

Computational Assignment: Modified Hartree Approximation in Solving Closed-Shell Atoms

Course: Phys 5400
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Objective and Methods

Primary goal: To numerically calculate bound electronic state energies and eigenfunctions in selected atoms (He, Ne, Mg and Ar) by employing the modified Hartree approximation.

Deliverables: energies (and comparison with book values and experiment values), selected radial wavefunctions, effective potential.

Physical Model

To solve the closed-shell atom electronic states, we refer to the Hartree-Fock method as described in the textbook [1], where the general mean-field eigenequation

$$\sum_{\delta} \left\{ \langle \alpha | \hat{T} | \delta \rangle + \langle \alpha | \hat{U}_{\text{ext}} | \delta \rangle + \sum_{\mu\nu} \langle \alpha \mu | \hat{V} | \delta \nu \rangle n_{\mu\nu}^{\text{HF}} \right\} z_{\delta}^n = \varepsilon_n z_{\alpha}^n \quad (1)$$

becomes, in the atomic case,

$$\begin{aligned} \varepsilon_n \phi_n(\mathbf{r}, m_s) = & -\frac{\hbar^2}{2m} \nabla^2 \phi_n(\mathbf{r}, m_s) + U_{\text{ext}}(r) \phi_n(\mathbf{r}, m_s) + \underbrace{\left[\int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \sum_{m'_s} n^{\text{HF}}(\mathbf{r}' m'_s, \mathbf{r}' m'_s) \right]}_{v_H(\mathbf{r})} \phi_n(\mathbf{r}, m_s) \\ & - \underbrace{\sum_{m'_s} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') n^{\text{HF}}(\mathbf{r}' m'_s, \mathbf{r} m_s) \phi_n(\mathbf{r}', m'_s)}_{\hat{v}_F \phi_n(\mathbf{r}, m_s)}. \end{aligned} \quad (2)$$

For this assignment, the modified Hartree is employed, where the last term (exchange) of Eq. (2) is neglected. Since the exchange term contains a negative term that exactly cancels the part of v_H coming from the orbital's own density, thus implying Pauli exclusion, we can modify v_H trivially by removing that term to approximate the full HF. It then can be shown that we can completely separate the radial components from the problem and that

$$v_H(r) = 4\pi \sum_{n\ell} \int_0^\infty dr' r'^2 \frac{n_{n\ell}^{\text{HF}}(r')}{\max(r, r')}, \quad n_{n\ell}^{\text{HF}}(r) = \frac{1}{4\pi} 2(2\ell + 1) \phi_{n\ell}^2(r). \quad (3)$$

We then modify v_H by removing the contribution from one electron in the subshell of interest, yielding

$$v_{n\ell}^{\text{MH}}(r) = v_H(r) - 4\pi \frac{1}{2(2\ell + 1)} \int_0^\infty dr' r'^2 \frac{n_{n\ell}^{\text{HF}}(r')}{\max(r, r')} \quad (4)$$

Combining the kinetic energy, the nuclear Coulomb potential and the spherically symmetric modified Hartree potential, the radial modified Hartree equation for each subshell (n, ℓ) is

$$\varepsilon_{n\ell} \phi_{n\ell}(r) = \left\{ -\frac{1}{2} \left[\frac{1}{r} \frac{d^2}{dr^2} (r \cdot) - \frac{\ell(\ell + 1)}{r^2} \right] - \frac{Z}{r} + v_{n\ell}^{\text{MH}}(r) \right\} \phi_{n\ell}(r). \quad (5)$$

This equation is solved self-consistently. We begin with an initial approximation to the orbitals $\{\phi_{n\ell}(r)\}$, for example hydrogenic functions. From these we construct the radial density $n_{n\ell}^{\text{HF}}(r)$ and the corresponding modified Hartree potential $v_{n\ell}^{\text{MH}}(r)$, with which we solve Eq.(5) for a new set of orbitals and eigenvalues $\{\phi_{n\ell}^{\text{new}}, \varepsilon_{n\ell}^{\text{new}}\}$, enforce normalization and orthogonality, and then recompute the density and the potentials, etc. The cycle is repeated until the orbitals and eigenvalues no longer change within a prescribed tolerance.

Computational Methods

Solution of eigenvalues. A logarithmic radial grid is used. Following the book, we introduce

$$u = \ln r, \quad r = e^u, \quad h_{n\ell}(u) = r^{3/2} \phi_{n\ell}(r), \quad (6)$$

yielding

$$\varepsilon_{n\ell} h_{n\ell}(u) = \left\{ -\frac{1}{2} \left[\frac{1}{r} \frac{d^2}{du^2} \frac{1}{r} - \frac{(\ell + \frac{1}{2})^2}{r^2} \right] - \frac{Z}{r} + v_{n\ell}^{\text{MH}}(u) \right\} h_{n\ell}(u). \quad (7)$$

A uniform grid of u is placed on $[u_{\min}, u_{\max}]$ where $e^{u_{\min}} \approx 0$, $u_i = i \Delta u$, $i = 0, \dots, N-1$ with $\Delta u = u_{\max}/(N-1)$, and enforce Dirichlet endpoints by solving only on the interior points $i = 1, \dots, N-2$. The second derivative is approximated by the standard three-point finite-difference formula, so that the kinetic operator is a tridiagonal matrix. This together with the diagonal potential terms yields the symmetric tridiagonal $(N-2) \times (N-2)$ Hamiltonian H . The resulting eigenvalue problem is solved using the **Eigen** C++ library. The function **Eigen::SelfAdjointEigenSolver** returns all eigenvalues and eigenvectors; to pick up the subshell (n, ℓ) in interest, the number of nodes is counted (the desired number being $(n - \ell - 1)$).

Normalization. The orbital is normalized such that $\int_{-\infty}^{\infty} |h_{n\ell}(u)|^2 du = 1$. Then the reduced eigenfunction is transformed back to the physical radial wavefunction $\phi_{n\ell}(r_i) = \frac{h_{n\ell}(u_i)}{r_i^{3/2}}$, which is then used to construct $v_{n\ell}^{\text{MH}}(u)$ for the next cycle.

Self-Consistency Algorithm. (1) *Initial guess.* We use an approximation to the hydrogenic polynomials for each subshell (n, ℓ) as the initial guess,

$$\phi_{n\ell}^{\text{initial}}(r) \propto r^\ell \exp\left(-\frac{Z}{n} r\right) \quad (8)$$

which is normalized and used to calculate Hartree potentials for the first iteration.

(2) *Calculation of $v_{n\ell}^{\text{MH}}(u)$:* The integral in Eq.(4) is calculated using a simple trapezoidal rule. However, during testing runs, simply updating $v_{n\ell}^{\text{MH}}(u)$ as the calculated result caused the error where the system cycles between 2 or among 3 points instead of converging. To stabilize the SCF cycle, $v_{n\ell}^{\text{MH}}(u)$ are updated using a linear mixing, such that at iteration p

$$v_{n\ell}^{\text{MH},(p)}(u) \rightarrow (1 - \alpha) v_{n\ell}^{\text{MH},(p-1)}(u) + \alpha v_{n\ell}^{\text{MH},(p)}(u), \quad (9)$$

where α is chosen to be equal to 0.3.

(3) *Convergence criterion.* The maximum change of the orbital energies between successive iterations is monitored in every iteration:

$$\Delta\varepsilon^{(p)} = \max_{n,\ell} |\varepsilon_{n\ell}^{(p)} - \varepsilon_{n\ell}^{(p-1)}|. \quad (10)$$

The SCF cycle is terminated when $\Delta\varepsilon^{(p)} \leq 10^{-8}$ Ha.

Energies & Wavefunctions. For each atom, energies $\varepsilon_{n\ell}$ are reported in Hartrees and compared to the values given in the textbook. For plotting the wavefunctions, it is convenient to work with the reduced radial functions $u_{n\ell}(r) = r \phi_{n\ell}(r) = \frac{h_{n\ell}(u_i)}{\sqrt{r_i}}$ on the interval $r_{\min} \leq r \leq r_{\max}$. To assess the quality of the modified-Hartree orbitals we compare them to high-accuracy Hartree-Fock reference orbitals from the Roothaan-HF parametrization of Bunge *et al.* [2] In that work, each atomic subshell (n, ℓ) is represented as a linear combination of normalized Slater-type orbitals (STOs),

$$R_{n\ell}^{(\text{Bunge})}(r) = \sum_j C_{j\ell} S_{j\ell}(r), \quad S_{j\ell}(r) = N_{j\ell} r^{n_{j\ell}-1} e^{-Z_{j\ell} r}, \quad (11)$$

with tabulated exponents $Z_{j\ell}$, integers $n_{j\ell}$, coefficients $C_{j\ell}$, and normalization constants $N_{j\ell} = (2Z_{j\ell})^{n_{j\ell}+1/2} / \sqrt{(2n_{j\ell})!}$.

Results

The simulation was conducted serially via the code **run.cpp** in the project repository. $N = 1500$, $u_{\min} = -8.0$, $u_{\max} = 6.0$. Atoms He, Ne, Mg and Ar are tested.

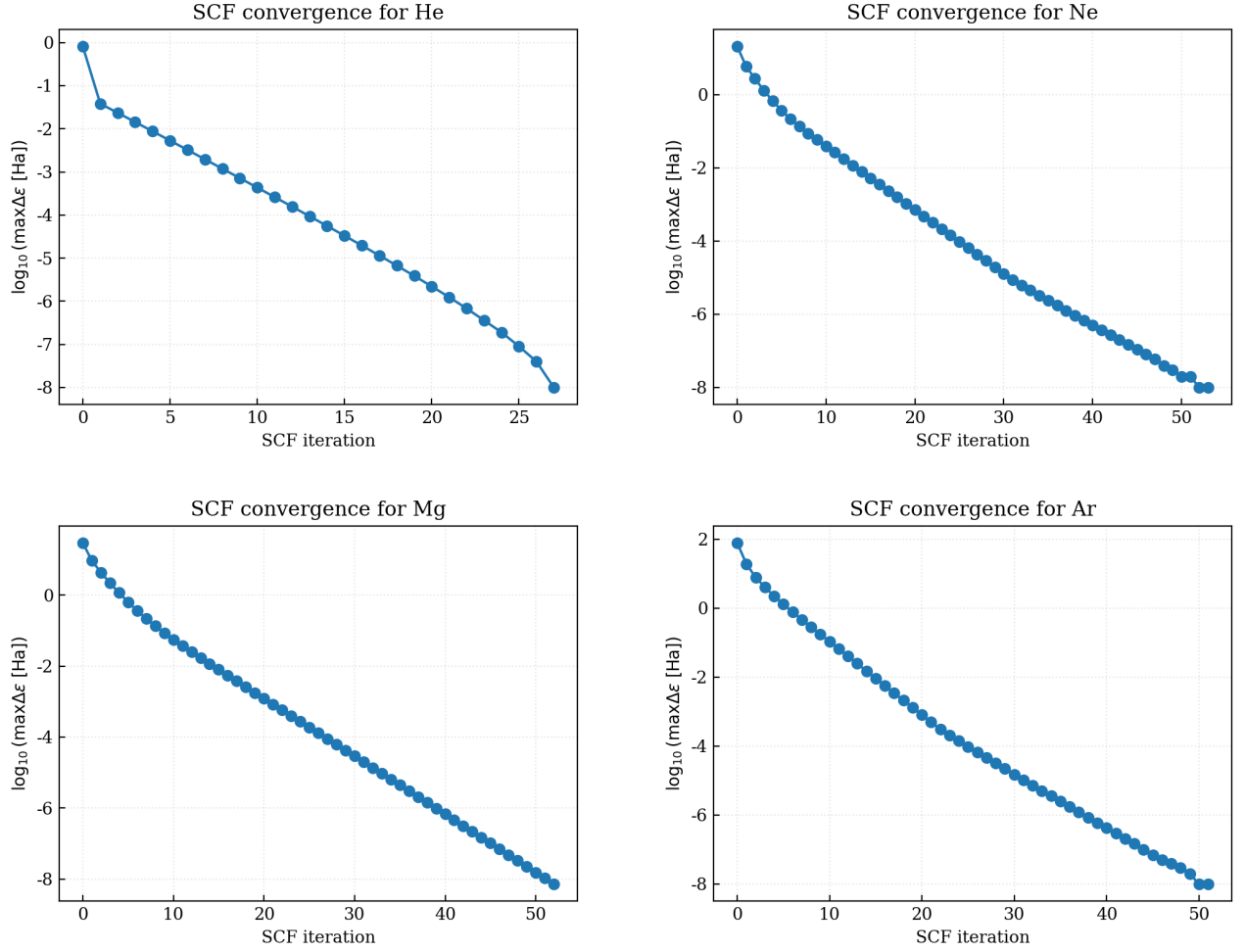


Figure 1: Convergence history (logarithmic) of the modified Hartree self-consistency for He, Ne, Mg and Ar atoms.

Atom	Orbital	This work	HF (Textbook)	Experiment
He	1s	-0.9156	-0.918	-0.9040
Ne	1s	-32.44	-32.77	-31.70
	2s	-1.400	-1.930	-1.782
	2p	-0.629	-0.850	-0.793
Mg	1s	-48.188	-49.03	-47.91
	2s	-2.977	-3.768	-3.26
	2p	-1.936	-2.283	-1.81
	3s	-0.230	-0.253	-0.2811
Ar	1s	-115.28	-118.6	-117.87
	2s	-10.86	-12.32	-12.00
	2p	-8.962	-9.571	-9.160
	3s	-0.9253	-1.277	-1.075
	3p	-0.420	-0.591	-0.579

Table 1: Removal energies (in a.u.) comparing this work with HF values from the book and experiment.

SCF convergence. Figure 1 shows the evolution of the SCF residual $\log_{10}(\max \Delta \epsilon)$ for He, Ne, Mg and Ar. All four systems exhibit a smooth, almost straight line on the logarithmic scale, corresponding to a geometric convergence. All atoms require at most 53 iterations to reach the same criterion without divergent behavior, showing that the simple linear mixing algorithm of the effective potentials with $\alpha = 0.3$ is reasonable.

Orbital energies. Overall, the algorithm successfully reproduces the gross shell structure and the ordering of

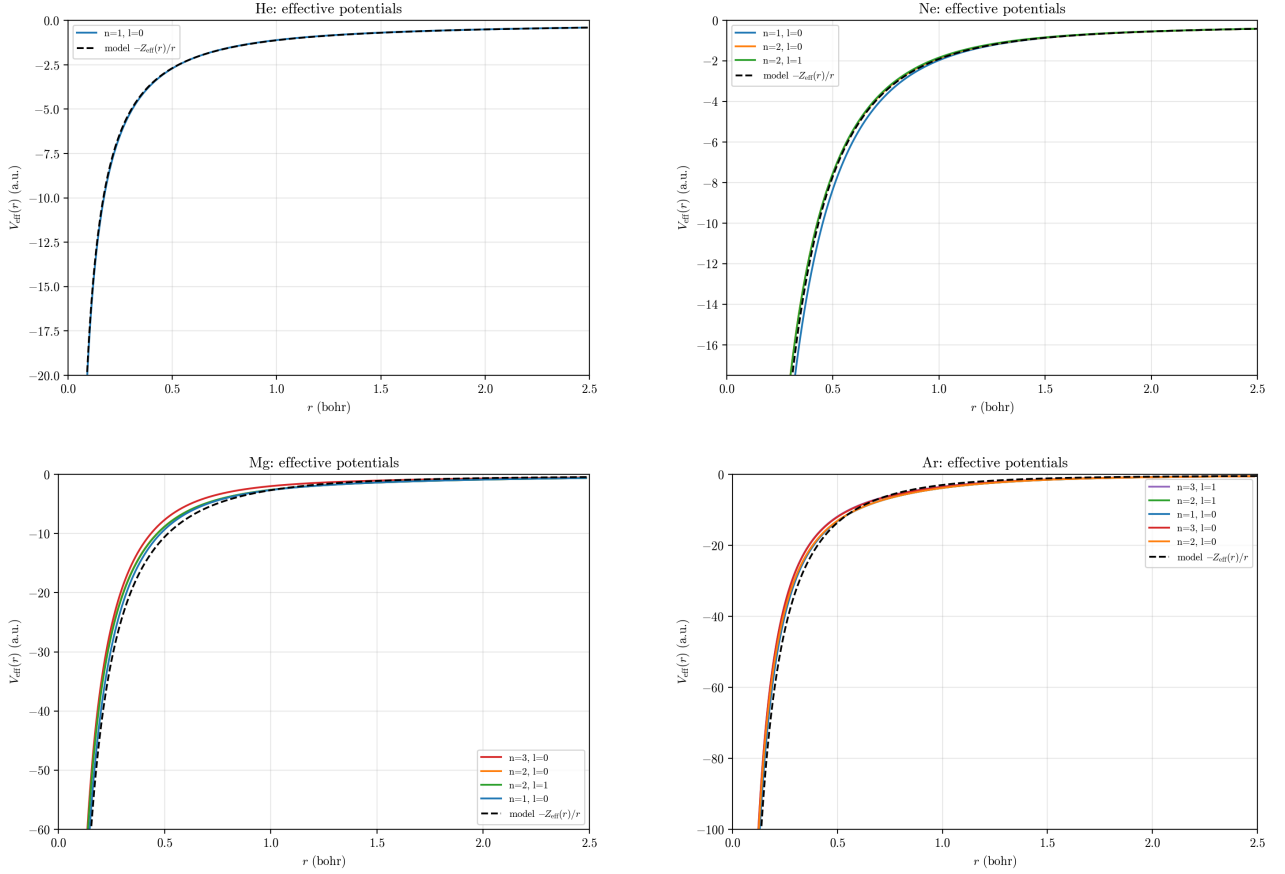


Figure 2: Effective potentials of the subshells of He, Ne, Mg and Ar atoms, compared to the simple exponentially mixed potentials obtained from the last assignment.

subshell energies (Table 1). For the innermost $1s$ orbitals the agreement is usually good. In He the calculated $1s$ energy differs from the HF reference by less than 0.3% and by about 1% from the experimental value. The $1s$ energies for Ne, Mg and Ar yielded errors of a few percent. This is largely because screening effects are small for these core orbitals and thus that the modified Hartree potential captures most of the mean field. For the more weakly bound $2s$, $2p$, $3s$ and $3p$ orbitals, our energies are less negative than the HF values and, generally, the experiment values as well. By neglecting the Fock term, the effective potential of the modified Hartree is less attractive than the full HF potential and therefore leads to less bound energies than the full HF. Interestingly, since the full HF energies are usually more bound than experiment because of the neglected correlation and relaxation effects, the modified Hartree energies are fortuitously balanced and not so far from the experiment values.

Effective potentials. Figure 2 shows the resulting self-consistent effective potentials $-\frac{Z}{r} + v_{n\ell}^{\text{MH}}(r)$ for each subshell, compared to the simple model potential $-[1 + (Z - 1)e^{-r/r_0}]/r$ with r_0 unchanged up to atoms as used in the previous assignment. For He, the modified Hartree potential aligns well with the simple exponential model. For Ne, Mg and Ar, it can be seen that the less bound orbitals have potentials that are less attractive, especially in the intermediate region. However, both $r \rightarrow 0$ and $r \rightarrow \infty$ regimes align with the simple exponential, consistent with the assumption that the potential goes to $-Z/r$ and $-1/r$ at these two limits respectively.

Radial wavefunctions. Figure 3 compares the reduced radial functions $u_{n\ell}(r) = r\phi_{n\ell}(r)$ obtained from the modified-Hartree calculation with the high-accuracy Roothaan-HF reference orbitals of Bunge *et al.* For all atoms the overall shapes and node structures are reproduced correctly: each subshell (n, ℓ) has the correct number of radial nodes $k = n - \ell - 1$, and the positions of maxima and nodes for the inner shells match the reference curves very well.

In summary, the modified-Hartree approximation used here provides a computationally simple, fully local model that reproduces the qualitative shell structure, effective potentials and radial wavefunctions of He, Ne, Mg and Ar, and yields somewhat accurate energies for core orbitals.

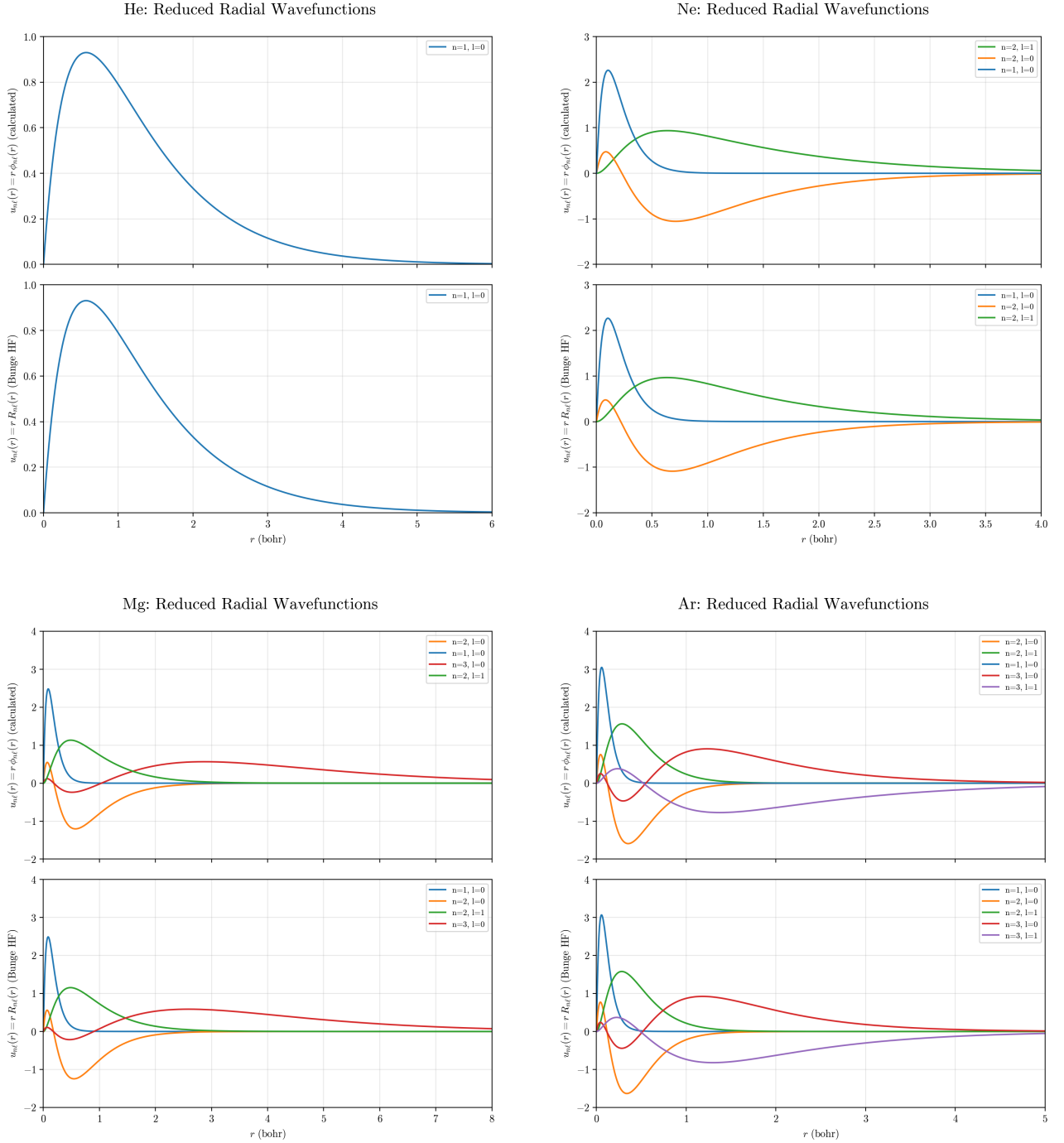


Figure 3: Reduced radial wavefunctions of the subshells of He, Ne, Mg and Ar atoms.

All code used in this project is available in the following GitHub repository:

https://github.com/Lihao-Liu2014/Modified_Hartree

References

- [1] Willem H. Dickhoff and Dimitri Van Neck. *Many-Body Theory Exposed!: Propagator Description of Quantum Mechanics in Many-Body Systems*. World Scientific, Singapore, 2 edition, 2008.
- [2] C. F. Bunge, J. A. Barrientos, and A. V. Bunge. Roothaan-hartree-fock ground-state atomic wave functions: Slater-type orbital expansions and expectation values for $z = 2-54$. *Atomic Data and Nuclear Data Tables*, 53:113–162, 1993.