A rapidly converging algorithm for solving the Kohn-Sham and related equations in electronic structure theory

J. Auer† and E. Krotscheck‡†

†Institut für Theoretische Physik, Johannes Kepler Universität Linz, A-4040 Linz, Austria
‡Institute for Nuclear Theory, University of Washington, Seattle, WA 98195-1550, USA

Abstract

We describe a rapidly converging algorithm for solving the Kohn–Sham equations and equations of similar structure that appear frequently in calculations of the structure of inhomogeneous electronic many–body systems. The algorithm has its roots the Hohenberg-Kohn theorem and solves directly for the electron density; single–particle wave functions are only used as auxiliary quantities. The method has been implemented for symmetric “slabs” of jellium as well as for spherical jellium clusters. Starting from very rough guesses for the initial electron density, convergence is reached within a few iterations. The iterations are driven by the static electric susceptibility.

1 INTRODUCTION

Density–functional theory [1] is a popular method for studying properties of inhomogeneous many–electron systems. Central to the execution of the theory is the solution of the Kohn-Sham equation, which is an effective Schrödinger equation for a set of single–particle wave functions \( \phi_i(\mathbf{r}) \)

\[
-\frac{\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) + V_H[\rho](\mathbf{r}) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),
\]

which are characterized by a set of quantum numbers \( i \). \( V_H(\mathbf{r}) \) in Eq. (1.1) is an effective one–body potential that describes both the influence of an external field and many–body interactions and depends implicitly on the density of
the system. In density functional theory, this effective one–body (“Hartree”)–
potential is

\[ V_H(r) = V_C(r) + V_{xc}(r) \]  

(1.2)

where \( V_C(r) \) is the Coulomb potential

\[ V_C(r) = \int d^3r' \frac{e^2}{|r-r'|} \left[ \rho(r') - \rho_+(r') \right] , \]  

(1.3)

and \( V_{xc}(r) \) is the “exchange–correlation” correction. \( \rho_+(r') \) is the charge den-
sity of the positive background.

From the single–particle wave functions \( \phi_i(r) \) one constructs the physical one–
body density

\[ \rho(r) = \sum_i n(i) |\phi_i(r)|^2 ; \]  

(1.4)

the \( n(i) \) are the occupation numbers of the single–particle states.

Structurally similar equations also appear in microscopic theories of inhomoge-
neous, correlated electrons [2,3]. In fact, equations equivalent to the Kohn–
Sham equation appear in the theory of basically all inhomogeneous quantum
many–particle systems such as nuclei, quantum liquid clusters, and quantum
liquid films. We disregard, for the time being, non–localities like a Fock–term
and will comment on how to include such complications further below.

In this paper we will develop a rapidly converging iterative scheme that solves,
very much in the spirit of the Hohenberg-Kohn theorem, directly for the density \( \rho(r) \).

It is plausible to try to solve Eqs. (1.1)-(1.4) iteratively: One calculates, from
an initial guess for the density \( \rho(r) \), the single–particle orbitals \( \phi_i(r) \) from Eq.
(1.1), from these a new single–particle density (1.4), and iterates the proce-
dure until convergence is reached. This procedure converges well for atoms
and other systems that are dominated by an \textit{external} field, but the conver-
gence can be very slow for metallic clusters, self–bound systems, or in cases
where local charge–neutrality is important. Judicious “mixing” of consecutive
iterations is needed [4,5] with admixtures of the “new” solutions of less than
1 percent for clusters of a few hundred electrons. A specialized “gradient iter-
ation method” [6,7] improves the stability of the process considerably, but
still takes very many iterations to converge. This situation is unsatisfactory
because one should think that, \textit{because} these systems are very stable in na-
ture, one should be able to mimic nature and to design a stable and rapidly converging numerical algorithm to obtain ground state configurations.

The cause for the sometimes delicate convergence properties is rather clear in electronic systems: The configuration with local charge neutrality will minimize the potential energy which can, on the other hand, be enormous if local charge neutrality is not maintained. The quantum kinetic energy causes only a small violation of local charge neutrality. In other words, the quantity that drives the configuration towards the correct ground state is the potential energy, whereas the simple iterative procedure (1.1), (1.4) focuses on the kinetic energy.

2 Algorithm

Our procedure to solve the coupled equation Eq. (1.1)–(1.4) has its roots in the Hohenberg-Kohn theorem [8] that states, among others, that the one-body density $\rho(\mathbf{r})$ is the only truly independent variable. We therefore design an algorithm that solves, by a Newton-Raphson procedure, directly for $\rho(\mathbf{r})$.

Consider the functional

$$
F[\rho](\mathbf{r}) \equiv \sum_{i} n_{i}(\mathbf{r}) |\phi_{i}[\rho](\mathbf{r})|^{2} - \rho(\mathbf{r})
$$

(2.1)

where the $\phi_{i}[\rho](\mathbf{r})$ are the solutions of Eq. (1.1) for the density $\rho(\mathbf{r})$. The exact solution of Eq. (1.1) is the density that satisfies

$$
F[\rho](\mathbf{r}) = 0.
$$

(2.2)

Non-linear equations of the type (2.2) can be solved iteratively by the Newton-Raphson algorithm. Assume that we have an $k$-th guess for the density, say $\rho^{(k)}(\mathbf{r})$. A next iteration $\rho^{(k+1)}(\mathbf{r}) \equiv \rho^{(k)}(\mathbf{r}) + \delta \rho^{(k)}(\mathbf{r})$ is defined by the condition

$$
0 = F[\rho^{(k+1)}](\mathbf{r}) = F[\rho^{(k)} + \delta \rho^{(k)}](\mathbf{r})

= F[\rho^{(k)}](\mathbf{r}) + \int d^{3}r' \frac{\delta F[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}')} \delta \rho^{(k)}(\mathbf{r}') + O((\delta \rho^{(k)})^{2}).
$$

(2.3)

Defining

$$
\frac{\delta F[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}')} = -\epsilon(\mathbf{r}, \mathbf{r}'; 0),
$$

(2.4)
the density correction \( \delta \rho^{(k)}(r) \) is determined by

\[
F[\rho^{(k)}](r) = \int d^3r' \epsilon(r, r'; 0) \delta \rho^{(k)}(r').
\]

(2.5)

which is, upon discretization, a system of linear equations which can be solved
by standard methods.

The remaining task is the calculation and physical interpretation of the kernel
\( \epsilon(r, r'; 0) \). For any set of single particle orbitals \( \{\phi_i(r)\} \) representing a \( k \)-th
iteration \( \{\phi_i^{(k)}(r)\} \), we have

\[
\epsilon(r, r'; 0) = \delta(r - r') - \sum_i n(i) \left[ \phi_i(r) \frac{\delta \phi_i^*(r)}{\delta \rho(r')} + \text{c. c.} \right].
\]

(2.6)

The variations of the single–particle wave functions are obtained by first order
perturbation theory:

\[
\frac{\delta \phi_i(r)}{\delta \rho(r')} = -\int d^3r'' \sum_{j \neq i} \frac{\phi_j(r) \phi_j^*(r'') \phi_i(r'') \delta V_H(r'')}{\varepsilon_j - \varepsilon_i} \frac{\delta \rho(r)}{\delta \rho(r')}.
\]

(2.7)

Inserting (2.7) in the second term of Eq. (2.6), we find

\[
\sum_i n(i) \left[ \phi_i(r) \frac{\delta \phi_i^*(r)}{\delta \rho(r')} + \text{c. c.} \right] = -\int d^3r'' \left[ \sum_{ij} n(j) \bar{n}(j) \frac{\phi_i(r) \phi_i^*(r') \phi_j(r'') \delta V_H(r'')}{\varepsilon_j - \varepsilon_i} + \text{c. c.} \right] \frac{\delta V_H(r'')}{\delta \rho(r')}.
\]

(2.8)

Two new quantities have been introduced in the last line of Eq. (2.8): In
the density variation of the Hartree–potential we recover a local and static
approximation for the effective “particle–hole” interaction,

\[
V_{p-h}(r, r') \equiv \frac{\delta V_H(r)}{\delta \rho(r')}.
\]

(2.9)

We also have identified, by inspection, the sum over states and wave functions
in Eq. (2.8) with the zero–frequency Lindhard–function \( \chi_0(r, r'; 0) \) of the non–
interacting system. The introduction of an occupation number factor \( \bar{n}(j) \equiv 1 - n(j) \) above is legitimate since all terms in the double sum where \( j \) is an
occupied state cancel out due to the antisymmetry of the energy denominator.
Hence, the Newton-Raphson procedure suggests a density correction \( \delta \rho^{(k)}(r) \) given by the linear integral equation (2.5), where \( F \left[ \rho^{(k)} \right](r) \) is the functional (2.1) and

\[
\epsilon(r, r'; 0) = \delta(r - r') - \int d^3 r'' \chi_0(r, r''; 0)V_{p-h}(r'', r')
\]

(2.10)

is the static dielectric function of a non-uniform electron gas [9].

3 Numerical Considerations

A number of simplifications that are independent of the geometry can be applied to the algorithm to speed up the calculation; the justification for such simplifications is based on the observations that

- The equilibration of the configuration is dominated by the Coulomb term \( V_C(r) \),
- The dielectric function \( \epsilon(r, r'; 0) \) does not need to be evaluated very accurately for the iterations to converge, and
- The ground state density is reasonably smooth.

Generally, and in particular in the local density approximation, it is not a problem to calculate the variation \( \delta V_H(r)/\delta \rho(r') \). However, we found that the inclusion of the exchange–correlation term \( \delta V_{xc}(r)/\delta \rho(r') \) does not noticeably improve the convergence of the procedure: It is sufficient to use the Coulomb interaction

\[
V_{p-h}(r, r') \approx \frac{e^2}{|r - r'|}.
\]

(3.1)

This simplification allows us to use the same algorithm in microscopic calculations [3] for which the computation of the variation of the exchange–correlation energy with respect to the density is more time consuming. Since the Coulomb term is vastly dominant, the non–local Fock term could also be included in the same manner and should not cause difficulties that are worse than the iterative solution.

Since the kernel \( \epsilon(r, r'; 0) \) does not need to be very accurate for the convergence of the procedure, there is also no need to recalculate it after every iteration. This is especially true if one is already close to the ground state density. In fact, one can save the \( L - U \) decomposition of \( \epsilon(r, r'; 0) \), and needs to carry out only the back-substitution step during every iteration. Moreover, during
all those iterations when $\epsilon(\mathbf{r}, \mathbf{r}'; 0)$ is not recalculated, Eq. (1.1) needs to be solved for the occupied states only.

Finally, because the ground state density should be reasonably smooth, it is unnecessary to include very high lying single–particle states in the state sum (2.8). In fact, since the electron density falls off exponentially into the vacuum, it is in most cases sufficient to restrict the sum over particle states to those with negative energies. Even for very crude initial densities, we found that it is safe to include states with energies no higher than 0.2 Ry.

With these considerations taken into account, the solution of Eq. (1.1) for any trial density $\rho(\mathbf{r})$ is the most time consuming part of the algorithm.

We conclude this section by remarking that the iterative solution conserves the particle number due to

$$\int d^3r \chi_0(\mathbf{r}, \mathbf{r}'; 0) = 0.$$  \hspace{1cm} (3.2)

It is therefore an important precaution to start the iterations with an initial density $\rho(\mathbf{r})$ that has the correct particle number.

4 Application for spherical jellium clusters

The feasibility of the calculation depends, of course, on the possibility to exploit the symmetries of the ground state and to reduce the three-dimensional eigenvalue problem (1.1) to a simpler task. If this can be accomplished, the calculation of the static dielectric function $\epsilon(\mathbf{r}, \mathbf{r}'; 0)$ and the implementation of the Newton-Raphson iterations is equally feasible.

We have implemented the algorithm for the symmetric slabs of jellium studied in Ref. [3], and for spherically symmetric jellium clusters which have in the past decade received much attention [10–12]. The convergence properties of the procedure are basically the same; we therefore describe the details for the cluster problem.

In this geometry, the states $\phi_i(\mathbf{r})$ are characterized by a radial quantum number $i$ and the angular momentum $\ell$, i.e. $i = \{i, \ell\}$. We consider closed–shell clusters, hence each state with angular momentum $\ell$ is $2(2\ell + 1)$-fold degenerate. Since the system is spherically symmetric, the Hartree– (or Kohn–Sham) equations decouple

$$\phi_i(\mathbf{r}) = \phi_i(\mathbf{r}) Y_{\ell,m}(\theta, \phi) = \frac{u_{i,\ell}(r)}{r} Y_{\ell,m}(\theta, \phi).$$  \hspace{1cm} (4.1)
Eq. (1.1) is a radial Schrödinger equation (note that we work in atomic units)

\[
- \frac{d^2 u_{i,\ell}(r)}{dr^2} + \frac{\ell(\ell + 1)}{r^2} u_{i,\ell}(r) + V_H[\rho(r)] u_{i,\ell}(r) = \varepsilon_{i,\ell} u_{i,\ell}(r)
\]

(4.2)

and the density is

\[
\rho(r) = \frac{1}{2\pi} \sum_{i,\ell} n(i, \ell)(2\ell + 1) |\phi_{i,\ell}(r)|^2.
\]

(4.3)

The calculations follow exactly those of the derivation of the previous section; all angular integrations can be carried out due to the spherical symmetry. The angle-averaged Coulomb potential is

\[
V_C(r, r') = \int d\Omega \frac{2}{4\pi |r - r'|} = \frac{2}{\max(r, r')}
\]

(4.4)

and the angle-averaged static Lindhard function is

\[
\chi_0(r, r'; 0) = \int d\Omega \frac{2}{4\pi} \chi_0(r, r'; 0)
\]

\[
= -\frac{1}{4\pi^2} \sum_{\ell, i, j} (2\ell + 1)n(i, \ell)\bar{n}(j, \ell) \frac{\phi_{i,\ell}(r)\phi_{i,\ell}(r')\phi_{j,\ell}(r')\phi_{j,\ell}(r')}{\varepsilon_{j\ell} - \varepsilon_{i,\ell}}.
\]

(4.5)

In this geometry, the Newton-procedure becomes a matter of solving a one-dimensional linear equation.

We demonstrate the working of our algorithm for the jellium model for Na clusters with 40 and 2018 electrons. To facilitate the comparison with earlier work, we use the local density approximation and the energy functional of Ref. [13]. The jellium background density \(\rho_+(r)\) was taken to be a step function; as a worst-case scenario we assumed, as starting density, the same density profile for the electrons. During the iterations, the static susceptibility was re-calculated for the first two steps only and then kept fixed.

Fig. 1 shows the density corrections \(\delta \rho(r)\) during the first five iterations for the 2018 electron model; results for the average density correction as well as the kinetic, potential, and exchange–correlation energy are given in Table 1 as a function of the iteration number. These results agree, within numerical accuracy, with those found in the literature [7,12]. Further documentation of the algorithm is provided in Fig. 2 where we show the difference between the energy obtained in the \(k\)-th iteration and the converged result. Also shown is the \(rms\) error in the density as function of the iteration number. Obviously, the rate of convergence is practically independent of the cluster size, and
comparable for different quantities of physical interest. We re-iterate that the replacement of the Coulomb potential by the full particle–hole interaction did not improve the convergence noticeably, updating the static susceptibility after every step reduced the number of iterations needed to obtain the accuracy shown in Fig. 1 to 16.

5 Summary

We have described in this note a rapidly converging algorithm for solving the Kohn-Sham and similar equations. While we have focused here on electronic systems, the algorithm is not restricted to those. Practically the same procedure has been implemented in our work on bosonic liquid films [14] and droplets [15], the only difference being that only one state is occupied in that case. In self–bound systems, the “particle–hole interaction” cannot be replaced by the Coulomb potential, but otherwise the convergence properties of the Newton–Raphson algorithm are the same.

For the implementation of our method, we have relied heavily on “canned” software, specifically BLAS and LAPACK routines for solving the band-symmetric eigenvalue problems (1.1), (4.2) and for computing the L-U decomposition of the static dielectric function. The most time–consuming part of the algorithm is the solution of the eigenvalue equations (1.1). If needed, much computation time can be saved by choosing specialized algorithms, such as the “imaginary timestep method [16]”, inverse iterations [17] or the Lanczos algorithm [18] that compute only the lowest lying states and work particularly well when good estimates for these states are known.

We hasten to point out that none of the measures to speed up the computation is essential for the implementation of our algorithm for the simple systems considered here that can be reduced to one–dimensional problems. Even when the static dielectric function is updated every time, each iteration is a matter of a few seconds on a reasonable personal computer. Efficiency considerations will become truly useful only for higher–dimensional problems like non–spherical clusters.

Finally, we emphasize again that a central quantity of our algorithm is the static dielectric function $\epsilon(r, r'; 0)$ which is an independently interesting physical quantity that one might wish to compute anyway. Our algorithm also highlights the reason for the delicate convergence of the normal iteration method: the dielectric function is vastly dominated by the potential energy term $\int d^3r''\chi_0(r, r'; 0)V_{p-h}(r'', r')$ whereas this term is neglected by the conventional iterative procedure.
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Fig. 1. The figure shows the density corrections $\delta \rho(r)/\rho_0$ for the electron density of a jellium cluster with $r_s = 4.0$ and $N = 2018$ electrons during the first five iterations. The density is normalized to the density $\rho_0$ of the jellium background, and the starting density was the same as the background density. The jellium edge is at $r = 50.55$ a.u.
Fig. 2. The figure shows the relative energy corrections $\Delta E/E_\infty = \left| E^{(k)}/E_\infty - 1 \right|$, where $E_\infty$ is the converged result, and $E^{(k)}$ is the energy obtained in $k$-th iteration, and the rms error $\epsilon = \sqrt{\sum_i |\delta \rho(r_i)|^2/(N\rho_0)}$ of the density. Results are shown for two jellium cluster with $r_s = 4.0$, for $N = 2018$ (solid lines) and $N = 40$ (dashed lines). In both cases, the starting density was the same as the background density.
Table 1
Convergence behavior of our iterations for a spherical jellium cluster with $r_s = 4$ and $N = 2018$ electrons. All energies are given in Rydberg units per electron. $\epsilon$ is the *rms* error $\epsilon = \sqrt{\sum_i |\delta \rho(r_i)|^2/N\rho_0}$, the $r_i$ are the mesh points, $N$ is the number of mesh points, and $\rho_0$ the jellium density.

| Iteration | $\epsilon$ | $\langle T \rangle$ | $\langle V \rangle$ | $\langle E_{sc} \rangle$ | $\langle E \rangle$ |
|-----------|------------|----------------------|---------------------|----------------------|---------------------|
| 1         | 3.60E-3    | 0.14501              | 0.00000             | -0.29998             | -0.15498            |
| 2         | 6.31E-4    | 0.13726              | 0.00055             | -0.29869             | -0.16087            |
| 3         | 2.35E-4    | 0.13637              | 0.00065             | -0.29820             | -0.16118            |
| 4         | 9.12E-5    | 0.13581              | 0.00074             | -0.29802             | -0.16147            |
| 5         | 3.52E-5    | 0.13559              | 0.00078             | -0.29795             | -0.16158            |
| 6         | 1.32E-5    | 0.13551              | 0.00080             | -0.29793             | -0.16162            |
| 7         | 4.84E-6    | 0.13548              | 0.00080             | -0.29792             | -0.16164            |
| 8         | 1.75E-6    | 0.13547              | 0.00081             | -0.29792             | -0.16164            |
| 9         | 6.21E-7    | 0.13546              | 0.00081             | -0.29792             | -0.16164            |