

Reconstruction of atomic effective potentials from isotropic scattering factors

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We present a method for the approximate determination of one-electron effective potentials of many-electron systems from a finite number of values of the isotropic scattering factor. The method is based on the minimum cross-entropy technique. An application to some neutral ground-state atomic systems has been done within a Hartree-Fock framework.

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The one-particle density $\rho(\mathbf{r})$ of a many-electron system plays a fundamental role in the description of different physical and chemical properties and it is the basic quantity in the development of density functional theories [1]. Hunter proposed [2] a Schrödinger-like equation for the electron density $\rho(\mathbf{r})$, which is the basis for an exact dynamical model of the motion of a single electron in a many-electron system. This model is the starting point for interpreting the structure of many-electron systems in terms of the effective three-dimensional potential $U(\mathbf{r})$ that “feels” each electron of the system [2–4].

The analytical reconstruction of the above effective potential from incomplete experimental information in various areas, such as atomic and molecular physics, would be useful. Here we will consider the elastic scattering factor (or form factor) $F(\mathbf{k})$ defined by

$$F(\mathbf{k}) = \int \rho(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (1)$$

This form factor can be obtained for atoms and molecules in both elastic x-ray scattering and electron scattering experiments [5]. For coherent x-ray scattering, the intensity of the scattered radiation is, in the first Born approximation, proportional to the absolute square of $F(\mathbf{k})$, where \mathbf{k} denotes the difference between the wave vectors of incident and scattered radiation. For atomic systems it is usual to work with the isotropic form factor (also called the spherically averaged atomic structure factor),

$$F(k) = \frac{1}{4\pi} \int F(\mathbf{k}) d\Omega_k,$$

where $d\Omega_k = \sin\theta_k d\theta_k d\phi_k$. This function is normalized by the requirement $F(0) = \int \rho(\mathbf{r}) d\mathbf{r} = \int_0^\infty D(r) dr = N$, where $D(r)$ is the radial charge density $D(r) = 4\pi r^2 \rho(r)$, $\rho(r)$ being the spherically averaged charge density and N the number of electrons. These spherical averages are the relevant quantities in the description of atomic systems in the absence of an external field. Due to the spherical symmetry of the system, the Fourier transformation (1) reduces to

$$F(k) = 4\pi \int_0^\infty \rho(r) j_0(kr) r^2 dr = \int_0^\infty D(r) j_0(kr) dr, \quad (2)$$

where $j_0(s)$ is the spherical Bessel function of order zero. However, these experimental data are only accessible for a finite and discrete set of values of the momentum transferred $k = |\mathbf{k}|$, as well as up to a maximum value k_{\max} that depends on the type of experiment involved.

The aim of this work is to propose a general method to obtain a one-electron effective potential from a limited set of values $\{F(k_i)\}$ ($i=0, \dots, n$) of the isotropic form factor $F(k)$. In doing so we employ the minimum cross-entropy principle [6,7]. First, we obtain a general effective potential for a N -electron system using the above technique. Then, we show numerical results for some particular atomic systems. Atomic units will be used along with this work.

As we point out above, Hunter derived [2] the following Schrödinger-like equation satisfied by the square root of the electron density of a N -electron system:

$$-\frac{\nabla^2 \rho(\mathbf{r})}{4} - \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} + U_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) = E \rho(\mathbf{r}), \quad (3)$$

where $U_{\text{eff}}(\mathbf{r})$ is a local effective potential. Given the density $\rho(\mathbf{r})$, $V_{\text{eff}}(\mathbf{r}) \equiv U_{\text{eff}}(\mathbf{r}) - E$ can be found simply by inverting Eq. (3),

$$V_{\text{eff}}(\mathbf{r}) = \frac{\nabla^2 \rho(\mathbf{r})}{4\rho(\mathbf{r})} - \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho^2(\mathbf{r})} = \frac{\nabla^2 \sqrt{\rho(\mathbf{r})}}{2\sqrt{\rho(\mathbf{r})}}, \quad (4)$$

so that for the spherically averaged charge density $\rho(r)$ we have

$$V_{\text{eff}}(r) = -\frac{1}{8\rho^2(r)} \left\{ -2\rho(r) \frac{d^2 \rho(r)}{dr^2} - \frac{4}{r} \rho(r) \frac{d\rho(r)}{dr} + \left(\frac{d\rho(r)}{dr} \right)^2 \right\}. \quad (5)$$

Sagar *et al.* [3] showed that the one-electron potential $V_{\text{eff}}(r)$ reveals the shell structure of atoms and ions and that, in general, it is useful for the interpretation of molecular and atomic structure.

In this work we obtain an analytical approximation to this effective potential $V_{\text{eff}}(r)$ from the isotropic form factor at $n+1$ values of the momentum transferred, $\{F(k_i)\}_{i=0}^n$. In order to reach this aim, we will first calculate the approxi-

mated density of the system based on the concept of minimum cross-entropy and then we will obtain an analytical approximation for the effective potential.

The minimum cross-entropy principle [7] is based on the concept of cross entropy or relative entropy $S[D, D_0]$ between two densities defined over a set X , $D(r)$, and $D_0(r)$, with the same normalization over X ,

$$S[D, D_0] \equiv \int_X D(r) \ln \frac{D(r)}{D_0(r)} dr. \quad (6)$$

We have to point out that $S[D, D_0]$ is always non-negative, convex, and equals zero only when $D(r) = D_0(r)$. Our *prior knowledge* about our system is assumed to be incorporated into a *prior distribution* $D_0(r)$. For a given prior density $D_0(r)$, the distribution $D(r)$ that satisfies some given constraints and minimizes the relative entropy is the *closest one* to $D_0(r)$ among all those that fulfill the constraints [8,9]. As constraints, we use $n+1$ values of the isotropic form factor $F(k_i)$, $i=0, 1, \dots, n$, in the points k_0, k_1, \dots, k_n ; so let us consider the nonlinear system of equations,

$$F(k_i) = \int_0^\infty D(r) j_0(k_i r) dr, \quad i=0, \dots, n. \quad (7)$$

We will always choose $k_0=0$. Then, we have the first condition

$$F(0) = \int_0^\infty D(r) dr = N \quad (8)$$

for an N -electron system. Then the minimum cross-entropy solution [i.e., that which minimizes the relative entropy functional,

$$S[D, D_0] = \int_0^\infty D(r) \ln \left[\frac{D(r)}{D_0(r)} \right] dr$$

with the constraints in Eq. (7)] is given by

$$D_n(r) = D_0(r) \frac{N}{Z} \exp \left\{ - \sum_{i=1}^n \lambda_i j_0(k_i r) \right\}, \quad (9)$$

where

$$Z = \int_0^\infty D_0(r) \exp \left\{ - \sum_{i=1}^n \lambda_i j_0(k_i r) \right\} dr \quad (10)$$

and $\lambda_1, \lambda_2, \dots, \lambda_n$ are multipliers that have to be evaluated numerically from the nonlinear set of equations,

$$\int_0^\infty D_n(r) j_0(k_i r) dr = F(k_i), \quad i=1, \dots, n. \quad (11)$$

It is worth pointing out that there are no known conditions to be fulfilled by the set of constraints in order to find a unique solution for this problem. We always reach numerically a solution independent of the number of constraints and

using different *a priori* densities. For a deep study of the minimum cross-entropy method see Refs. [6, 8, 10].

The effective potential will be written, in this approximation, in terms of the input data $k_0=0, k_1, \dots, k_n$, the numerically calculated Lagrange multipliers $\lambda_1, \dots, \lambda_n$ for each n , and the *a priori* density. For this purpose we will use two different *a priori* radial densities $D_0(r) = 4\pi r^2 \rho_0(r)$ in the case of an atomic system. To choose these two densities we will take into account that in the limit $r \rightarrow 0$ the effective potential acting on each electron is just the unscreened Coulomb potential $-Z/r$ due to the nucleus. As $r \rightarrow \infty$, we would like the potential to have the ionization potential (ϵ) of the system as its asymptotic value [2]. The first property is reproduced by the *a priori* distribution $\rho_0^{(1)}(r) = \rho(0) e^{-2Zr}$ and the second one by $\rho_0^{(2)}(r) = [N \langle r^{-2} \rangle / 2\pi] e^{-\sqrt{8\epsilon}r}$. We have to point out that the distribution $\rho_0^{(1)}(r)$ is a known rigorous lower bound for the one-particle density for any value of the position r [11] and $\rho_0^{(2)}(r)$ behaves asymptotically as the exact density (through the ionization potential). In fact there is a lower bound to the effective atomic potential in terms of the nuclear charge and the ionization potential [11],

$$V_{\text{eff}}(r) \geq -\frac{Z}{r} + \epsilon, \quad r \in (0, \infty). \quad (12)$$

To obtain the analytical approximation to the effective potential $V_{\text{eff}}(r)$, we only have to introduce the expression given by Eq. (9) in Eq. (5),

$$V_{\text{eff}}^{(n)}(r) = \sum_{i=1}^n \frac{b}{4r} \lambda_i \cos(k_i r) - \sum_{i=1}^n \lambda_i \frac{b - k_i^2 r}{4r^2 k_i} \sin(k_i r) + \frac{b^2}{8} - \frac{b}{2r} + \frac{1}{8} \left[\sum_{i=1}^n \frac{\lambda_i}{r} \left(\cos(k_i r) - \frac{\sin(k_i r)}{k_i r} \right) \right]^2, \quad (13)$$

where $b=2Z$ if we are using $\rho_0^{(1)}(r)$ as *a priori* density, or $b=\sqrt{8\epsilon}$ if we are using the second one $\rho_0^{(2)}(r)$.

Notice that this technique can also be applied to other N -particle systems for which we can obtain experimentally the spherically averaged form factor $F(k)$ using appropriate *a priori* information. In particular, it would be possible in molecular and nuclear systems.

Recently it has appeared in the literature (see Ref. [12], and references cited therein) a number of methods for the approximate reconstruction of effective potentials in one-particle systems starting with incomplete information for one-particle systems. These approximations for the effective potential are always of polynomial character so suffering the disadvantage that the potentials to approximate must be divergent as r goes to infinity.

In order to illustrate our method, we shall consider two ground-state neutral atoms, helium ($N=2$) and lithium ($N=3$). We have examined the approximate reconstruction of the effective potential that governs the motion of a single electron using as input data the values $\{F(k_i)\}_{i=0}^n$ for different values of n . The input values of $F(k_i)$ have been calculated by means of the accurate Roothaan-Hartree-Fock

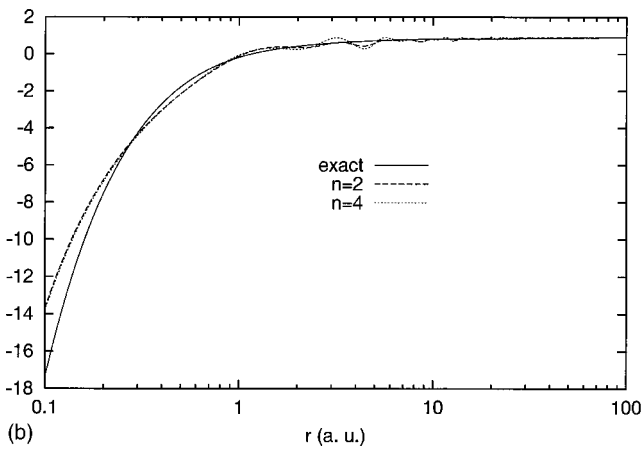
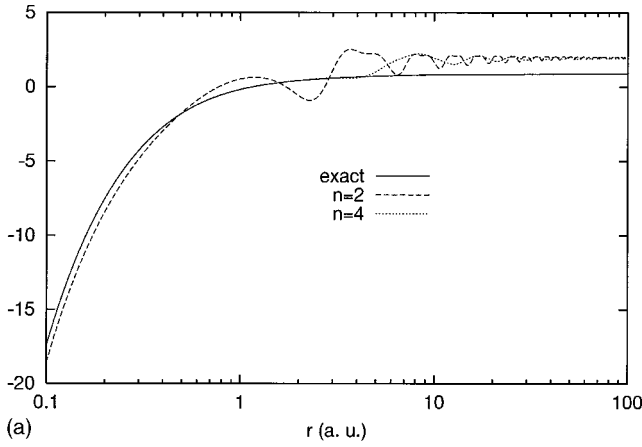


FIG. 1. Comparison between the exact (RHF) and approximated effective potentials for the ground-state helium ($Z=N=2$) using $F(k_i)$, $i=0, \dots, n$ with $n=2, 4$ and (a) $\rho_0^{(1)}(r)$ as the *a priori* information and (b) $\rho_0^{(2)}(r)$ as the *a priori* information. Atomic units are used.

(RHF) wave functions of Koga *et al.* [13]. We have used equidistant values of k ranging from 0 to 3 a.u., namely, $k_i = 3i/n$ for $i=0, \dots, n$.

In Figs. 1(a) and 2(a) we can see the good accuracy of the approximation $V_{\text{eff}}^{(n)}(r)$ (for helium with $n=2, 4$ and lithium with $n=2, 6$), when $r \rightarrow 0$. The reason is that in these cases we have introduced the *a priori* density $\rho_0^{(1)}(r)$ that takes into account the potential that governs the motion of an electron near the nucleus. In fact it is observed from Eq. (13) and the MacLaurin expansion of the approximate potential $V_{\text{eff}}^{(n)}(r)$ that $V_{\text{eff}}^{(n)}(r) \rightarrow -(Z/r)$ as $r \rightarrow 0$ for any n . We have compared with the exact effective potential in a RHF framework cited above. Equation (13) tells us the asymptotic behavior of $V_{\text{eff}}^{(n)}$ when we use $\rho_0^{(1)}(r)$, i.e., $b=2Z$; so that approximation is finite but it has not the ionization potential as its asymptotic value.

The behavior as $r \rightarrow \infty$ can be reproduced by introducing the *a priori* density $\rho_0^{(2)}(r)$; so in Eq. (13) we take $b = \sqrt{8}\epsilon$ (where we have used the RHF value of ϵ for each system [13]) and consequently $V_{\text{eff}}^{(n)}(r) \rightarrow \epsilon$ as $r \rightarrow \infty$ for any value of n . In Figs. 1(b) and 2(b) the approximation using $\rho_0^{(2)}(r)$ as a *a priori* density is exemplified for helium with n

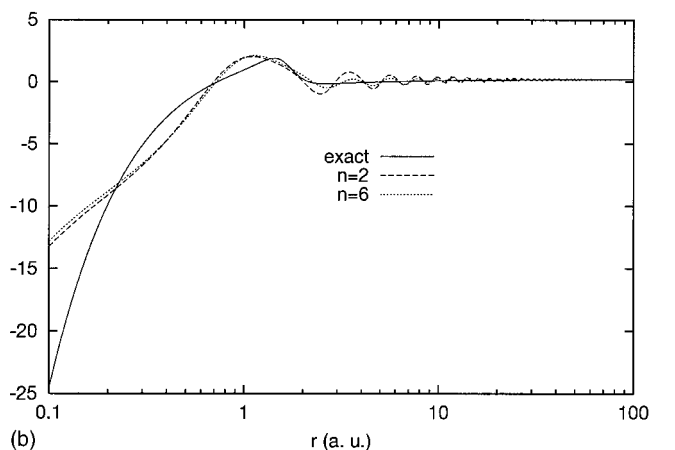
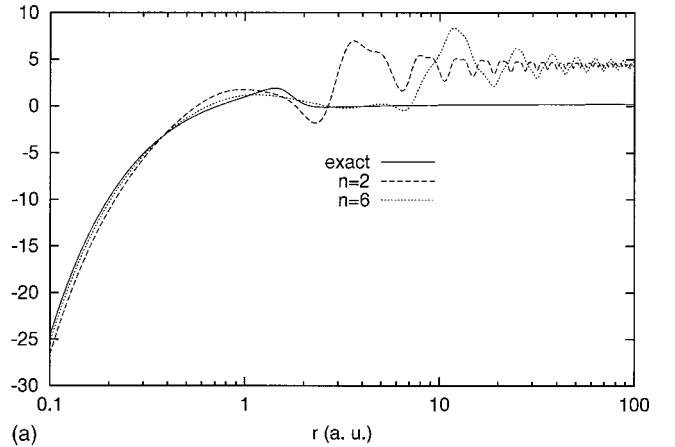


FIG. 2. Comparison between the exact (RHF) and approximated effective potentials for the ground-state lithium ($Z=N=3$) using $F(k_i)$, $i=0, \dots, n$ with $n=2, 6$ and (a) $\rho_0^{(1)}(r)$ as the *a priori* information and (b) $\rho_0^{(2)}(r)$ as the *a priori* information. Atomic units are used.

$n=2, 4$ and lithium with $n=2, 6$. In all these cases when we take into account more information, i.e. a greater value of n , the results improve. Here again we have compared with the exact effective potential calculated in a RHF framework.

In summary we have developed a universal method to obtain an analytical effective potential for N -particle systems from the experimental values of the form factor and an *a priori* density. This method uses the minimum cross-entropy technique, and it has the advantage of introducing *a priori* information of the system in study and of giving approximations that are bounded asymptotically. Furthermore, we have illustrated the applicability of the method by the explicit reconstruction of the ground-state density of two specific atomic systems (He, Li) within the RHF framework.

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