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ELLIPTIC PRECONDITIONER FOR ACCELERATING THE SELF CONSISTENT FIELD ITERATION IN KOHN-SHAM DENSITY FUNCTIONAL THEORY

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Abstract. We discuss techniques for accelerating the self consistent field (SCF) iteration for solving the Kohn-Sham equations. These techniques are all based on constructing approximations to the inverse of the Jacobian associated with a fixed point map satisfied by the total potential. They can be viewed as preconditioners for a fixed point iteration. We point out different requirements for constructing preconditioners for insulating and metallic systems respectively, and discuss how to construct preconditioners to keep the convergence rate of the fixed point iteration independent of the size of the atomistic system. We propose a new preconditioner that can treat insulating and metallic system in a unified way. The new preconditioner, which we call an elliptic preconditioner, is constructed by solving an elliptic partial differential equation. The elliptic preconditioner is shown to be more effective in accelerating the convergence of a fixed point iteration than the existing approaches for large inhomogeneous systems at low temperature.

Key words. Kohn-Sham density functional theory, self consistent field iteration, fixed point iteration, elliptic preconditioner

AMS subject classifications. 65F08, 65J15, 65Z05

1. Introduction. Electron structure calculations based on solving the Kohn-Sham density functional theory (KSDFT) [20, 24] play an important role in the analysis of electronic, structural and optical properties of molecules, solids and other nano structures. The Kohn-Sham equations define a nonlinear eigenvalue problem

$$\begin{aligned} &H[\rho]\psi_i = \varepsilon_i \psi_i, \\ &\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad \int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\,\mathrm{d}\mathbf{r} = \delta_{ij}, \end{aligned} \tag{1.1}$$

where ε_i are the Kohn-Sham eigenvalues (or quasi-particle energies) and ψ_i are called the Kohn-Sham wavefunctions or orbitals. These eigenfunctions define the electron

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density $\rho(\mathbf{r})$, which in turn defines the Kohn-Sham Hamiltonian

$$H[\rho] = -\frac{1}{2}\Delta + \mathcal{V}[\rho] + V_{\text{ion}},$$

where Δ is the Laplacian operator, $\mathcal{V}(\rho)$ is a nonlinear function of ρ, and V_{ion} is a potential function that is independent of ρ. The parameters f_i's that appear in the definition of ρ, which are often referred to as the occupation number, are defined by

$$f_i = \frac{1}{1 + \exp(\beta(\varepsilon_i - \mu))}, \tag{1.2}$$

where β is proportional to the inverse of the temperature T and μ is called the chemical potential chosen to ensure that f_i's satisfy

$$\sum_i f_i = \int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} = N, \tag{1.3}$$

for a system that contains N electrons. The right hand side of (1.2) is known as the Fermi-Dirac function evaluated at ε_i. When β is sufficiently large, the Fermi-Dirac function behaves like a step function that drops from 1 to 0 at μ (which lies between ε_N and ε_{N+1}.) Spin degeneracy is omitted here for simplicity.

In this paper, we assume the Kohn-Sham (1.1) is defined within the domain $\Omega = [0, L]^3$ with periodic boundary conditions, and the number of electrons N is proportional to the volume of the domain.

Because the eigenvalue problem (1.1) is nonlinear, it is often solved iteratively by a class of algorithms called *self-consistent field iterations* (SCF). The SCF iteration can be viewed as a fixed point iteration applied to a nonlinear system of equations defined in terms of the potential or charge density. The function evaluation in each step of the SCF iteration is relatively expensive. Hence, it is desirable to reduce the total number of SCF iteration by accelerating its convergence. Furthermore, we would like the convergence rate to be independent of the size of the system. In the past few decades, a number of acceleration schemes have been proposed [3, 37, 22, 12, 19, 27, 38, 4, 32]. However, none of the existing methods provide a satisfactory solution to the convergence issues to be examined in this paper, especially the issue of size dependency.

The purpose of the paper is twofold. First, we summarize a number of ways to accelerate the SCF iteration. Many of the schemes we discuss already exist in both the physics and the applied mathematics literature [26, 25, 4, 47, 13, 39, 44]. We analyze the convergence properties of these acceleration schemes. In our analysis, we assume a good starting guess to the charge density or potential is available. Such a starting guess is generally not difficult to obtain in real applications. As a result, the convergence of the SCF iteration can be analyzed through the properties of the Jacobian operator associated with the nonlinear map defined in terms of the potential or density. Acceleration schemes can be developed by constructing approximations to the Jacobian or its inverse. These acceleration schemes can also be viewed as preconditioning techniques for solving a system of nonlinear equations.

It turns out that the SCF iteration exhibits quite different convergence behavior for insulating and metallic systems [14, 36]. These two types of systems are distinguished by the gap between ε_N and ε_{N+1} as the number of electrons N, or equivalently the system size increases to infinity. For insulating systems,

$$\lim_{N\to\infty} E_g > 0, \tag{1.4}$$

where $E_g = \varepsilon_{N+1} - \varepsilon_N$, whereas for metallic systems, $\lim_{N\to\infty} E_g = 0$. Different accelerating (or preconditioning) techniques are required for insulating and metallic systems.

The second purpose of this paper is to propose a new method for preconditioning the SCF iteration. The new preconditioner, which we call the elliptic preconditioner, provides a unified treatment of insulating and metallic systems. It can also be applied to complex materials that contain both an insulating and a metallic component and is solved at low temperature. This type of systems is considered to be difficult [38] for a standard Kohn-Sham solver.

The paper is organized as follows. In section 2, we introduce the fixed point iteration for solving the Kohn-Sham problem, and the simple mixing method as the simplest acceleration method. More advanced preconditioning techniques are discussed in section 3. In section 4, we discuss the convergence behavior of the acceleration methods. Based on these discussions, a new preconditioner called the elliptic preconditioner is presented in section 5. The performance of the elliptic preconditioner is compared to existing techniques for one dimensional model problems and a realistic three dimensional problem in section 6. We conclude and discuss future work in section 7.

In this paper, the Kohn-Sham orbitals $\{\psi_i\}$ are assumed to be in $H^1(\Omega)$. In practical calculations, they are discretized in a finite dimensional space such as the space spanned by a set of planewaves. As a result, each operator corresponds to a finite dimensional matrix. To simplify our discussion, we will not distinguish operators defined on $H^1(\Omega)$ from the corresponding matrices obtained from discretization unless otherwise noted. This applies to both differential and integral operators. For example, we may simply denote $f(\mathbf{r}) = \int A(\mathbf{r},\mathbf{r}')g(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$ by $f = Ag$.

2. Fixed point iteration and simple mixing. It follows from the spectral theory that the charge density ρ defined in (1.1) can be written as

$$\rho(\mathbf{r}) = \left[1 + e^{\beta(H[\rho]-\mu I)}\right]^{-1}(\mathbf{r},\mathbf{r}). \tag{2.1}$$

That is, $\rho(\mathbf{r})$ is the diagonal part of the Fermi-Dirac function evaluated at the Kohn-Sham Hamiltonian. The right-hand side of (2.1) defines a fixed point map from ρ to itself.

A similar map can be defined in terms of $V = \mathcal{V}(\rho)$ since ρ is implicitly a function of V, which we will denote by $\rho = F(V)$. The analysis we present below and the acceleration strategies we propose are applicable to both the density fixed point map (2.1) and the potential fixed point map

$$V = \mathcal{V}[F(V)]. \tag{2.2}$$

Without loss of generality, we will focus on the potential fixed point map (2.2) in the rest of the paper.

Note that the function $\mathcal{V}(\rho)$ has the form

$$\mathcal{V}[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}' + V_{\mathrm{xc}}[\rho(\mathbf{r})], \tag{2.3}$$

where the first term corresponds to the electron-electron repulsion, and V_{xc} is known as an *exchange-correlation* potential that accounts for many-body effects of the electrons. In this paper, we assume V_{xc} depends on ρ only. This is known as the local density

approximation (LDA) [10, 35]. The definition of $V_{\rm xc}$ is not unique. A number of expressions are available in the physics literature [6, 28, 34]. However, for the purpose of this paper, we do not need to be concerned with the explicit form of $V_{\rm xc}$. It should be noted that $V_{\rm xc}$ is often much smaller in magnitude compared to the electron-electron repulsion.

The simplest method for seeking the solution of (2.2) is the fixed point iteration. In such an iteration, we start from some input potential V_1, and iterate the following equation

$$V_{k+1} = \mathcal{V}\left[F(V_k)\right], \tag{2.4}$$

until (hopefully) the difference between V_{k+1} and V_k is sufficiently small.

When V_k is sufficiently close to the fixed point solution V^*, we may analyze the convergence of the fixed point iteration (2.4) by linearizing the function $\mathcal{V}[F(\cdot)]$ defined in (2.2) at V^*.

If we define $\delta V_k = V_k - V^*$, subtracting V^* from both sides of (2.4) and approximating $\mathcal{V}[F(V_k)]$ by its first-order Taylor expansion at V^* yields

$$\delta V_{k+1} \approx \left.\frac{\partial \mathcal{V}}{\partial V}\right|_{V=V^*} \delta V_k, \tag{2.5}$$

where $(\partial\mathcal{V}/\partial V)|_{V=V^*}$ is the Jacobian of $\mathcal{V}[F(V)]$ with respect to V evaluated at V^*.

It follows from the chain rule that

$$\frac{\partial \mathcal{V}}{\partial V} = \frac{\partial \mathcal{V}}{\partial \rho}\frac{\partial F}{\partial V}.$$

Taking the functional derivative of $\mathcal{V}[F(V)]$ given in (2.3) with respect to $\rho(\mathbf{r})$ yields

$$\frac{\partial \mathcal{V}}{\partial \rho}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\partial V_{\rm xc}}{\partial \rho}(\mathbf{r},\mathbf{r}'). \tag{2.6}$$

The first term on the right hand side of (2.6) is the Coulomb kernel. It will be denoted by $v_c(\mathbf{r},\mathbf{r}')$ below. The second term is the functional derivative of the exchange-correction potential with respect to ρ. It is often denoted by $K_{\rm xc}(\mathbf{r},\mathbf{r}')$.

In the physics literature, the functional derivative of F with respect to V is often referred to as the independent particle polarizability matrix, and denoted by $\chi\left(\mathbf{r},\mathbf{r}'\right)$. At zero temperature, $\chi\left(\mathbf{r},\mathbf{r}'\right)$ is given by the Adler-Wiser formula [1, 46]

$$\chi(\mathbf{r},\mathbf{r}') = 2\sum_{n=1}^{N}\sum_{m=N+1}^{\infty} \frac{\psi_n(\mathbf{r})\psi_m^*(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}')}{\varepsilon_n-\varepsilon_m}, \tag{2.7}$$

where (ε_i,ψ_i), $i=1,2,...$, are the eigenpairs defined in (1.1). Note that χ is negative semidefinite since $\varepsilon_n \le \varepsilon_m$.

Eq. (2.5) can be iterated recursively to yield

$$\delta V_{k+1} \approx \left(\frac{\partial \mathcal{V}}{\partial \rho}\chi\right)^k \delta V_1. \tag{2.8}$$

Therefore, a necessary condition that guarantees the convergence of the fixed point iteration is

$$\sigma\left(\frac{\partial \mathcal{V}}{\partial \rho}\chi\right) < 1,$$

where $\sigma(A)$ is the spectral radius of the operator (or matrix) A.

Unfortunately this condition is generally not satisfied as we will show later. However, a simple modification of the fixed point iteration can be made to overcome potential convergence failure as long as $\sigma\left(\frac{\partial \mathcal{V}}{\partial \rho}\chi\right)$ is bounded.

The modification takes the form

$$V_{k+1} = V_k - \alpha\left(V_k - \mathcal{V}\left[F(V_k)\right]\right), \tag{2.9}$$

where α is a scalar parameter. The updating formula given above is often referred to as simple mixing. When V_j are sufficiently close to V^*, the error propagation of simple mixing scheme is

$$\delta V_{k+1} \approx \delta V_k - \alpha\left(I - \frac{\partial \mathcal{V}}{\partial \rho}\chi\right)\delta V_k. \tag{2.10}$$

Notice that $I - (\partial\mathcal{V}/\partial\rho)\chi$ is simply the Jacobian of the residual function $V - \mathcal{V}[F(V)]$ with respect to V. We will denote this Jacobian by J. Its value at V^* will be denoted by J_*. In the physics literature, this Jacobian is often referred to as a *dielectric* operator [1, 46], and denoted by ε.

It follows from (2.10) that simple mixing will lead to convergence if

$$\sigma\left(I - \alpha J_*\right) < 1. \tag{2.11}$$

If $\lambda(J_*)$ is an eigenvalue of J_*, then the condition given in (2.11) implies that

$$|1 - \alpha\lambda(J_*)| < 1. \tag{2.12}$$

Consequently, $\lambda(J_*)$ must satisfy

$$0 < \alpha < \frac{2}{\lambda(J_*)}. \tag{2.13}$$

Note that (2.13) is only meaningful when $\lambda(J_*) > 0$ holds. Therefore, $\lambda(J_*) > 0$ is often referred to as the *stability condition* of a material [5, 30, 31]. Furthermore, when $\lambda(J_*)$ is bounded, it is always possible to find a parameter α to ensure the convergence of the modified fixed point iteration even though the convergence may be slow.

We should comment that the stability condition $\lambda(J_*) > 0$ holds in most cases because $K_{\rm xc}$ is typically much smaller in magnitude compared to v_c, which is positive definite, and χ is negative semidefinite. When the stability condition fails, phase transition may occur, such as the transition from uniform electron gas to Wigner crystals in the presence of low electron density [45]. Such case is beyond the scope of the current study. Nonetheless, $\lambda(J_*)$ can become very large in practice even when the stability condition holds, especially for metallic systems of large sizes, as we will show in section 4. A large $\lambda(J_*)$ requires α to be set to a small value to ensure convergence. Even though convergence can be achieved, it may be extremely slow.

3. Preconditioned fixed point iteration and quasi-Newton acceleration. The simple mixing scheme selects α as a scalar in (2.9). If we replace the scalar α by the inverse of the Jacobian matrix of the function $V - \mathcal{V}[F(V)]$ evaluated at V_k, we obtain a Newton's update of V. When V_k is in the region where the linear approximation given by (2.5) is sufficiently accurate, the Newton's method converges quadratically to the solution of (2.2).

3.1. Jacobian-free Krylov Newton. The difficulty with applying Newton's method directly is that the Jacobian matrix $J_k = I - \frac{\partial \mathcal{V}[F(V)]}{\partial V}|_{V=V_k}$ or its inverse cannot be easily evaluated. However, we may apply a Jacobian-free Krylov Newton technique [23] to obtain the Newton's update

$$\Delta_k = J_k^{-1} r_k, \quad \text{where} \quad r_k = V_k - \mathcal{V}\left[F(V_k)\right],$$

by solving the linear system

$$J_k \Delta_k = r_k \tag{3.1}$$

iteratively using, for example, the GMRES algorithm [40]. The matrix vector multiplication of the form $y \leftarrow J_k x$, which is required in each GMRES iteration, can be approximated by finite difference

$$y \approx x - \frac{\mathcal{V}[F(V_k + \epsilon x)] - \mathcal{V}[F(V_k)]}{\epsilon},$$

for an appropriately chosen scalar ϵ.

The finite difference calculation requires one additional function evaluation of $\mathcal{V}[F(V_k + \epsilon x)]$ per GMRES step. Therefore, even though the Newton's method may exhibit quadratic convergence, each Newton iteration may be expensive if the number of GMRES steps required to solve the correction equation (3.1) is large. The convergence rate of GMRES method for solving the linear system (3.1) is known to be given by [29]

$$\|\Delta_k^n - \Delta_k\| \leq C \left(\frac{\sqrt{\kappa(J_k)} - 1}{\sqrt{\kappa(J_k)} + 1} \right)^n \|\Delta_k^0 - \Delta_k\|, \tag{3.2}$$

where $\kappa(J_k) = \frac{\lambda_{\max}(J_k)}{\lambda_{\min}(J_k)}$ is the condition number of J_k, and Δ_k^n is the approximation of Δ_k at the nth step of the GMRES iteration. As we will show in Section 4, the condition number $\kappa(J_k)$ can grow rapidly with respect to the size of the system, especially for metallic systems. Therefore the number of iterations required by an iterative solver also grows with respect to the size of the system unless preconditioning strategies are employed.

3.2. Broyden's and Anderson's method. An alternative to the Newton's method for solving (2.2) is a quasi-Newton method that replaces J_k^{-1} with an approximate Jacobian inverse C_k that is easy to compute and apply. In such a method, the updating strategy becomes

$$V_{k+1} = V_k - C_k \left(V_k - \mathcal{V}[F(V_k)]\right). \tag{3.3}$$

The simple mixing scheme discussed in the previous section can be viewed as a quasi-Newton method in which C_k is set to αI. More sophisticated quasi-Newton updating schemes can be devised by using Broyden's techniques [21] to construct better approximations to J_k or J_k^{-1}. In the Broyden's second method, C_k is obtained by performing a sequence of low-rank modifications to some initial approximation C_0 of the Jacobian inverse using a recursive formula [13, 32] derived from the following constrained optimization problem

$$\begin{aligned} \min_{C} \quad & \frac{1}{2}||C - C_{k-1}||_F^2 \\ \text{s.t.} \quad & S_k = C Y_k, \end{aligned} \tag{3.4}$$

where C_{k-1} is the approximation to the Jacobian constructed in the $(k-1)$th Broyden iteration. The matrices S_k and Y_k above are defined as

$$S_k = (s_k, s_{k-1}, \cdots, s_{k-\ell}), \quad Y_k = (y_k, y_{k-1}, \cdots, y_{k-\ell}), \tag{3.5}$$

where s_j and y_j are defined by $s_j = V_j - V_{j-1}$ and $y_j = r_j - r_{j-1}$ respectively.

It is easy to show that the solution to (3.4) is

$$C_k = C_{k-1} + (S_k - C_{k-1}Y_k)Y_k^\dagger, \tag{3.6}$$

where $Y_k^\dagger$ denotes the pseudo-inverse of Y_k, i.e., $Y_k^\dagger = (Y_k^T Y_k)^{-1} Y_k^T$.

A special case of the Broyden's method is the Anderson's method [3] in which C_{k-1} is fixed to an initial approximation C_0 at each iteration. It follows from Eq. (3.3) that the Anderson's method updates the potential as

$$V_{k+1} = V_k - C_0(I - Y_k Y_k^\dagger)r_k - S_k Y_k^\dagger r_k, \tag{3.7}$$

In particular, if C_0 is set to αI, we obtain the Anderson's method

$$V_{k+1} = V_k - \alpha(I - Y_k Y_k^\dagger)r_k - S_k Y_k^\dagger r_k.$$

commonly used in KSDFT solvers.

3.3. Pulay's method. An alternative way to derive the Broyden's method is through a technique called Direct Inversion of Iterative Subspace (DIIS). The technique is originally developed by Pulay for accelerating a Hartree-Fock calculation [37]. Hence it is often referred to as *Pulay mixing* in the condensed matter physics community. The motivation of the Pulay's method is to minimize the difference between V and $\mathcal{V}[F(V)]$ within a subspace $\mathcal{S}$ that contains previous approximations to V. In Pulay's original work [37], the optimal approximation to V from $\mathcal{S}$ is expressed as $V_{\text{opt}} = \sum_{j=k-\ell-1}^{k} \alpha_j V_j$, where V_j $(j = k-\ell-1, ..., k)$ are previous approximations to V, and the coefficients α_j chosen to satisfy the constraint $\sum_{j=k-\ell-1}^{k} \alpha_j = 1$.

When V_j's are all sufficiently close to the solution of (2.2), $\mathcal{V}[F(\alpha_j V_j)] \approx \alpha_j \mathcal{V}[F(V_j)]$ holds. Hence we may obtain α_j (and consequently V_{opt}) by solving the following quadratic program

$$\begin{array}{cc} \min_{\{\alpha_j\}} & \|\sum_{j=k-\ell-1}^{k} \alpha_j r_j\|_2^2 \\ \text{s.t.} & \sum_{j=k-\ell-1}^{k} \alpha_j = 1, \end{array} \tag{3.8}$$

where $r_j = V_j - \mathcal{V}[F(V_j)]$.

Note that (3.8) can be reformulated as a unconstrained minimization problem if V_{opt} is required to take the form $V_{\text{opt}} = V_k + \sum_{j=k-\ell}^{k} \beta_j (V_j - V_{j-1})$, where β_j can be any unconstrained real number. Again, if we assume $\mathcal{V}[F(V)]$ is approximately linear at V_j and let $b = (\beta_{k-\ell}, ..., \beta_k)^T$, minimizing $\|V_{\text{opt}} - \mathcal{V}[F(V_{\text{opt}})]\|$ with respect to $\{\beta_j\}$ yields $b = -Y_k^\dagger r_k$, where Y_k is same as that defined in (3.5).

In [25, 26], the Pulay's method for updating V is defined as

$$V_{k+1} = V_{\text{opt}} - C_0(V_{\text{opt}} - \mathcal{V}[F(V_{\text{opt}})]), \tag{3.9}$$

where C_0 is an initial approximation to the inverse of the Jacobian (at the solution). Substituting $V_{\text{opt}} = V_k - S_k Y_k^\dagger r_k$ into (3.9) yields exactly the Anderson's updating formula (3.7).

3.4. Preconditioned fixed point iteration. If V_* is the solution to (2.2), then subtracting it from both sides of the quasi-Newton updating formula

$$V_{k+1} = V_k - C_k \left(V_k - \mathcal{V}[F(V_k)]\right)$$

yields

$$\delta V_{k+1} \approx \delta V_k - C_k J_* \delta V_k = (I - C_k J_*)\delta V_k, \tag{3.10}$$

where J_* is the Jacobian of the function $V - \mathcal{V}[F(V)]$ at V_* and C_k is the approximation to J_*^{-1} constructed at the kth step. If C_k is a constant matrix C for all k, we can rewrite (3.10) as

$$\delta V_{k+1} = (I - CJ_*)^k \delta V_1. \tag{3.11}$$

Ideally, we would like to choose C to be J_*^{-1} so that the quasi-Newton iteration would converge in one iteration. However, this is generally not possible (since we do not know V_*.) But, if C is sufficiently close to J_*^{-1}, we may view C as a preconditioner for a preconditioned fixed point iteration defined by (3.11).

A desirable property for C is that $|\sigma(I - CJ_*)| < 1$ or

$$0 < \sigma(CJ_*) < 2. \tag{3.12}$$

Because $J_* = I - (\partial\mathcal{V}/\partial\rho)\chi$, we may construct C by seeking approximations to $\partial\mathcal{V}/\partial\rho$ and χ first and inverting the approximate Jacobian in (3.10). This is the approach taken by Ho, Ihm and Joannopoulos in [19], which is sometimes known as the HIJ approach. The HIJ approach approximates the matrix χ by using Alder-Wiser formula given in Eq. (2.7) which requires computing all eigenvalues and eigenvectors associated with the Kohn-Sham Hamiltonian defined at V_k. The resulting computational cost for constructing χ alone is $\mathcal{O}(N^4)$ due to the explicit construction of each pair of occupied and unoccupied states. Such a preconditioning strategy is not practical for large problems.

An alternative to the HIJ approach is to use the extrapolar method proposed in [4]. This method approximates the high energy unoccupied states by planewaves. As a result, the number of occupied and unoccupied state pairs is reduced. However, the overall algorithm still scales as $\mathcal{O}(N^4)$, and the preconditioning strategy will become increasingly more expensive as system size increases.

A more efficient preconditioner that works well for simple metallic systems is the Kerker preconditioner [22]. The potential updating scheme associated with this preconditioner is often known as the Kerker mixing scheme. The construction of the Kerker preconditioner is based on the observation that the Coulomb operator v_c can be diagonalized by the Fourier basis (planewaves), and the eigenvalues of the Coulomb operator are $4\pi/q^2$, where $q = |\mathbf{q}|$ is the magnitude of a sampled wave vector associated with the Fourier basis function of the form $e^{i\mathbf{q}\cdot\mathbf{r}}$. Furthermore, for simple metals the polarizability operator χ can be approximately diagonalized by the Fourier basis. The eigenvalues of χ are bounded from below and above. Therefore, without taking into account the contribution from $K_{\rm xc}$, the eigenvalues of J_* are $1 + 4\pi\gamma/q^2 = (q^2 + 4\pi\gamma)/q^2$ for some constant $\gamma > 0$ which is related to the Thomas-Fermi screening length [49]. But the true value of γ is generally unknown.

By neglecting the effect of $K_{\rm xc}$ in $\partial V/\partial\rho$, the Kerker scheme sets C to

$$C = \alpha\mathcal{F}^{-1} D_K \mathcal{F}, \tag{3.13}$$

where $\mathcal{F}$ is the matrix representation of the discretized Fourier basis that diagonalizes both v_c and χ, and the diagonal matrix D_K contains $q^2/(q^2+4\pi\hat{\gamma})$ on its diagonal, for some appropriately chosen constant $\hat{\gamma}$, and α is a parameter chosen to ensure (3.12) is satisfied.

As a result, the eigenvalues of CJ associated with the Kerker preconditioner are approximately $\alpha(q^2+4\pi\gamma)/(q^2+4\pi\hat{\gamma})$. When q is small, the corresponding eigenvalue of CJ is approximately $\alpha\gamma/\hat{\gamma}$. When q is large, the corresponding eigenvalue of CJ is approximately α. By choosing an appropriate $\alpha \in (0,1)$ we can ensure that all eigenvalues are within $(0,2)$ even when $\hat{\gamma}$ is not completely in agreement with the true γ.

The behavior of χ for simple insulating systems is very different from that for simple metallic systems. For simple insulating systems, the eigenvalues of χ corresponding to small q modes behave like $-\xi q^2$ where $\xi > 0$ is a constant [14, 36]. As a result, the spectral radius of J is bounded by a constant when the contribution from the exchange-correlation is negligible. Therefore, we can choose $C = \alpha I$ with an appropriate α to ensure the condition (3.12) is satisfied. The optimal choice of α will be discussed in the next section.

We should also note that when C_k is allowed to change from one iteration to another through the use of quasi-Newton updates, the convergence of the preconditioned fixed point (or quasi-Newton) iteration can be Q-superlinear [33].

4. Convergence rate and size dependency. In the previous section, we identified the condition under which a preconditioned fixed-point iteration applied to the Kohn-Sham problem converges. In this section, we discuss the optimal rate of convergence and its dependency on the size of the physical system. Ideally, we would like to construct a preconditioner to ensure the rate of convergence to be independent of the system size.

4.1. The convergence rate of the simple mixing scheme. When the preconditioner is chosen to be $C = \alpha I$ (i.e., simple mixing), the convergence of the preconditioned fixed point iteration is guaranteed if α satisfies the condition given in (2.13). It is easy to show that the optimal choice of α, which is the solution to the following problem

$$r = \min_{\alpha} \max_{\lambda(J_*)} |1 - \alpha\lambda(J_*)|,$$

must satisfy

$$|1 - \alpha\lambda_{\max}| = |1 - \alpha\lambda_{\min}|, \tag{4.1}$$

where $\lambda_{\max}$ and $\lambda_{\min}$ are the largest and smallest eigenvalues of J_* respectively.

The solution to (4.1) is

$$\alpha = \frac{2}{\lambda_{\max} + \lambda_{\min}}. \tag{4.2}$$

Therefore, the optimal convergence rate of simple mixing is simply [12]

$$r = \frac{\lambda_{\max} - \lambda_{\min}}{\lambda_{\max} + \lambda_{\min}} = \frac{\kappa(J_*) - 1}{\kappa(J_*) + 1}, \tag{4.3}$$

where $\kappa(J_*) = \lambda_{\max}/\lambda_{\min}$ is the condition number of the Jacobian at the solution.

4.2. The convergence rate of the Anderson/Pulay scheme. The convergence rate of the Broyden's method can be shown to be Q-superlinear when it is applied to a smooth function, and when the starting guess of the solution is sufficiently close to the true solution and the starting guess of Jacobian is sufficiently close to the true Jacobian at the solution [33]. However, in the Anderson or Pulay scheme, we reset the previous approximation to the Jacobian to $C_0 = \alpha I$ at each iteration. Therefore, its convergence may not be superlinear in general.

One interesting observation made by a number of researchers [2, 12] is that $V_{k+1} - V^*$ lies in the Krylov subspace $\{V_0 - V^*, J_*(V_0 - V^*), ..., J_*^k(V_0 - V^*)\}$ when V_0 is sufficiently close to V^*, and V_{k+1} is constructed to have a minimum $\|V_{k+1} - V^*\|$ in this subspace in the Anderson/Pulay scheme even though we do not know this subspace explicitly. (Since we do not know V^* or J_*.) Therefore, one can draw a connection between the Anderson/Pulay scheme and the GMRES [40] algorithm for solving a linear system of equations [13, 39, 44]. As a result, if the Anderson or Pulay scheme converges, the convergence rate can be shown to be bounded by

$$r = \frac{\sqrt{\kappa(J_*)} - 1}{\sqrt{\kappa(J_*)} + 1}.$$

Clearly, when $\kappa(J_*)$ is large, the Anderson/Pulay acceleration scheme is superior to the simple mixing scheme.

When a good initial approximation to the inverse of the Jacobian (e.g. the Kerker preconditioner), C_0 is available, it can be combined with the Anderson/Pulay acceleration scheme to make the fixed point iteration converge more rapidly.

4.3. The dependency of the convergence rate on system size. A natural question that arises when we apply a preconditioned fixed point iteration to a large atomistic system is whether the convergence rate depends on the size of the system.

For periodic systems, the size of the system is often characterized by the number of unit cells in the computational domain. To simplify our discussion, we assume the unit cell to be a simple cubic cell with a lattice constant L. For non-periodic systems such as molecules, we can construct a fictitious (cubic) supercell that encloses the molecule and periodically extend the supercell so that properties of the system can be analyzed through Fourier analysis. In both cases, we assume the number of atoms in each supercell is proportional to L^3.

Because the convergence rates of both the simple mixing and the Anderson's method depend on the condition number of J_*, we should examine the dependency of $\kappa(J_*)$ with respect to L. When a good initial guess to the Jacobian C_0 is available, we should examine the dependency of $\kappa(C_0 J_*)$ with respect to L.

Recall that $J_* = I - (v_c + K_{\rm xc})\chi$, where v_c is positive definite, $K_{\rm xc}$ is symmetric but not necessarily positive definite and χ is symmetric negative definite.

The $K_{\rm xc}$ term is typically much smaller compared to v_c. When $K_{\rm xc}$ is small enough that $v_c + K_{\rm xc}$ remains positive definite, which is often true, the eigenvalues of J_* satisfy $\lambda(J_*) > \bar{\lambda} > 0$ where $\bar{\lambda}$ is independent of the system size. The inequality $\lambda_{\min} > \bar{\lambda} > 0$ gives the stability condition of the system.

The dependency of $\lambda_{\max}$ on L is generally difficult to analyze. However, for simple model systems such as a jellium system (or uniform electron gas) in which $K_{\rm xc}(\mathbf{r}, \mathbf{r}') = K_{\rm xc}^* \delta(\mathbf{r}, \mathbf{r}')$ for some constant $K_{\rm xc}^*$, we may use Fourier analysis to show that the eigenvalues of J_* are simply

$$\lambda_{\mathbf{q}} = 1 + \left(\frac{4\pi}{q^2} + K_{\rm xc}^*\right) \gamma F_L(q) \tag{4.4}$$

where $q = |\mathbf{q}|$, γ is a constant, and $F_L(q)$ is known as the *Lindhard* response function [49]. The Lindhard function satisfies

$$\lim_{q\to 0} F_L(q) = 1, \quad \lim_{q\to\infty} F_L(q) = 0, \tag{4.5}$$

Hence by taking $q = \frac{2\pi}{L}$, $\lambda_{\max}(J_*)$ is determined by $1 + \gamma(L^2/\pi + K^*_{\rm xc})$. As a result, the convergence of a fixed point iteration preconditioned by simple mixing and/or modified by the Anderson's method tends to become slower for a jellium system as the system size increases.

When the Kerker preconditioner is used, the eigenvalues of CJ_* are

$$\lambda_{\mathbf{q}} = \alpha \frac{q^2 + \gamma F_L(q)(4\pi + K^*_{\rm xc} q^2)}{q^2 + 4\pi\hat{\gamma}}. \tag{4.6}$$

They are approximately α when q is large, and are determined by $\alpha F_L(q)\gamma/\hat{\gamma}$ when q is small. Since the smallest q satisfies $q = 2\pi/L$, the convergence rate of the Kerker preconditioned fixed point iteration is independent of system size for a jellium system. The same conclusion can be reached for simple metals such as Na or Al which behave like free electrons [49]. Therefore, the Kerker preconditioner is an ideal preconditioner for simple metals.

However, the Kerker preconditioner is not an appropriate preconditioner for insulating systems. Although in general the Jacobian associated with the insulating system cannot be diagonalized by the Fourier basis, it can be shown that $e^{i\mathbf{q}\cdot\mathbf{r}}$ is an approximate eigenfunction of χ with the corresponding eigenvalue $-\xi q^2$ [14, 36]. If we ignore the contribution from $K_{\rm xc}$, $e^{i\mathbf{q}\cdot\mathbf{r}}$ is also an approximate eigenfunction of J_* with the corresponding eigenvalue $1 + (4\pi/q^2)q^2\xi = 1 + 4\pi\xi$ for small q's. If C is chosen to be the Kerker preconditioner, then the corresponding eigenvalue of CJ_* is

$$\lambda_{\mathbf{q}} = \frac{q^2}{q^2 + 4\pi\hat{\gamma}}(1 + 4\pi\xi).$$

As the system size L increases, the smallest q, which satisfies $q = 2\pi/L$, becomes smaller. Consequently, the corresponding eigenvalue of CJ_* approaches zero. The convergence rate, which is determined by $\sigma(1 - CJ_*)$, deteriorates as the system size increases.

For insulating system, a good preconditioner is simply αI, where α is chosen to be close to $1/(1 + 4\pi\xi)$ (in general, we do not know the value of ξ). When such a preconditioner is used the convergence the fixed point iteration becomes independent of the system size.

5. Elliptic preconditioner. As we have seen above, insulating and metallic systems call for different types of preconditioners to accelerate the convergence of a fixed point iteration for solving the Kohn-Sham problem. A natural question one may ask is how we should construct a preconditioner for a complex material that may contain both insulating and metallic components or metal surfaces.

Before we answer this question, let us introduce a new framework that unifies the construction of preconditioners for both insulating and metallic systems. Our preconditioner is of the random phase approximation (RPA) type [4], i.e, we construct C to approximate $\tilde{J}_*^{-1}$, where $\tilde{J}_* = I - v_c\chi$, instead of J_*^{-1}.

Note that we may rewrite $\tilde{J}_*^{-1}$ as

$$\tilde{J}_*^{-1} = (v_c^{-1} - \chi)^{-1} v_c^{-1}.$$

Since $v_c^{-1} = -\Delta/(4\pi)$, applying $\tilde{J}_*^{-1}$ to a vector r_k simply amounts to solving the following equation

$$(-\Delta - 4\pi\chi)\tilde{r}_k = -\Delta r_k. \tag{5.1}$$

For metallic systems, we replace χ in (5.1) by a constant $-\hat{\gamma}$ with $\hat{\gamma} > 0$. The solution to the modified equation

$$(-\Delta + 4\pi\hat{\gamma})\tilde{r}_k = -\Delta r_k \tag{5.2}$$

yields exactly the same quasi-Newton correction produced by the Kerker preconditioner.

For isotropic insulating system, we replace χ by $\xi\Delta$ in (5.1). The resulting equation becomes

$$-(1 + 4\pi\xi)\Delta\tilde{r}_k = -\Delta r_k, \tag{5.3}$$

which can be solved directly as

$$\tilde{r}_k = \frac{1}{1 + 4\pi\xi} r_k. \tag{5.4}$$

Such a solution corresponds to simple mixing with α set to $1/(1 + 4\pi\xi)$.

For a complex material that consists of both insulating and metallic components, it is desirable to choose approximation of χ that is spatially dependent. To this end, we construct a new preconditioner by replacing the Laplacian operator on the left hand side of (5.1) with $-\nabla \cdot (a(\mathbf{r})\nabla)$ and χ with $b(\mathbf{r})$ respectively. As a result, a quasi-Newton correction can be obtained by solving

$$\left(-\nabla \cdot (a(\mathbf{r})\nabla) + 4\pi b(\mathbf{r})\right)\tilde{r}_k = -\Delta r_k. \tag{5.5}$$

in each preconditioned fixed point iteration. Here $a(\mathbf{r})$ and $b(\mathbf{r})$ are real functions. If we choose $a(\mathbf{r}) = 1 + 4\pi\xi$ as a constant and $b(\mathbf{r}) = 0$, we obtain the simple mixing defined by Eq. (5.4). Similarly, if we choose $a(\mathbf{r}) = 1$ and $b(\mathbf{r}) = \hat{\gamma}$ as a constant, we recover the Kerker mixing scheme defined by Eq. (5.2).

The asymptotic behavior of χ with respect to the sizes of both insulating and metallic systems suggests that $a(\mathbf{r})$ and $b(\mathbf{r})$ should be chosen to satisfy $a(\mathbf{r}) \geq 1$ and $b(\mathbf{r}) \geq 0$. In this case, the operator defined on the left hand size of (5.5) is a strongly elliptic operator. Such an operator is symmetric positive semi-definite. Therefore we will refer to the preconditioner defined by Eq. (5.5) as an "elliptic preconditioner" for the self consistent field iteration.

The implementation of the elliptic preconditioner only requires solving an elliptic equation. In general $a(\mathbf{r}), b(\mathbf{r})$ are spatially dependent, and solving the elliptic preconditioner requires more than just a Fourier transform and scaling operation as is the case for the Kerker preconditioner. However, it is generally much less time consuming than evaluating the Kohn-Sham map or constructing χ or J_k. In particular, fast algorithms such as multigrid [7], fast multipole method (FMM) [17], Hierarchical matrix [18] solver and Hierarchical semi-separable (HSS) matrix [11] can be applied to solve Eq. (5.5) with $\mathcal{O}(N)$ arithmetic operations. Even if we cannot achieve $\mathcal{O}(N)$ complexity, Eq. (5.5) can often be solved efficiently by Krylov subspaces iterative methods as we will show in the next section.

Our numerical experience suggests that simple choices of $a(\mathbf{r})$ and $b(\mathbf{r})$ can produce satisfactory convergence result for complicated systems. For example, if we place

a metallic system in vacuum to ascertain its surface properties [41], we can choose $b(\mathbf{r})$ to be a nonzero constant in the metallic region, and almost 0 in the vacuum part. The resulting piecewise constant function can be smoothed by convolving it with a Gaussian kernel. Similarly, $a(\mathbf{r})$ can be chosen to be 1 in the metallic region, and a constant larger than 1 in the vacuum region.

6. Numerical results. In this section, we demonstrate the performance of the elliptic preconditioner proposed in the previous section, and compare it with other acceleration schemes through two examples. The first example consists of a one-dimensional (1D) reduced Hartree-Fock model problem that can be tuned to exhibit both metallic and insulating features. The second example is a three-dimensional (3D) problem we construct and solve in KSSOLV [48], which is a MATLAB toolbox for solving Kohn-Sham equations for small molecules and solids.

6.1. One dimensional reduced Hartree-Fock model. The 1D reduced Hartree-Fock model was introduced by Solovej [43], and has been used for analyzing defects in solids in [8, 9]. The simplified 1D model neglects the contribution of the exchange-correlation term. Nonetheless, typical behaviors of an SCF iteration observed for 3D problems can be exemplified by this 1D model. In addition to neglecting the exchange-correlation potential, we also use a pseudopotential to represent the electron-ion interaction. This makes our 1D model slightly different from that presented in [43].

The Hamiltonian in our 1D reduced Hartree-Fock model is given by

$$H[\rho] = -\frac{1}{2}\frac{d^2}{dx^2} + \int K(x,y)(\rho(y) + m(y))\,\mathrm{d}y \tag{6.1}$$

Here $m(x) = \sum_{i=1}^{M} m_i(x - R_i)$, with the position of the i-th nuclei denoted by R_i. Each function $m_i(x)$ takes the form

$$m_i(x) = -\frac{Z_i}{\sqrt{2\pi\sigma_i^2}} e^{-\frac{x^2}{2\sigma_i^2}}, \tag{6.2}$$

where Z_i is an integer representing the charge of the i-th nucleus. The parameter σ_i represents the width of the nuclei in the pseudopotential theory. Clearly as $\sigma_i \to 0$, $m_i(x) \to -Z_i\delta(x)$ which is the charge density for an ideal nucleus. In our numerical simulation, we set σ_i to a finite value. The corresponding $m_i(x)$ is called a *pseudo charge density* for the i-th nucleus. We refer to the function $m(x)$ as the total pseudo-charge density of the nuclei. The system satisfies charge neutrality condition, *i.e.*

$$\int \rho(x) + m(x)\,\mathrm{d}x = 0. \tag{6.3}$$

Since $\int m_i(x)\,\mathrm{d}x = -Z_i$, the charge neutrality condition (6.3) implies

$$\int \rho(x)\,\mathrm{d}x = \sum_{i=1}^{M} Z_i = N, \tag{6.4}$$

where N is the total number of electrons in the system. To simplify discussion, we omit the spin contribution here.

Instead of using a bare Coulomb interaction, which diverges in 1D, we adopt a Yukawa kernel

$$K(x,y) = \frac{2\pi e^{-\kappa|x-y|}}{\kappa\epsilon_0}, \tag{6.5}$$

which satisfies the equation

$$-\frac{d^2}{dx^2}K(x,y) + \kappa^2 K(x,y) = \frac{4\pi}{\epsilon_0}\delta(x-y). \tag{6.6}$$

As $\kappa \to 0$, the Yukawa kernel approaches the bare Coulomb interaction given by the Poisson equation. The parameter ϵ_0 is used to make the magnitude of the electron static contribution comparable to that of the kinetic energy.

The parameters used in the reduced Hartree-Fock model are chosen as follows. Atomic units are used throughout the discussion unless otherwise mentioned. For all the systems tested below, the distance between each atom and its nearest neighbor is set to 10 a.u.. The Yukawa parameter $\kappa = 0.01$ is small enough so that the range of the electrostatic interaction is sufficiently long, and ϵ_0 is set to 10.00. The nuclear charge Z_i is set to 2 for all atoms. Since spin is neglected, $Z_i = 2$ implies that each atom contributes to 2 occupied bands. The Hamiltonian operator is represented in a planewave basis set. The temperature of the system is set to 100 K, which is usually considered to be very low, especially for the simulation of metallic systems.

By adjusting the parameters $\{\sigma_i\}$, the reduced Hartree-Fock model can be tuned to resemble an insulating, metallic or hybrid system. We apply the elliptic preconditioner with different choices of $a(x)$ and $b(x)$ to all three cases. In the case of an insulator and a metal, both $a(x)$ and $b(x)$ are chosen to be constant functions. For the hybrid system, $a(x)$ and $b(x)$ are constructed by convolving a step function with a Gaussian kernel as shown in Figure 6.1. The σ_i values used for all these cases are listed in Table 6.1 along with the constant values chosen for $a(x)$ and $b(x)$ in the insulating and metallic cases. For the hybrid case, we partition the entire domain $[0, 320]$ into two subdomains: $[0, 160]$ and $[160, 320]$. The σ_i value is set to 6.0 in the first subdomain and 2.0 in the second subdomain.

case	σ_i	$a(x)$	$b(x)$	$\hat{\gamma}$
insulating	2.0	1.0	0.0	0.50
metallic	6.0	1.0	0.5	0.50
hybrid	2.0/6.0	see Fig. 6.1 (a)	see Fig. 6.1 (b)	0.42

Table 6.1: Test cases and SCF parameters used for the 1D model.

For all three cases, we apply the Anderson's method, the Anderson's method combined with the Kerker preconditioner, and the Anderson's method combined with the elliptic preconditioner to the SCF iteration. The α parameter used in the Anderson scheme is set to 0.50 in all tests. The $\hat{\gamma}$ parameter is set to 0.50 for the insulating and metallic cases, and 0.42 for the hybrid case.

The converged electron density ρ associated with the three 1D test cases as well as the 74 smallest eigenvalues associated with the Hamiltonian defined by the converged ρ are shown in Figure 6.2. The first 64 eigenvalues correspond to occupied states, and the rest correspond to the first 10 unoccupied states.

For the insulator case, the electron density fluctuates between 0.08 and 0.30. There is a finite gap between the highest occupied eigenvalue (ε_{64}) and the lowest unoccupied eigenvalue (ε_{65}). The band gap is $E_g = \varepsilon_{65} - \varepsilon_{64} = 0.067$ a.u.. The electron density associated with the metallic case is relatively uniform in the entire domain. The corresponding eigenvalues lie on a parabola (which is the correct distribution for uniform electron gas.) In this case, there is no gap between the occupied eigenvalues

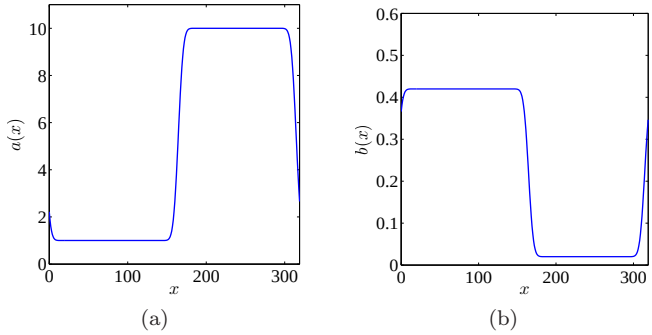


Fig. 6.1: (a) The choice of $a(x)$ and (b) the choice of $b(x)$ used by the elliptic preconditioner for a system with mixed metallic and insulating region.

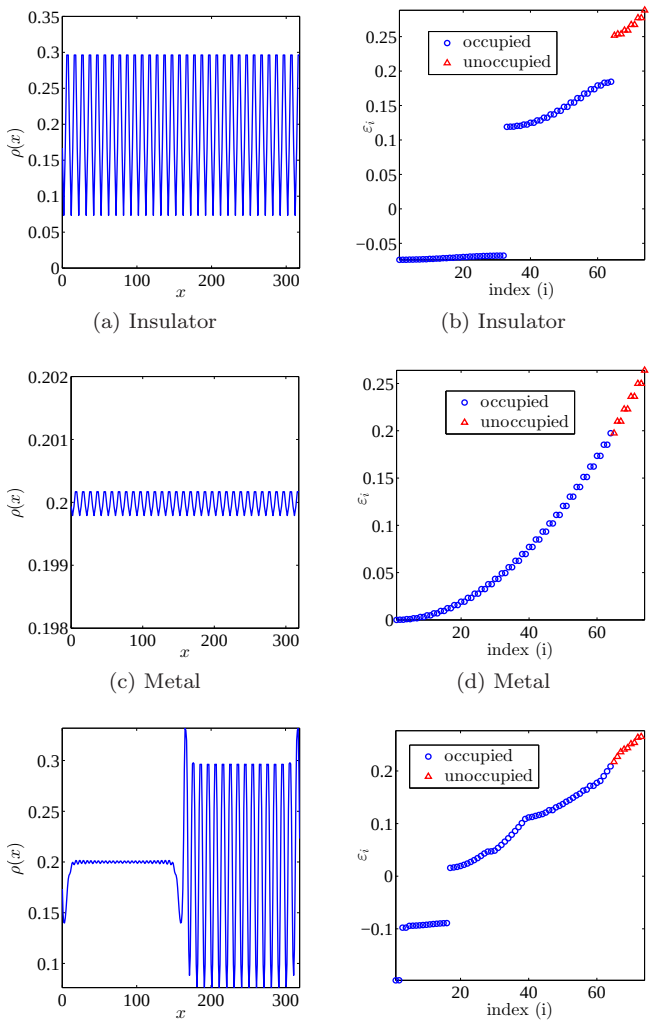
and the unoccupied eigenvalues. For the hybrid case, the electron density is uniformly close to a constant in the metallic region (except at the boundary), and fluctuates in the insulating region. There is no gap between the occupied and unoccupied states.

In Figure 6.3, we show the convergence behavior of all three acceleration schemes for three test cases by plotting the relative self-consistency error in potential against the iteration number. In each one of the subfigures, the blue line with circles, the red line with triangles and the black line with triangles correspond to tests performed on a 32-atom, 64-atom and 128-atom system respectively. We observe that the combination of the Anderson's method and the elliptic preconditioner gives the best performance in all test cases. In particular, the number of SCF iterations required to reach convergence is more or less independent from the type of system and system size. We can clearly see that the use of the Kerker preconditioner leads to deterioration in convergence speed when the system size increases for insulating and hybrid systems. On the other hand, the Anderson's method alone is not sufficient to guarantee the convergence of SCF iteration for metallic and hybrid systems. All these observed behaviors are consistent with the analysis we presented in the previous section.

6.2. Three dimensional sodium system with vacuum. In this subsection, we compare the performance of different preconditioning techniques discussed in section 3 when they are applied to a 3D problem constructed in KSSOLV [48], a MATLAB toolbox for solving Kohn-Sham problems for molecules and solids. We have chosen to use the KSSOLV toolbox because of its ease of use, especially for prototyping new algorithms. The results presented here can be reproduced by other more advance DFT software packages such as Quantum ESPRESSO [15], with some additional programming effort.

The model problem we construct consists of a chain of sodium atoms placed in a vacuum region that extends on both ends of the chain. The sodium chain contains a number of body-centered cubic (BCC) unit cells. The dimension of the unit cell along each direction is 8.0 a.u.. Each unit cell contains two sodium atoms. To examine the size dependency of the preconditioning techniques, we tested both a 16-unit cell (32-atoms) model and a larger 32-unit cell (64 atoms) model. The converged electron density on the $x = 0$ plane (or the [100] plane in crystallography terminology) associated with the 32-atom model is shown in Figure 6.4.

Figure 6.6 shows how the Anderson's method, the combination of the Anderson's



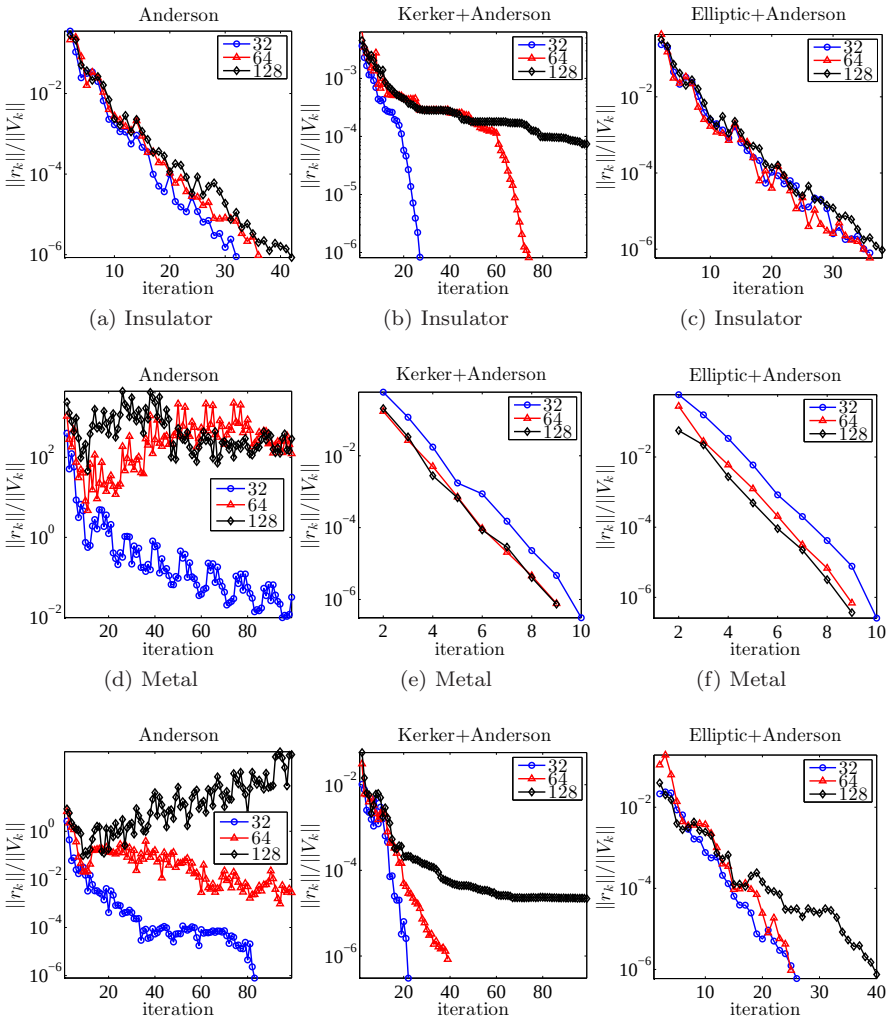
(a) Insulator (b) Insulator

(c) Metal (d) Metal

(e) Metal+Insulator (f) Metal+Insulator

Fig. 6.2: The electron density $\rho(x)$ of a 32-atom (a) insulating system (c) metallic and (e) hybrid metal-insulator in the left panel. The corresponding occupied (blue circles) and unoccupied eigenvalues (red triangles) are shown in the right panel in subfigure (b), (d), (f), respectively.

method and the Kerker preconditioner and the combination of the Anderson's method and the elliptic preconditioner behave for both the 32-atom and the 64-atom sodium systems. For the 32-atom problem, the parameter α for the Anderson's method is set to 0.4. The parameter $\hat{\gamma}$ required in both the Kerker preconditioner and the elliptic preconditioner is set to 0.05. For the 64-atom problem, the parameter α is set to 0.8. For simplicity the function $a(x)$ required in the elliptic preconditioner is set to a constant function $a(x) = 1.0$. The $b(x)$ function (shown in Figure 6.5 for the 32-atom problem) is constructed by convolving a square wave function with a value of 0.05 in the sodium region and 0 in the vacuum region with a Gaussian kernel. The SCF



(a) Insulator (b) Insulator (c) Insulator

(d) Metal (e) Metal (f) Metal

(g) Metal+Insulator (h) Metal+Insulator (i) Metal+Insulator

Fig. 6.3: The convergence of the Anderson's method, the Anderson's method with the Kerker preconditioner, and the Anderson's method with the elliptic preconditioner for insulators in subfigures (a), (b), (c), for metals in subfigures (d), (e), (f), and for hybrid systems in subfigures (g), (h), (i), respectively.

iteration is declared to be converged when the relative self-consistency error in the potential is less than 10^{-6}.

As we can clearly see from Figure 6.6, the use of the Anderson's method with the elliptic preconditioner leads to rapid convergence. Furthermore, the number of iterations (around 30) required to reach convergence does not change significantly as we move from the 32-atom problem to the 64-atom problem.

Using the Anderson's method alone enables us to reach convergence in 60 iterations for the 32-atom problem. However, it fails to reach convergence within 100

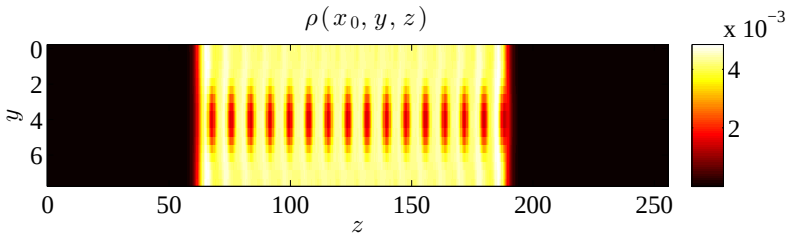


Fig. 6.4: The $x = 0$ slice of the electron density $\rho(x, y, z)$ of the 32-atom sodium system with large vacuum regions at both ends.

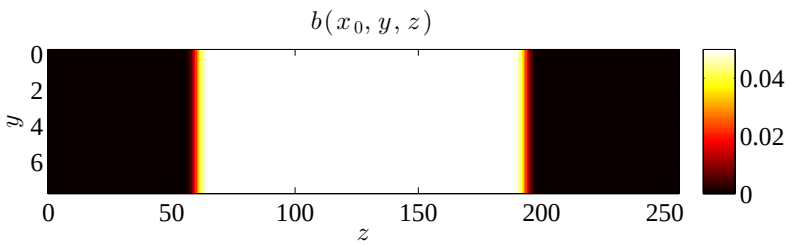


Fig. 6.5: The $x = 0$ slices of the function $b(x, y, z)$ used in the elliptic preconditioner for a 32-atom sodium system with large vacuum regions at both ends.

iterations for the 64-atom case. When the Anderson's method is combined with the Kerker preconditioner, the SCF iteration converges very slowly for both the 32-atom and the 64-atom problems.

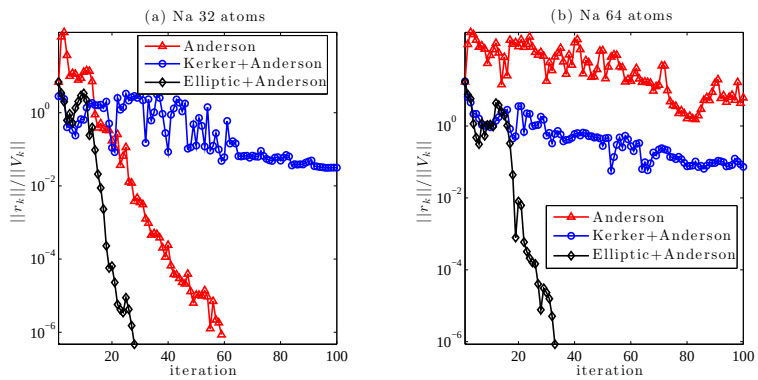


Fig. 6.6: The convergence of the Anderson's method, the Anderson's method with the Kerker preconditioner, and the Anderson's method with the elliptic preconditioner for quasi-1D Na systems with a large vacuum region with 32 Na atoms (a) and 64 Na atoms (b).

7. Concluding Remarks. We discussed techniques for accelerating the convergence of the self-consistent iteration for solving the Kohn-Sham problem. These

techniques make use of the spectral properties of the Jacobian operator associated with the Kohn-Sham fixed point map. They can also be viewed as preconditioners for a fixed point iteration. We pointed out the crucial difference between insulating and metallic systems and different strategies for constructing preconditioners for these two types of systems. A desirable property of the preconditioner is that the number of fixed point iterations is independent of the size of the system. We showed how this property can be maintained for both insulators and metals. Furthermore, we proposed a new preconditioner that treats insulating and metallic systems in a unified way. This preconditioner, which we refer to as an elliptic preconditioner, is constructed by solving an elliptic PDE with spatially dependent variable coefficients. Constructing preconditioners for insulating and metallic systems simply amounts to setting these coefficients to appropriate functions. The real advantage of this type of preconditioner is that it allows us to tackle more difficult problems that contain both insulating and metallic components at low temperature. We showed by simple numerical examples that this is indeed the case. In the near future, we plan to implement the elliptic preconditioner for standard electronic structure calculation software packages such as QUANTUM ESPRESSO [15], ABINIT [16] and SIESTA [42] etc..

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