



# A Green's function quantum average atom model



C.E. Starrett

Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM, 87545, USA

## ARTICLE INFO

### Article history:

Received 23 March 2015

Received in revised form

20 April 2015

Accepted 6 May 2015

Available online 21 May 2015

### Keywords:

Average atom

Greens function

Warm dense matter

Dense plasmas

Density functional theory

## ABSTRACT

A quantum average atom model is reformulated using Green's functions. This allows integrals along the real energy axis to be deformed into the complex plane. The advantage being that sharp features such as resonances and bound states are broadened by a Lorentzian with a half-width chosen for numerical convenience. An implementation of this method therefore avoids numerically challenging resonance tracking and the search for weakly bound states, without changing the physical content or results of the model. A straightforward implementation results in up to a factor of 5 speed-up relative to an optimized orbital based code.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Average atom models are widely used to calculate equation of state [1–5] and other properties [6–11] of dense plasmas. They are density functional theory based models, and despite being less physically realistic than corresponding density functional theory molecular dynamics based methods [12–14], they are still very useful as they give a reasonable description of the plasma over a wide range of temperatures and densities and are much less computationally expensive.

Average atoms models come in a wide variety. They can be purely orbital free in character, for example using the Thomas-Fermi approximation [15], or use orbital based, Kohn-Sham density functional theory [1,4,10,16,17]. For a long time orbital based models had numerical problems due to the presence of narrow resonances in the continuum of free states. This led to erroneous discontinuities in the predicted pressure when resonance states occurred. Sophisticated algorithms were developed to track and accurately sample these resonances [2], resulting in a continuous prediction of pressure. These resonance trackers increase the computational cost and are complicated to program.

In this article we reformulate an orbital based average atom model in terms of the single-particle Green's function. The Green's function has a useful property that it is analytic in the upper half energy plane and has a non-negative imaginary part (i.e. the Hergoltz property). This means that integrals over energy along the real axis can instead be deformed into the complex energy plane, along any (numerically convenient) contour. The advantage to this is that

the Green's function lying along the real axis is broadened at complex energies by a Lorentzian of half-width equal to the imaginary part of the complex energy. Therefore any structures that need to be resolved for accurate real energy integrations, including narrow resonances, are broadened automatically in the complex plane. The contour integration over energy can therefore be easily evaluated without adaptive grids for resonance tracking.

As an added benefit, bound states are treated numerically in exactly the same way as continuum states in the Green's function approach. Along the real energy axis, the density of states (DOS) of a bound state is a Dirac delta function at the bound state eigenenergy, and a search algorithm must be used to find all bound states. In the complex plane the DOS becomes a continuous Lorentzian, so no search algorithm is necessary.

While this reformulation is interesting in its own right, for the reasons just discussed it also offers a significant numerical speed-up and a reduction in computational complexity, without changing the physical content or indeed the results. For clarity, let us repeat; the converged results from this Green's function approach are identical to the corresponding orbital based model (within numerical tolerance).

To our knowledge this is the first formulation and numerical evaluation of an average atom model in terms of Green's functions, though it has been noted previously that the average atom orbitals can be interpreted as spectral functions of the Green's functions [18]. However, the Green's function formulation of a 'single-center' problem and the use of complex energy integration is not new, and has been extensively used in solid-state physics for many decades

[19–21]. There it is part of a broader method known as Korringa-Kohn-Rostoker Green's Function (KKR-GF), which has recently found its first application in dense plasma physics [22].

The structure of this article is as follows: In section 2 we briefly review the average atom model that is used throughout this article to demonstrate the Green's function method. However the method is equally applicable to other Kohn-Sham based average atom models [1,2,10,11,23]. In section 3 we give the main equations for the Green's function formulation. We demonstrate the contour integration method and the broadening of resonances and bound states both theoretically and in a numerical example. In section 4 we give our conclusions. Two appendices are provided, discussing the calculation of wavefunctions and automatic contour generation.

## 2. Average atom physical model

In the present average atom model we consider a sphere of radius  $R$  (volume  $V$ ) containing an nucleus of charge  $Z$  at its center (the origin) and electrons of density  $n_e(\mathbf{r})$ . The sphere is charge neutral, i.e.

$$\int_V d\mathbf{r} n_e(\mathbf{r}) = Z \quad (1)$$

The non-relativistic Kohn-Sham Hamiltonian is

$$\mathcal{H}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V^{\text{eff}}(\mathbf{r}) \quad (2)$$

Here the effective interaction is given by

$$V^{\text{eff}}(\mathbf{r}) = \left( V^{\text{el}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r}) \right) e^2 \quad (3)$$

where the electrostatic part is

$$V^{\text{el}}(\mathbf{r}) = -\frac{Z}{r} + \int_V d\mathbf{r}' \frac{n_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

and the exchange and correlation part is

$$V^{\text{xc}}(\mathbf{r}) = \frac{\delta F^{\text{xc}}}{\delta n_e(\mathbf{r})} \quad (5)$$

For the exchange and correlation free energy  $F^{\text{xc}}$  we have used the finite temperature expression of [24]. By construction the potentials and electron densities are spherically symmetric.

In orbital based average atom calculations one solves the Schrödinger equation for the one-electron orbitals  $\psi_\epsilon(\mathbf{r})$  at energy  $\epsilon$ , and constructs the electron density with

$$n_e(r) = 2 \int_{-\infty}^{\infty} d\epsilon f(\epsilon) |\psi_\epsilon(\mathbf{r})|^2 \quad (6)$$

where  $f_\epsilon$  is the Fermi-Dirac occupation factor

$$f(\epsilon) = \frac{1}{\exp(\beta(\epsilon - \mu)) + 1} \quad (7)$$

and  $\beta = 1/(k_B T)$  is the inverse temperature.  $\mu$  is the ideal (non-interacting) contribution to the electronic chemical potential. The part of the integral in equation (6) from  $-\infty$  to 0 reduces to a finite summation over all bound states since their density of states are Dirac delta functions at their eigen-energies [25]. The integral from 0 to  $\infty$  is over the continuum of positive energy states.

The self-consistent procedure for solving these equations is as follows:

1. Start with an initial guess at the potential  $V^{\text{eff}}(r)$
2. Solve the Schrödinger equation for the orbitals  $\psi_\epsilon$ .
3. Construct an electron density from these orbitals (equation (6)) and vary  $\mu$  until charge neutrality is satisfied (equation (1))
4. Calculate a new potential from this electron density using equations (3)–(5)
5. Using a linear combination of the new and old potentials as a new guess for  $V^{\text{eff}}$ , iterate steps 2 through 4 until the new potential is the same as the old one to within a numerical tolerance.

Calculation of the electron density with equation (6) requires searching for bound states and accurately evaluating the integral over continuum states. The integrand for this latter can be highly structured and therefore require a large number of energy points and a sophisticated algorithm to make sure that sharp features are found and accurately resolved [2].

In the following section it is shown that the electron density can be evaluated using a Green's function approach which guarantees that structures in the continuum integration are smooth and slowly varying and moreover, ameliorates the search for bound states.

## 3. Green's function formulation

In terms of the one-electron Green's function  $G(\mathbf{r}, \mathbf{r}', z)$ , the spherically symmetric electron density is given by Ref. [21].

$$n_e(r) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{\infty} dz f(z) G(r, r, z) \quad (8)$$

where the integral over (complex) energy  $z$  is along the real axis,  $f(z)$  is the Fermi-Dirac occupation factor (equation (7)) and the Green's functions is given by

$$G(\mathbf{r}, \mathbf{r}', z) = -i p \sum_L R_l(r_<, z) H_l(r_>, z) Y_L(\mathbf{r}) Y_L^*(\mathbf{r}') \frac{4\pi\epsilon_0\hbar}{m_e e^4} \quad (9)$$

Here  $\mathbf{r}$  and  $\mathbf{r}'$  are spatial coordinates,  $p = \sqrt{(2m_e z / \hbar^2)}$  is the momentum,  $L = \{l, m\}$  is combined notation for the orbital angular momentum and magnetic quantum numbers,  $Y_L$  are the spherical harmonics, and  $r_{<(>)} = \min(\max)(r, r')$ .  $R_l(r) = P_l(r)/r$  and  $H_l(r) = I_l(r)/r$ , where  $P_l$  and  $I_l$  are the regular and irregular solutions of the radial Schrödinger equation (appendix Appendix: A)

$$\left[ -\frac{\hbar^2}{2m_e} \left( \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} \right) + V^{\text{eff}}(r) - z \right] \begin{Bmatrix} P_l(r) \\ I_l(r) \end{Bmatrix} = 0 \quad (10)$$

We note that since  $z$  is in general complex, so are  $P_l$  and  $I_l$ . The wave functions  $R_l$  and  $H_l$  are normalized such that for  $r \geq R$  they take the field free form, i.e.

$$R_l(r) = j_l(pr) - i p h_l^+(pr) t_l(p) \quad (11)$$

$$H_l(r) = h_l^+(pr) \quad (12)$$

where  $h^+ = j_l + i \eta_l$  is the spherical Hankel function,  $j_l$  is the spherical Bessel function and  $\eta_l$  is the spherical Neumann function.  $t_l$  is the so-called t-matrix element, defined in appendix Appendix: A. It is straightforward to show that the Green's function expression for the electron density (equation (8)) recovers the usual orbital

Download English Version:

<https://daneshyari.com/en/article/1772344>

Download Persian Version:

<https://daneshyari.com/article/1772344>

[Daneshyari.com](https://daneshyari.com)