_k = Z'_k^T g_k = \begin{pmatrix} v_k \\ 0 \end{pmatrix} \]  

(2.41)
12. Update the reduced Hessian using the BFGS formula:

\[ u'_k = Z^T_k g_{k+1} = \begin{pmatrix} u_k \\ \rho_{k+1} \end{pmatrix}. \] (2.42)

There is no loss of information here, since \( g_k, g_{k+1} \in Z_k'. \)

13. Go to 2.

14. \( k = k + 1 \)

15. Go to 4.

- While \( 0 \leq k \leq m - 1 \), this algorithm is identical to the conventional one (§ 2.2) with \( H_0 = \sigma I \) within round-off errors. The two algorithms begin to differ once \( k \) reaches \( m \), but the deterioration of the convergence rate is minimized by constructing the subspace with the previous search directions rather than the gradients.
• For simplicity, the above algorithm includes minimal exception handling. Therefore, the original paper \cite{32} should be consulted for a more complete one. However, such exceptions are observed only in the very early stages of the first ionic step, where the quadratic model is not valid.

• One cycle requires approximately $2rN$ multiply-and-add operations, arising from eqs. (2.29) and (2.38). For practical values of $m (< 10)$, these costs will be much lower than those of evaluating the total energy in step 6.

• The basis functions should be appropriately scaled \cite{16,27} in advance, so that their contribution to the total energy is similar.

• The reduced Hessian $H_k$ is diagonalized in each cycle to guarantee its positive definiteness; nonpositive eigenvalues, if any, are modified appropriately. Then, it follows from eqs. (2.28) and (2.32) that $E' = -v_k^T H_k^{-1} v_k < 0$, because $H_k^{-1}$ is also positive definite and $|v_k| = |g_k| \geq \epsilon$. Furthermore, the average eigenvalue of the reduced Hessian, denoted by $\lambda_k$, is also calculated and stored for later use.

• We explain the choice of $\sigma$ used in step 1 and 12 here. Since $\sigma$ is the approximate curvature along the new direction \cite{32}, a reasonable estimate is needed to achieve high performance. Therefore, a number of strategies have been proposed to choose optimal $\sigma$ \cite{30,31,32}, most of which provide dynamical estimates. Nevertheless, we use a constant $\sigma$ during each ionic step unless otherwise noted, which is determined as follows: In the first ionic step, $\sigma$ is estimated from the coarse grid iterations \cite{22}. At the end of each ionic step, the sequence $\{\lambda_k\}$ is further averaged to give the new $\sigma$ for the next ionic step. $\sigma$ obtained in this way varies only slowly with ionic steps, while providing stable and high performance in the systems we have studied so far. Comparison is also made with the dynamical estimates in § 3.

2.5 Data compression

The memory usage of the algorithm illustrated in the previous section is dominated by the $m$ previous search directions, which amount to $mN$ elements. While this is much smaller than the storage of the full Hessian (= $N^2$), it is still a serious obstacle in large-scale simulations. In what follows, we present a simple algorithm to compress the previous search directions without sacrificing the efficiency of the original method. In this algorithm, one search direction is compressed in each cycle, by taking advantage of its structure. If $p(N)$, which is being compressed, is viewed as a two-dimensional array $p(N_b, N_c)$, the size of $p(i, j)$ for a given basis function ($j$) is expected to be similar for all orbitals ($i$). Based on this idea, the largest element of $|p(i, j)|$ with respect to $i$ is chosen as the scale factor. Moreover, $N_{br}$ is defined as the number of bits assigned to each element of $p$ after compression.
Then, the scale factor \( \omega(N_G) \) and the compressed array \( p_i(N_B, N_G) \) are given by

\[
\text{real}*8 \quad \omega(j) = \left( \max_{1 \leq i \leq N_B} |p(i,j)| \right) / I_{\text{max}} \tag{2.49}
\]

and

\[
\text{integer} \quad p_i(i,j) = \text{round} \left( \frac{p(i,j)}{\omega(j)} \right) + I_{\text{max}} \tag{2.50}
\]

respectively, where \( I_{\text{max}} = 2^{N_\text{bit}} - 1 \) and \( 0 \leq p_i(i,j) \leq 2I_{\text{max}} = 2^{N_\text{bit}} - 2 \). Therefore, each element of \( p_i \) is representable by \( N_\text{bit} \) bits. The original values of \( p \) are recovered approximately by

\[
p(i,j) \approx \omega(j) (p_i(i,j) - I_{\text{max}}).
\]

In this method, the quality of the compression can be controlled by a single parameter, \( N_\text{bit} \). Furthermore, the largest element for each \( j \), which is the most important one, remains exact.

The total storage for the \( m \) search directions after compression is \( mN_\text{bit}N'/8 \) bytes, if appropriately packed with bit operations. If \( m = N_\text{bit} = 8 \), for instance, this amounts to only one double-precision array of size \( N' \). Note also that the storage for the scale factors is minor.

In the current implementation, \( p_k \) is compressed in step 3 when added to \( B'_k \). At the same time, the last column of \( T'_k \) is calculated directly from the compressed \( p_k \) (rather than using \( q_k \)) to maintain the consistency of the QR-decomposition. However, the uncompressed \( p_k \) is also retained and used in step 3.

Unfortunately, some inconsistency seems inevitable in the update of the reduced Hessian, since \( s_k \) and \( y_k \) no longer belong to \( Z'_k \). Nevertheless, \( E' < 0 \) remains valid as long as the reduced Hessian is positive definite and the latest \( g \) and \( p \) are uncompressed. Therefore, the stability of the minimization is guaranteed even if the previous search directions are highly compressed.

### §3. Results

As a test of our implementation under realistic conditions, we performed a series of Born-Oppenheimer dynamics\(^{36}\) for bulk diamond at 220 K in a periodic cubic supercell of 64 atoms within the local density approximation\(^{1, 2}\). The wavefunctions were expanded by the adaptive finite-element method\(^{11, 12}\) with an average cutoff energy of 43 Ry, which corresponds to \( N_G = 8 \times 14^3 = 21,952 \). Since \( N_B \) is equal to 128, \( N' \) amounts to approximately 2,800,000 in this system. The Brillouin zone was sampled only at the \( \Gamma \)-point, and the separable pseudopotentials were used\(^{37, 38}\). The convergence criterion (\( \epsilon \)) was chosen so that \( |E_{k+1} - E_k| \simeq 2 \times 10^{-8} \) Ry/atom when \( |g_{k+1}| < \epsilon \) was satisfied. Convergence to the ground state was accelerated by the enhanced extrapolation scheme\(^{39}\) which provides accurate initial wavefunctions with the help of population analysis.

The equations of motion for the ions were integrated using the velocity-Verlet method\(^{40}\) with a timestep of 80 a.u. (~2 fs). Starting from the same ionic configuration, each run lasted for 57
ionic steps, the last 50 steps of which were used to collect the statistics. Moreover, $B, T,$ and $H$ were taken over from previous ionic steps unless otherwise noted. Therefore, these matrices were saturated during this period in all runs.

We first show the average number of iterations ($N_{\text{iter}}$) and total energy evaluations ($N_E$) needed to optimize the electronic-structures for the conjugate gradient method using the Polak-Ribiere formula \cite{14} and the quasi-Newton method using the BFGS formula in Table II. The convergence rate of the quasi-Newton method as measured by $N_{\text{iter}}$ is already comparable to that of the conjugate gradient method for $m = 2$, and becomes better as $m$ is increased. However, there is no point in using $m$ much larger than $N_{\text{iter}}$ (say, 20), because the Hessian is dominated by the contribution from previous ionic steps. In practice, any reasonable choice of $m$, e.g. 5-8, will provide near-optimal performance, since $N_{\text{iter}}$ depends only weakly on $m$ in this range. Note also that the CPU-time is more closely related to $N_E$ than $N_{\text{iter}}$. Therefore, the quasi-Newton method was much faster than the conjugate gradient method for all $m$ we tried. Specifically, $N_E = 2N_{\text{iter}} + 1$ in the conjugate gradient method, because at least one line search was forced to maintain the conjugacy of the search directions. In contrast, $N_E = N_{\text{iter}} + 1$ in the quasi-Newton method, which means that no line search was required in step 7.

The algorithm presented in §2.4 has a number of options which are not uniquely determined. Therefore, we examine some of them here, as shown in Table III. (a) is the reference run performed with $m = 7$, taken from Table II. (b)-(d) were performed under the same conditions as (a) except for the following points: (b) A line search with a parabolic fit was forced in each cycle to see if the convergence rate is improved. However, $N_E$ was almost doubled without any reduction of $N_{\text{iter}}$. Therefore, it is not justified to perform a line search in the quasi-Newton method, which is consistent with previous findings.\cite{30} (c) The Hessian was discarded at the end of each ionic step. Since the convergence rate deteriorates significantly, the inheritance of the Hessian seems to be profitable. (d) We tried $\sigma_k = |y_k|^2/y_k^T s_k$, which gave good results in Refs. \cite{31,32}. However, this choice requires more iterations on average, presumably because $\sigma_k$ varies too rapidly with $k$. The norm of the gradient also decays less smoothly in this case.

So far the previous search directions have been uncompressed, i.e. stored as 64-bit double-precision arrays. The effect of compression is examined here in a series of runs for $m = 3$ and 7, with different $N_{\text{bit}}$. As shown in Table IV, the performance is maintained after compression by a factor of 8-16, especially for $m = 7$. Moreover, no instability occurred up to $N_{\text{bit}} = 3$. We also show the distribution of the search direction after compression with $N_{\text{bit}} = 8$ in Fig. 1. The distribution function $d(x)$ is defined as the number of elements of $p$, such that $p_i(i) = x$, where $1 \leq i \leq N$ and $0 \leq x \leq 2^{8} - 2 = 254$. Therefore, $\sum_x d(x) = N$, and there are two singularities at $x = 0$ and 254. The width of the distribution is approximately equal to $I_{\text{max}}$, which indicates that our choice of the scale factor (eq.(2.49)) is appropriate.
Finally, in order to examine the generality of our implementation, part of the runs were repeated for an isolated cytosine molecule ($C_4H_5N_3O$) in a cubic supercell of $(16 \text{ a.u.})^3$, with a timestep of $40 \text{ a.u.} \approx 1 \text{ fs})$. The average cutoff energy was $39 \text{ Ry}$, which corresponds to $N_a = 21, N_o = 8 \times 16^3 = 32,768$, and $N \sim 700,000$. The results shown in Table V suggest that the performance of the quasi-Newton method in this system is somewhat more robust against compression, but is qualitatively similar to the previous results in other respects.

§4. Summary

We have shown in this article that the quasi-Newton method using the BFGS formula is the method of choice for large-scale electronic-structure calculations, if combined with efficient memory management. The advantages of the quasi-Newton method over the conjugate gradient method are summarized as follows: (i) The Hessian of the previous ionic step can be taken over to accelerate the convergence. (ii) Practically no line search is required, which reduces the cost of each step significantly.

Although there is room for fine-tuning the algorithm and more extensive tests are necessary, the quasi-Newton method will provide significant speedups of the first-principles codes, together with other techniques like the enhanced extrapolation scheme and the constrained molecular dynamics.

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Table I. Notation for the full/reduced vectors. Note that $v$ and $u$ denote the previous and the current gradients, respectively.

| full     | reduced |
|----------|---------|
| gradient | $g$     | $v, u$ |
| search direction | $p$ | $q$ |
| update vectors    | $\Delta \Psi$ | $s$ |
|                   | $\Delta g$ | $y$ |
| wavefunction      | $\Psi$ | - |

Table II. The performance of the conjugate gradient method and the quasi-Newton method is compared in the molecular-dynamics simulations of bulk diamond. $N_{iter}$ and $N_E$ denote the number of iterations and total energy evaluations averaged over 50 ionic steps, respectively.

| method                  | $N_{iter}$ | $N_E$ |
|-------------------------|------------|-------|
| Conjugate gradient      | 14.3       | 29.6  |
| BFGS, $m = 2$           | 14.9       | 15.9  |
| 3                       | 13.8       | 14.8  |
| 4                       | 13.8       | 14.8  |
| 5                       | 12.9       | 13.9  |
| 6                       | 12.4       | 13.4  |
| 7                       | 12.1       | 13.1  |
| 8                       | 11.9       | 12.9  |
| 9                       | 11.7       | 12.7  |
| 10                      | 11.6       | 12.6  |
| 20                      | 12.4       | 13.4  |
Table III. A number of variants are compared for the BFGS with $m = 7$. (a) Reference run from Table II. (b) A line search with a parabolic fit was forced in each cycle. (c) The Hessian was discarded at the end of each ionic step. (d) $\sigma_k = |y_k|^2 / y_k^T s_k$ was used as the curvature for the new direction.

| method | $N_{\text{iter}}$ | $N_E$ |
|--------|------------------|-------|
| (a)    | 12.1             | 13.1  |
| (b)    | 12.2             | 25.4  |
| (c)    | 15.1             | 16.1  |
| (d)    | 14.3             | 15.4  |

Table IV. The effect of compression is compared for the BFGS with $m = 3$ and 7.

| $m$ | $N_{\text{init}}$ | $N_{\text{iter}}$ | $N_E$ |
|-----|------------------|------------------|-------|
| 3   | 64               | 13.8             | 14.8  |
| 8   | 14.1             | 15.1             |       |
| 4   | 14.3             | 15.3             |       |
| 3   | 15.4             | 16.4             |       |
| 7   | 64               | 12.1             | 13.1  |
| 8   | 12.2             | 13.2             |       |
| 4   | 12.2             | 13.2             |       |
| 3   | 13.3             | 14.3             |       |
Table V. The results of selected runs from Table II-IV, repeated for an isolated cytosine molecule (C₄H₅N₃O).

| method     | N_{init} | N_{iter} | N_E  |
|------------|----------|----------|------|
| Conjugate gradient | –        | 13.1     | 27.1 |
| BFGS, \(m = 3\) | 64       | 13.0     | 14.0 |
|            | 8        | 13.0     | 14.0 |
|            | 4        | 13.0     | 14.0 |
|            | 3        | 13.3     | 14.3 |
| BFGS, \(m = 7\) | 64       | 10.7     | 11.7 |

Fig. 1. The distribution function \(d(x)\) of the compressed search direction \(p_t\) for \(N_{init} = 8\).
