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# Tartarus: A relativistic Green's function quantum average atom code

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ABSTRACT

A relativistic Green's Function quantum average atom model is implemented in the Tartarus code for the calculation of equation of state data in dense plasmas. We first present the relativistic extension of the quantum Green's Function average atom model described by Starrett [1]. The Green's Function approach addresses the numerical challenges arising from resonances in the continuum density of states without the need for resonance tracking algorithms or adaptive meshes, though there are still numerical challenges inherent to this algorithm. We discuss how these challenges are addressed in the Tartarus algorithm. The outputs of the calculation are shown in comparison to PIMC/DFT-MD simulations of the Principal Shock Hugoniot in Silicon. We also present the calculation of the Hugoniot for Silver coming from both the relativistic and nonrelativistic modes of the Tartarus code.



## 1. Introduction

There is a need for accurate calculation of equation of state (EOS) data for plasmas in a wide range of temperature and densities stemming from the study of astrophysical and laser generated plasmas. These dense plasmas exist at such high densities and temperatures that neither perturbative plasma or atomic physics approaches are able to fully describe the system. Average atom (AA) models attempt to account for the plasma environment while retaining a reasonable description of the electronic structure. These density functional theory based average atom models allow for the calculation of plasma thermodynamic properties at a wide range of temperature and density points without a large computational expense.

There are versions of AA models that do not account for the orbital nature of the electrons [2], but this lack of detail on the electronic structure leads to inaccuracies and loss of features in the resulting EOS calculations. AA models that account for orbital structure provide more physically accurate descriptions of the plasma but have long suffered from numerical challenges [3–7]. Chief among these difficulties has been the robust accounting for of resonance states in the continuum density of states. These so-called pressure ionized states are narrow in width and highly peaked, making them very important to the calculation of the electron structure. Robust and sophisticated algorithms have been developed to deal with these resonances by tracking their location and densely populating the integration grid in their vicinity [8].

In order to circumvent the numerical complexity and computational time added to fully treat the resonances in the continuum density of states, Starrett developed a nonrelativistic Green's function based AA model that utilizes the properties of Green's function to broaden any features in the density of states, which can include bound state features as well [1]. The need to carry out EOS calculations for heavy elements (high $Z$) requires a fully relativistic treatment of the electrons. In this paper, we outline the theory needed to transition from the nonrelativistic to the relativistic formalism and the numerical implementation of that model in the form of the Tartarus code. Though the main qualitative features of the model remain unchanged, the transition is not trivial. We especially focus on the details of the calculation of thermodynamic properties of the plasma using this formalism. Since the typical orbital approaches work well for higher angular momentum states where resonances do not occur, Tartarus uses a hybrid approach with the Green's function calculation applying to the lower angular momentum states where resonances are prevalent and orbital calculations used elsewhere.

As a means of validation, we present the consistency of the plasma pressure calculated by Tartarus via the virial theorem and numerical differentiation of the free energy. This shows the results are consistent with what has been seen in previous AA calculations [9]. Though Tartarus is able to quickly and robustly generate EOS data for a wide range of plasma species and conditions, the underlying AA model is not without approximations. More physically representative models use Kohn-Sham Density Functional Theory Molecular Dynamics (DFT-MD) to capture the electronic structure and ionic positions [10–12]. These methods lead to physically accurate results, but require simulations involving many separate atomic

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sites iterated over many time steps, with computational time scaling sharply with the temperature. This makes these calculations computationally expensive and unsuited for the generation of large sets of EOS data. Another high fidelity modeling approach is Path Integral Monte Carlo (PIMC) [13,14]. This method is also very expensive computationally, and computation time increases as temperature is lowered. These methods provide benchmark calculations with which to compare the results of less computationally expensive calculations. In the last part of the paper we show the comparison of a shock Hugoniot generated from a Tartarus EOS with simulations done using DFT-MD/PIMC calculations. This illustrates both the strengths and physical inaccuracies of the AA model. Tartarus in its current version is well tested for generating EOS data of plasmas ranging from 0.1 eV to 40,000 eV and for densities ranging from one-fifth of solid density to well over eight times solid density. Hartree atomic units ($\hbar = m_e = e = 1$) are used throughout the rest of the paper unless otherwise noted.

## 2. Theory

### 2.1. Average atom model and DKS-DFT orbitals

The average atom model as it is implemented in this work approximates the typical atom in a plasma with a sphere of radius $R = \left(\frac{3}{4\pi n_{ion}}\right)^{\frac{1}{3}}$ which defines the atomic sphere volume,$V$, where $n_{ion}$ is the ion number density of the plasma, and has at its center a nucleus of charge $Z$. Outside of the atomic sphere the effective potential seen by the electrons is zero. The sphere is required to be charge neutral.

Inside the sphere the electron density is determined using finite temperature relativistic density functional theory [15–17]. The Dirac–Kohn–Sham (DKS) electron orbitals are defined by

$$\hat{H}_D \vec{\psi}_\epsilon = \epsilon \vec{\psi}_\epsilon \tag{1}$$

where $\epsilon$ is the electron energy. The DKS–DFT Hamiltonian, $H_D$, is defined as

$$\hat{H}_D = \hat{T} + (\hat{\beta} - I_4)mc^2 + \hat{V}^{eff} \tag{2}$$

where $\hat{T}$ is the kinetic energy operator defined as

$$\hat{T} = c\vec{\alpha} \cdot \vec{p} \tag{3}$$

with

$$\alpha = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix} \tag{4}$$

Here $\vec{\sigma}$ are the Pauli matrices, $\vec{p}$ is the electron momentum, $I_j$ is the identity matrix of size $j$, $\hat{\beta}$ is defined as

$$\hat{\beta} = \begin{bmatrix} I_2 & 0 \\ 0 & -I_2 \end{bmatrix} \tag{5}$$

and $\hat{V}^{eff}$ is the effective DKS potential operator, $\hat{V}^{eff} = V^{eff}(\vec{r})I_4$, with $V^{eff}(\vec{r})$ defined as

$$V^{eff}(\vec{r}) = \left(V^{el}(\vec{r}) + V^{xc}(\vec{r})\right)e^2 \tag{6}$$

where the electrostatic part is

$$V^{el}(\vec{r}) = -\frac{Z}{r} + \int_V d\vec{r}' \frac{n_e(\vec{r}')}{|\vec{r} - \vec{r}'|} \tag{7}$$

and the exchange and correlation part is

$$V^{xc}(\vec{r}) = \frac{\delta F^{xc}}{\delta n_e(\vec{r})} \tag{8}$$

with $F^{xc}$ as the exchange and correlation free energy.

The DKS–DFT orbitals are vectors of size 4, commonly written as a two component vector,

$$\vec{\psi}_\epsilon = \begin{bmatrix} \vec{\psi}^A_\epsilon \\ \vec{\psi}^B_\epsilon \end{bmatrix} = \sum_{\kappa,m} \left[ g_\kappa(r,\epsilon)\vec{\chi}_{\kappa,m}(\hat{r}\,) i f_\kappa(r,\epsilon)\vec{\chi}_{-\kappa,m}(\hat{r}\,) \right] \tag{9}$$

where $\kappa$ is the relativistic angular momentum quantum number, $m$ is an index representing both the magnetic and spin quantum numbers, $\vec{\chi}_{\kappa,m}(\Omega)$ are the well known spherical spinors, $\vec{\psi}^A_\epsilon$ and $\vec{\psi}^B_\epsilon$ are the big and small components of the wavefunction, respectively, and $g_\kappa$ and $f_\kappa$ are the big and small components of the radial wavefunction, respectively, which are the solutions to the radial Dirac equations:

$$\begin{aligned} &[\epsilon - V^{eff}(r)]g_\kappa(r) + \hbar c \frac{1}{r}\left\{\frac{d}{dr} - \frac{\kappa}{r}\right\}(rf_\kappa) = 0 \\ &-\hbar c \frac{1}{r}\left\{\frac{d}{dr} + \frac{\kappa}{r}\right\}\left(rg_\kappa(r)\right) + [\epsilon - V^{eff}(r) + 2mc^2]f_\kappa(r) = 0 \end{aligned} \tag{10}$$

We can take advantage of the spherical symmetry in the model to analytically reduce the calculations of interest. In the orbital formalism, the radial electron number density can then be expressed as [8]

$$n_e(r) = \int_{-\infty}^{\infty} d\epsilon f(\epsilon,\mu) \sum_\kappa 2|\kappa|[g^2_\kappa(r,\epsilon) + f^2_\kappa(r,\epsilon)] \tag{11}$$

where $f(\epsilon,\mu)$ is the Fermi-Dirac occupation factor with chemical potential $\mu$, and the integral from $-\infty$ to 0 reduces to a summation over the discrete bound states.

In order to solve Eqs. 1–11, we use a self-consistent field (SCF) scheme. This requires repeated evaluation of the electron density, which consists of integration over the continuum energy spectrum as well as a search for bound states at negative energies. For an orbital based calculation, this requires resonance tracking for continuum states and a dense energy grid in order to resolve sharp features in the integrand, adding considerable computational time and complexity to the calculation. The GF approach avoids this burden by ensuring that the functions to be integrated are smooth and vary slowly in energy. Surprisingly, the integrals can be extended to negative energies, thus including bound states, with the integrand remaining smooth.

### 2.2. Green's function formalism

The transition to the Green's Function formalism in the average atom model is straightforward. The SCF procedure remains unchanged, but now the electron density is calculated via the GF by

$$n_e(r) = -\frac{1}{\pi}\Im \int_{-\infty}^{\infty} dz f(z,\mu) Tr G(r,r,z) \tag{12}$$

where $z = \epsilon + i\gamma$ is the complex energy (with $\gamma = 0$ for the integration in Eq. 12), $Tr$ denotes the trace operation, and $G(r, r, z)$ is the single-site, one-electron Green's function with spherical symmetry already applied. This is exactly the same expression as is used in the nonrelativistic formalism [1], and only the form of the GF changes for the relativistic model. The spherically symmetric trace of the relativistic GF can be written as

$$\begin{aligned} &Tr G(r,r,z) = -ip\left(1 + \frac{z}{2mc^2}\right) \\ &\times \textstyle\sum_\kappa \frac{2|\kappa|}{4\pi}[g^R_\kappa(r)g^I_\kappa(r) + f^R_\kappa(r)f^I_\kappa(r)] \end{aligned} \tag{13}$$

where $p = \sqrt{2z\left(1 + \frac{z}{2mc^2}\right)}$ is the magnitude of the momentum and the superscripts $R$ and $I$ refer to the regular and irregular solutions of the radial Dirac–Kohn–Sham equations, respectively, and the, in general complex, energy dependence of the solutions is left implicit. The regular solution is obtained by integrating outward from the origin and diverges at infinity, whereas the irregular