Preconditioned conjugate gradient method for the sparse generalized eigenvalue problem in electronic structure calculations

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The use of localized basis sets is essential in linear-scaling electronic structure calculations, and since such basis sets are mostly non-orthogonal, it is necessary to solve the generalized eigenvalue problem $Hx = \varepsilon Sx$. In this work, an iterative method for finding the lowest few eigenvalues and corresponding eigenvectors for the generalized eigenvalue problem based on the conjugate gradient method is presented. The method is applied to first-principles electronic structure calculations within density-functional theory using a localized spherical-wave basis set, first introduced in the context of linear-scaling methods [Comput. Phys. Commun. 102 (1997) 17]. The method exhibits linear convergence of the solution, the rate of which is improved by a preconditioning scheme using the kinetic energy matrix.
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1 Introduction

Linear-scaling electronic structure methods [1] are essential for calculations of large systems containing many atoms. One of the criteria for the success of such methods is the use of a high quality localized basis set, which is usually non-orthogonal. Using such a basis set, one can formulate the electronic structure problem as a generalized eigenvalue problem $Hx = \varepsilon Sx$ [2–4], which also arises naturally in many other scientific disciplines. The properties of H and S are that they are $N \times N$ Hermitian matrices and that S is also positive definite. For the case where only the lowest few eigenvalue-eigenvector pairs of large N

matrices are required, most direct diagonalization (e.g. Cholesky-Householder procedure) methods which use similarity transformations [2–5] are inefficient because all eigenvalue-eigenvector pairs are found. The computational effort scales as N^3, where N is the number of basis functions in the calculation. Iterative methods which concentrate on only the lowest few eigenvalue-eigenvector pairs are much more efficient [6–11], and are widely used to solve the standard symmetric eigenvalue problem. Iterative solution of the generalized eigenvalue problem usually proceeds by first performing a Cholesky decomposition of S to obtain a standard symmetric eigenvalue problem. However, in this work the generalized problem, cast into variational form, is solved by the conjugate gradient method without first transforming to symmetric form. The gradient method was proposed long ago by Hestenes and Karush [12,13] to solve the eigenvalue problem, where they used a steepest descent method to perform the minimization.

In this work, we first present an example of a generalized eigenvalue problem taken from first-principles electronic structure calculations. An iterative conjugate gradient minimization method which finds the lowest few eigenvalues and eigenvectors is then introduced. Although this method can be used for Hermitian H and Hermitian-positive-definite S, it will be most efficient when H and S are also sparse, a case which arises when large systems are studied with localized basis sets. We have taken the tensor nature of the search direction and other quantities into account. A preconditioning scheme related to that discussed by Bowler and Gillan in a previous Communication [14] to improve the convergence is proposed. To test the method we use a localized spherical-wave basis set introduced in another Communication [15] to perform first-principles calculations. Test cases are taken from the molecular chlorine and bulk silicon systems. The rate of convergence of the solutions is one of our main concerns here. Linear convergence of the solution is observed from the results of calculations.

2 Formulation of the problem

We give a brief account of electronic structure calculations within density-functional theory [16] which requires the generalized eigenvalue problem to be solved (see Ref. [17] for a more comprehensive description). For a system of M electrons, we need to solve self-consistently the Kohn-Sham equations which assume the following form

$$\hat{H}\psi_m(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2 + V_{\mathrm{eff}}(\mathbf{r})\right]\psi_m(\mathbf{r}) = \varepsilon_m\psi_m(\mathbf{r}), \tag{1}$$

where $\hat{H}$ is the Kohn-Sham Hamiltonian, with energy eigenvalues ε_m and corresponding eigenstates $\psi_m(\mathbf{r})$. The effective potential V_{eff} consists of three terms; the classical electrostatic or Hartree potential, the exchange-correlation potential, and the external potential [17]. The electron density is formed from the M lowest or occupied eigenstates

$$\rho(\mathbf{r}) = \sum_{m=1}^{M} |\psi_m(\mathbf{r})|^2 . \tag{2}$$

The eigenstates satisfy the orthogonality constraints where

$$\int \mathrm{d}\mathbf{r}\ \psi_m^*(\mathbf{r})\psi_n(\mathbf{r}) = \delta_{mn}, \tag{3}$$

for all m and n.

When a non-orthogonal basis set $\{\chi_\alpha(\mathbf{r})\}$ is used, the eigenstates are written as

$$\psi_n(\mathbf{r}) = \sum_\alpha {x_n}^\alpha\ \chi_\alpha(\mathbf{r}), \tag{4}$$

where α labels a basis function $\chi_\alpha(\mathbf{r})$. The right hand side of Eq. (4) has been written as a contraction between a contravariant quantity x_n and a covariant quantity $\chi(\mathbf{r})$. Substituting Eq. (4) into Eq. (1), taking inner products with the $\{\chi_\alpha(\mathbf{r})\}$, and using the definitions

$$S_{\alpha\beta} = \int \mathrm{d}\mathbf{r}\ \chi_\alpha^*(\mathbf{r})\chi_\beta(\mathbf{r}), \tag{5}$$

and

$$H_{\alpha\beta} = \int \mathrm{d}\mathbf{r}\ \chi_\alpha^*(\mathbf{r})\hat{H}\chi_\beta(\mathbf{r}), \tag{6}$$

we obtain the generalized eigenvalue problem

$$H_{\alpha\beta}{x_n}^\beta = \varepsilon_n S_{\alpha\beta}{x_n}^\beta. \tag{7}$$

In writing Eq. (7), we have adopted the Einstein summation notation where we sum over repeated Greek indices. The orthogonality conditions of the Kohn-Sham eigenstates in Eq. (3) translate into

$${x_m^*}^\alpha S_{\alpha\beta}{x_n}^\beta = \delta_{mn}. \tag{8}$$

When Eq. (7) is solved, a new output electron density $\rho_{\text{out}}^{(i)}$ is obtained and a new input electron density for the next iteration can be constructed by a linear (or more sophisticated [18]) mixing scheme e.g.

$$\rho_{\text{in}}^{(i+1)} = f\rho_{\text{out}}^{(i)} + (1-f)\rho_{\text{in}}^{(i)}, \tag{9}$$

where the optimum choice for f depends upon the eigenvalues of the static dielectric matrix of the system. The mixing of densities is carried out until Eq. (1) is solved self-consistently.

3 The iterative method

We shall now consider the case of a real, localized, non-orthogonal basis set, and assume that a real symmetric generalized eigenvalue problem is to be solved. To obtain the M lowest eigenstates, we minimize the objective function Ω which is the sum of M eigenvalues (formed by the Rayleigh quotients)

$$\Omega = \sum_{n=1}^{M} \varepsilon_n = \sum_{n=1}^{M} \frac{x_n{}^{\alpha} H_{\alpha\beta} x_n{}^{\beta}}{x_n{}^{\alpha} S_{\alpha\beta} x_n{}^{\beta}}, \tag{10}$$

subject to the orthogonality constraints of Eq. (8). Ω takes its minimum value when $\{x_i; i = 1, \ldots, M\}$ spans the same subspace as the M lowest eigenvectors of Eq. (7). Even though the procedure given below is for a single eigenvector update, it can be generalized easily to an M-eigenvector (or block) update (see Appendix A).

The derivative of Ω with respect to $x_m{}^{\gamma}$ is

$$\frac{\partial \Omega}{\partial x_m{}^{\gamma}} = \frac{2}{(x_m{}^{\alpha} S_{\alpha\beta} x_m{}^{\beta})} \left[H_{\gamma\mu} x_m{}^{\mu} - \varepsilon_m S_{\gamma\nu} x_m{}^{\nu} \right]. \tag{11}$$

Eq. (11) defines a covariant gradient

$$g_{n\alpha} = H_{\alpha\mu} x_n{}^{\mu} - \varepsilon_n S_{\alpha\nu} x_n{}^{\nu}. \tag{12}$$

As pointed out by White *et al.* [19], it is important to consider the tensor property of the search direction. We define the dual basis functions $\chi^{\alpha}(\mathbf{r})$ by the conditions

$$\int \mathrm{d}\mathbf{r}\ \chi^{\alpha}(\mathbf{r}) \chi_{\beta}(\mathbf{r}) = \delta^{\alpha}{}_{\beta}. \tag{13}$$

The metric tensor $S^{\alpha\beta}$ can be defined in terms of the dual basis functions where

$$S^{\alpha\beta} = \int \mathrm{d}\mathbf{r}\ \chi^{\alpha}(\mathbf{r})\chi^{\beta}(\mathbf{r}). \tag{14}$$

It can be shown that $S^{\alpha\beta}$ transforms covariant vectors into contravariant vectors and that $S^{\alpha\beta}S_{\beta\gamma} = \delta^{\alpha}{}_{\gamma}$. Hence we transform the covariant gradient $g_{n\alpha}$ into a contravariant gradient $g_n{}^{\alpha}$ by using the metric tensor $S^{\alpha\beta}$ where

$$g_n{}^{\alpha} = S^{\alpha\beta} g_{n\beta} = S^{\alpha\beta} H_{\beta\gamma} x_n{}^{\gamma} - \varepsilon_n x_n{}^{\alpha}. \tag{15}$$

The contravariant gradient can then be used to update the eigenvector coefficients in Eq. (4).

The constraints of Eq. (8) can be maintained (to first order) by ensuring that the search direction $g_n^{\perp\alpha}$ obtained from $g_n{}^{\alpha}$ is orthogonal to the space spanned by all the current approximate eigenvectors. By writing

$$g_n^{\perp\alpha} = S^{\alpha\beta} H_{\beta\gamma} x_n{}^{\gamma} - \varepsilon_n x_n{}^{\alpha} + \sum_m x_m{}^{\alpha} c_{mn}, \tag{16}$$

and imposing the requirement that $g_n^{\perp\alpha} S_{\alpha\beta} x_m{}^{\beta} = 0$ for all m and n, we find

$$c_{nm} = \varepsilon_n \delta_{nm} - x_n{}^{\alpha} H_{\alpha\beta} x_m{}^{\beta}. \tag{17}$$

We then have

$$g_n^{\perp\alpha} = S^{\alpha\beta} H_{\beta\gamma} x_n{}^{\gamma} - \sum_m x_m{}^{\alpha} \left(x_m{}^{\mu} H_{\mu\nu} x_n{}^{\nu} \right), \tag{18}$$

and

$$g_{n\,\alpha}^{\perp} = H_{\alpha\beta} x_n{}^{\beta} - S_{\alpha\beta} \sum_m x_m{}^{\beta} \left(x_m{}^{\mu} H_{\mu\nu} x_n{}^{\nu} \right). \tag{19}$$

We can use Eq. (18) as the steepest descent direction for constructing the conjugate gradients. However, the convergence of the solution depends strongly on the ratio of the largest and smallest eigenvalues of H [14,20]. Since the largest eigenvalues are dominated by the basis functions with large kinetic energy, we precondition the search direction using the kinetic energy matrix T where

$$T_{\alpha\beta} = -\frac{\hbar^2}{2m_{\mathrm{e}}} \int \mathrm{d}\mathbf{r}\ \chi_{\alpha}(\mathbf{r}) \nabla^2 \chi_{\beta}(\mathbf{r}). \tag{20}$$

We propose to obtain the preconditioned steepest descent direction ${G_n}^{\alpha}$ in the same manner as in Ref. [14] from the equation

$$ {G_n}^{\alpha} = (S + \frac{1}{\tau}T)^{\alpha\beta} g^{\perp}_{n\ \beta}, \tag{21} $$

which amounts to finding ${G_n}^{\alpha}$ by solving

$$ (S + \frac{1}{\tau}T)_{\alpha\beta} {G_n}^{\beta} = g^{\perp}_{n\ \alpha}. \tag{22} $$

τ sets the kinetic energy scale for the preconditioning: components of the gradient corresponding to basis functions with kinetic energy much lower than τ are unaffected by the preconditioning, whereas the contribution of components with kinetic energy much higher than τ is suppressed. The limit $\tau \to \infty$ thus corresponds to the case of no preconditioning, while the effect of preconditioning becomes stronger as $\tau \to 0$. Preconditioning which is too aggressive leads to a degradation of performance, and even the wrong answer being obtained, because it can reorder the lowest eigenvectors. We discuss the choice of τ in Sec. 4. This preconditioning scheme does not rely on the "diagonal approximation" used in Ref. [14], which is appropriate in that case because the overlap between different basis functions is not extensive. One can solve Eq. (22) by using the standard preconditioned conjugate gradient method for linear systems [4,21].

The search direction to be obtained from ${G_n}^{\alpha}$ is also required to be orthogonal to all approximate eigenvectors. By carrying out the same procedure as in Eq. (16), we find the gradient which is orthogonal to all approximate eigenvectors is given by

$$ {G^{\perp}_n}^{\alpha} = {G_n}^{\alpha} - \sum_m {x_m}^{\alpha} ({x_m}^{\beta} S_{\beta\gamma} {G_n}^{\gamma}). \tag{23} $$

In the conjugate gradient minimization method, ${G^{\perp}_n}^{\alpha}$ will be used to construct a conjugate search direction ${D_n}^{\alpha}$ where

$$ {D_n}^{\alpha} = -{G^{\perp}_n}^{\alpha} + \gamma \tilde{D}^{\alpha}_n \tag{24} $$

where $\tilde{D}_n$ is D_n from the previous iteration. We give the expression for γ in the Polak-Ribière formula where

$$ \gamma = \frac{{G^{\perp}_n}^{\alpha} S_{\alpha\beta} ({g^{\perp}_n}^{\beta} - {\tilde{g}^{\perp}_n}{}^{\beta})}{{\tilde{G}^{\perp}_n}{}^{\alpha} S_{\alpha\beta} {\tilde{g}^{\perp}_n}{}^{\beta}} = \frac{{G^{\perp}_n}^{\alpha} g^{\perp}_{n\ \alpha} - {G^{\perp}_n}^{\alpha} \tilde{g}^{\perp}_{n\alpha}}{{\tilde{G}^{\perp}_n}{}^{\alpha} \tilde{g}^{\perp}_{n\alpha}}. \tag{25} $$

The tilde signs again signify the quantities from the previous iteration. Line minimization (see Appendix B) of Ω is then performed along the direction $D_n^{\perp\alpha}$ where

$$D_n^{\perp\alpha} = D_n{}^{\alpha} - \sum_m x_m{}^{\alpha}(x_m{}^{\beta} S_{\beta\gamma} D_n{}^{\gamma}), \tag{26}$$

which is orthogonal to all approximate eigenvectors. We can systematically update each eigenvector sequentially until the minimum value of Ω is found. The single eigenvector update procedure described above can be generalized to a block update procedure where all approximate eigenvectors are updated simultaneously. The pseudo-code for the block update procedure can be found in Appendix A.

4 Tests of the algorithm

In this section, we present the results obtained from the calculations based on the block update procedure. Test cases are taken from the molecular chlorine and bulk crystalline silicon systems. The localized spherical-wave basis set [15] is used, where the basis functions are chosen to be centered on the atoms. We have used norm-conserving Troullier-Martins pseudopotentials [22] in the Kleinman-Bylander form [23], with angular momentum components up to $l = 2$. We use an LDA [24] for the exchange and correlation term. Periodicity of the supercell is assumed and the Γ point is used for the k-point sampling.

A chlorine molecule of bond length 2.0 Å is placed in a cubic box of side 10 Å. With a cutoff energy of 640 eV and the basis-function radius R of 4.0 Å, a total of $2 \times 139 = 278$ basis functions are used. In Fig. 1 we display the convergence of the sum of Kohn-Sham eigenvalues toward the "exact" value obtained from direct matrix diagonalization, as a function of the iteration number. The convergence of solution is seen to be linear when the number of iterations is smaller than the number of basis functions. To investigate the effect of preconditioning on the convergence of the solution, we have used a number of fixed τ values. It is seen that the performance of the method improves with moderate preconditioning. Fig. 1 shows that τ should be about 10 eV for good convergence. We have performed another calculation with τ updated according to the highest kinetic energy of all approximate eigenvectors, which converges to 24 eV. This is the natural choice for τ used in other preconditioning schemes, and the performance of this calculation (the curve labelled by open diamonds $\diamond$) is seen to be rather similar to that of the 'optimal' case with $\tau = 10$ eV. This method therefore allows τ to be chosen automatically, and optimized during the calculation, rather than being another parameter which the user must specify.

To investigate the importance of preserving the tensor nature of the search direction, we have performed calculations with the same cutoff energy of 640 eV on the molecular chlorine system, but this time with S set to the identity matrix (this corresponds to the case where tensor nature of the search direction is not preserved) and the off-diagonal elements of T set to zero (this corresponds to the diagonal approximation used in Ref. [14]) when we solve Eq. 22. The results of the calculations are presented in Fig. 2 where we have included the tensor-nature-preserving (TNP) curves for comparison. It is found that that the non-tensor-property-preserving (NTNP) cases fail to converge to the right solution. We conclude that it is essential to take tensor properties into account when one is dealing with a non-orthogonal basis set.

With a cutoff energy as high as 4800 eV (a total of $2\times392 = 784$ basis functions are used in these calculations), Fig. 3 clearly indicates that it is crucial to use the preconditioning scheme. A comparison between Figs. 1 and 3 reveals that when the optimal value of τ is used, the number of iterations to achieve the same accuracy remains roughly the same, even though the number of basis functions has more than doubled, which shows that the preconditioning scheme is indeed working.

Similar tests are performed on the bulk crystalline silicon system. The calculations on a 64-atom silicon unit cell are performed at the equilibrium lattice parameter of 5.43 Å with an energy cutoff of 200 eV. We have chosen R to be 3.1 Å which is sufficient for this purpose. These settings result in a total of $64 \times 55 = 3520$ basis functions for the calculations. In Fig. 4 we we note that our 'best' $\tau \sim 1$ eV is comparable with the value of 3.8 eV used by Bowler and Gillan [14]. We have performed another calculation with τ updated according to the highest kinetic energy of all approximate eigenvectors, which converges to 12 eV. The performance of this calculation is seen to be rather similar to that of the optimal cases with $\tau = 1$ or 10 eV.

5 Conclusions

In this work we have proposed an iterative conjugate gradient method to obtain the lowest few eigenvalues and corresponding eigenvectors of the generalized eigenvalue problem $Hx = \varepsilon Sx$, which exhibits linear convergence. A preconditioning scheme which uses the kinetic energy matrix is introduced to improve the convergence of the solutions. The scheme is controlled by a single parameter whose optimal value may be chosen automatically.

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Appendix A

The pseudo-code for solving the generalized eigenvalue problem $Hx = \varepsilon Sx$ based on the block update procedure is as follows, where H, S and T denote the $N \times N$ Hamiltonian, overlap and kinetic energy matrices respectively. Let $X^{(k)} = \left[X_1^{(k)}, X_2^{(k)}, \ldots, X_M^{(k)}\right]$ be an $N \times M$ matrix where $X_i^{(k)}$ is the i-th column of $X^{(k)}$, and k labels the iteration.

The procedure is then:

$k := 1$
Choose $X^{(1)}$
Choose convergence tolerance ϵ
Orthonormalize $X^{(1)}$ (Gram-Schmidt)
Calculate $\Omega^{(1)}$
Choose $\Omega^{(0)}$ such that $\left|\Omega^{(1)} - \Omega^{(0)}\right| > \epsilon$
$F^{(0)} := 0$
$A^{(0)} := 0$
$\gamma_1^{(0)} := 1$
while $\left|\Omega^{(k)} - \Omega^{(k-1)}\right| > \epsilon$ **do**
  $Y^{(k)} := HX^{(k)}$
  $Z^{(k)} := SX^{(k)}$
  $P^{(k)} := (X^{(k)})^T Y^{(k)}$
  $F^{(k)} := Y^{(k)} - Z^{(k)} P^{(k)}$
  Solve $(S + T/\tau) B^{(k)} = F^{(k)}$
  $C^{(k)} := (Z^{(k)})^T B^{(k)}$
  $G^{(k)} := B^{(k)} - X^{(k)} C^{(k)}$
  $\gamma_1^{(k)} := \mathrm{tr}\left((G^{(k)})^T F^{(k)}\right)$
  $\gamma_2^{(k)} := \mathrm{tr}\left((G^{(k)})^T F^{(k-1)}\right)$
  $\gamma^{(k)} := \left(\gamma_1^{(k)} - \gamma_2^{(k)}\right) / \gamma_1^{(k-1)}$
  $A^{(k)} := -G^{(k)} + \gamma^{(k)} A^{(k-1)}$
  $E^{(k)} := (Z^{(k)})^T A^{(k)}$
  $D^{(k)} := A^{(k)} - X^{(k)} E^{(k)}$

$\lambda_{\mathrm{opt}} := \mathrm{linmin}(X^{(k)}, D^{(k)})$ (see Appendix B)
$X^{(k+1)} := X^{(k)} + \lambda_{\mathrm{opt}} D^{(k)}$
Orthonormalize $X^{(k+1)}$ (Gram-Schmidt)
Calculate $\Omega^{(k+1)}$
$k := k + 1$
end

In some applications, individual eigenvalues are needed. They can be obtained by a subspace rotation method where we simply need to diagonalize the $M \times M$ matrix $X^T HX$. If U diagonalizes $X^T HX$ such that $U^T(X^T HX)U = \mathrm{diag}(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_M)$, we obtain the individual eigenvalues $\{\varepsilon_i; i = 1, \ldots, M\}$ with corresponding eigenvectors $X' = XU$.

Appendix B

To perform a line minimization from a point $X^{(k)}$ along a certain direction $D^{(k)}$, we wish to find λ_{opt}, the optimum value of λ which minimizes

$$f(\lambda) = \sum_{m=1}^{M} \frac{(X_m^{(k)} + \lambda D_m^{(k)})^T H (X_m^{(k)} + \lambda D_m^{(k)})}{(X_m^{(k)} + \lambda D_m^{(k)})^T S (X_m^{(k)} + \lambda D_m^{(k)})}. \tag{27}$$

This may be achieved in several ways. First, by calculating the derivative of f at $\lambda = 0$, $\left.\frac{\mathrm{d}f}{\mathrm{d}\lambda}\right|_{\lambda=0}$, taking a trial step λ_{t} to evaluate $f_{\mathrm{t}} = f(\lambda_{\mathrm{t}})$ and making a parabolic fit to determine λ_{opt}.

Alternatively, since

$$\frac{\mathrm{d}f}{\mathrm{d}\lambda} = \sum_{m=1}^{M} \frac{2(a_m + \lambda b_m + \lambda^2 c_m)}{(1 + \lambda^2 (D_m)^T S D_m)^2}, \tag{28}$$

where

$$\begin{aligned}
a_m = & \left[\left(X_m^{(k)}\right)^T S X_m^{(k)}\right] \left[\left(D_m^{(k)}\right)^T H X_m^{(k)}\right] - \\
& \qquad \left[\left(X_m^{(k)}\right)^T H X_m^{(k)}\right] \left[\left(D_m^{(k)}\right)^T S X_m^{(k)}\right], \qquad (29) \\
b_m = & \left[\left(X_m^{(k)}\right)^T S X_m^{(k)}\right] \left[\left(D_m^{(k)}\right)^T H D_m^{(k)}\right] - \\
& \qquad \left[\left(X_m^{(k)}\right)^T H X_m^{(k)}\right] \left[\left(D_m^{(k)}\right)^T S D_m^{(k)}\right], \qquad (30) \\
c_m = & \left[\left(X_m^{(k)}\right)^T S D_m^{(k)}\right] \left[\left(D_m^{(k)}\right)^T H D_m^{(k)}\right] -
\end{aligned}$$

$$\left[\left(X_m^{(k)}\right)^T HD_m^{(k)}\right]\left[\left(D_m^{(k)}\right)^T SD_m^{(k)}\right], \tag{31}$$

we find $\lambda_{\rm opt}$ as one of the roots of the quadratic equation

$$a + b\lambda + c\lambda^2 = 0, \tag{32}$$

where $a = \sum_m a_m$ etc.

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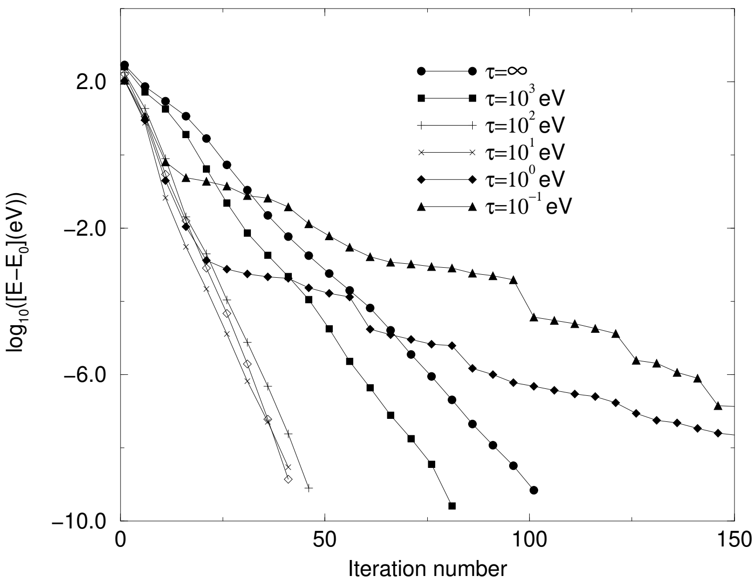

Fig. 1. Convergence of the sum of eigenvalues Ω (eV) as a function of iteration number for the chlorine molecule calculations using a cutoff energy of 640 eV. Ω_0 is the "exact" value from the direct matrix diagonalization. The curve labelled by empty diamonds ($\diamond$) corresponds to the calculation where τ is updated according to the highest kinetic energy of all approximate eigenvectors.

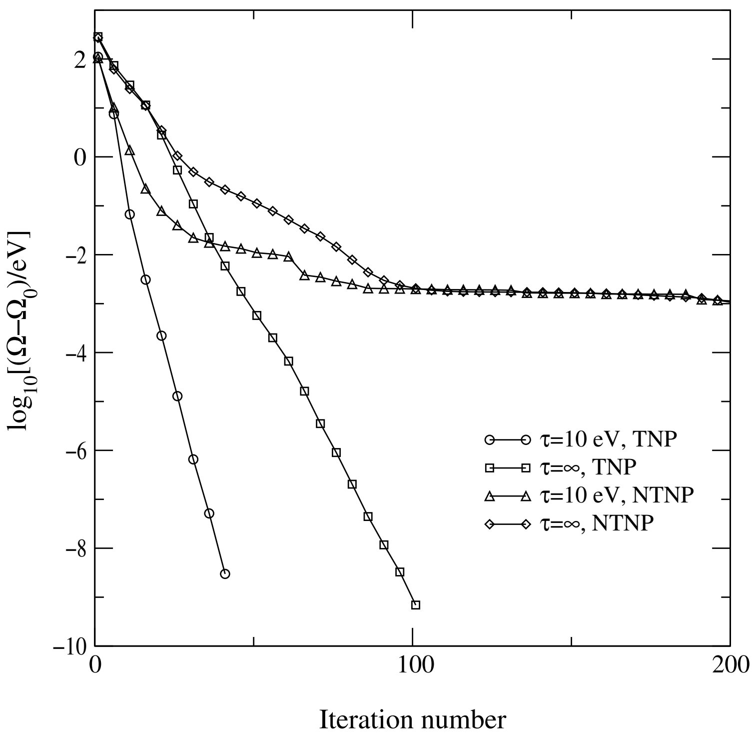

Fig. 2. Convergence of the sum of eigenvalues Ω (eV) as a function of iteration number for the chlorine molecule calculation using a cutoff energy of 640 eV. The curves show the difference between the tensor-nature-preserving (TNP) calculations and non-tensor-nature-preserving (NTNP) calculations.

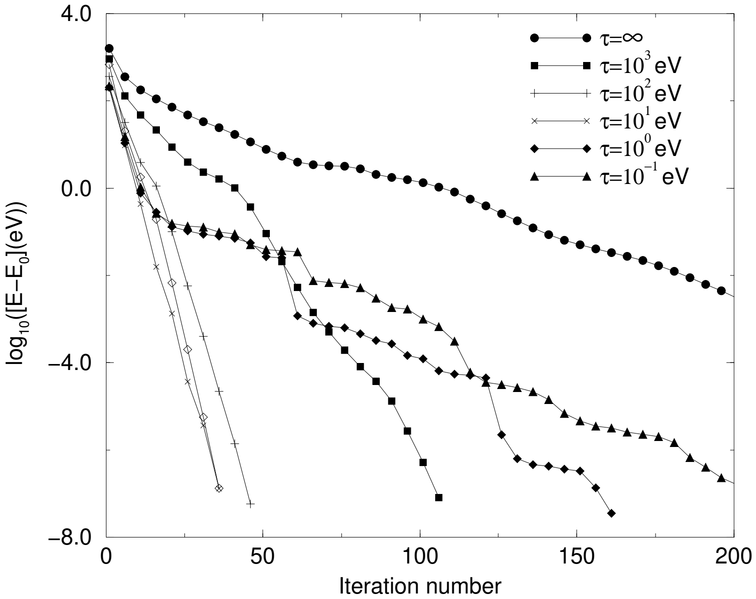

Fig. 3. Convergence of the sum of eigenvalues Ω (eV) as a function of iteration number for the chlorine molecule calculations using a cutoff energy of 4800 eV. Ω_0 is the "exact" value from the direct matrix diagonalization. The curve labelled by empty diamonds ($\diamond$) corresponds to the calculation where τ is updated according to the highest kinetic energy of all approximate eigenvectors.

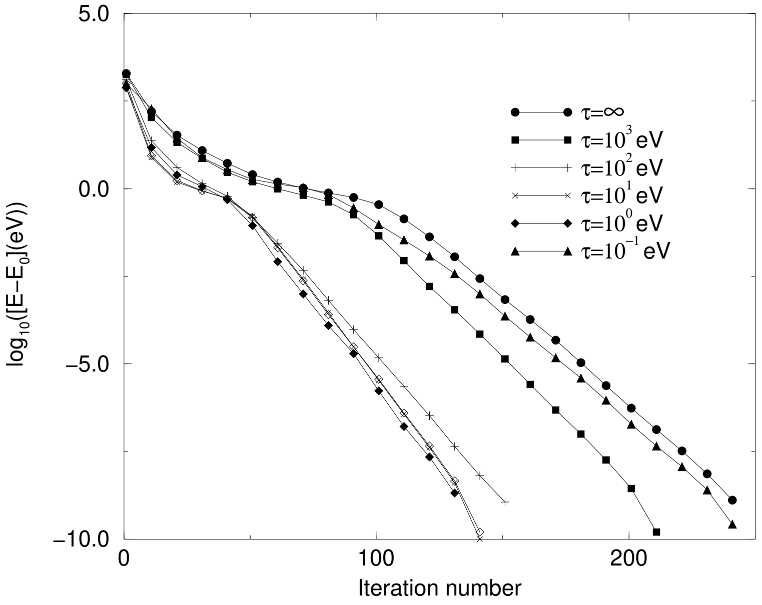

Fig. 4. Convergence of the sum of eigenvalues Ω (eV) as a function of iteration number for the 64-atom Si crystal calculations using a cutoff energy of 200 eV. Ω_0 is the "exact" value from the direct matrix diagonalization. The curve labelled by empty diamonds ($\diamond$) corresponds to the calculation where τ is updated according to the highest kinetic energy of all approximate eigenvectors.