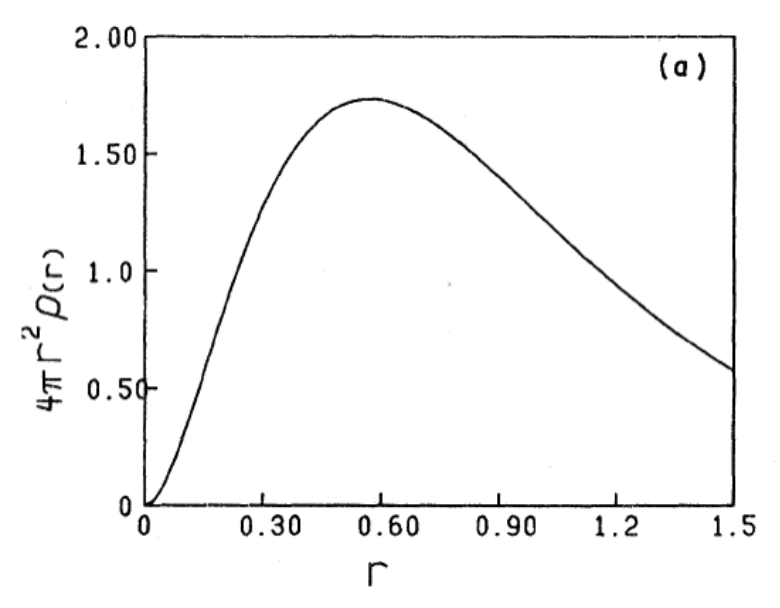
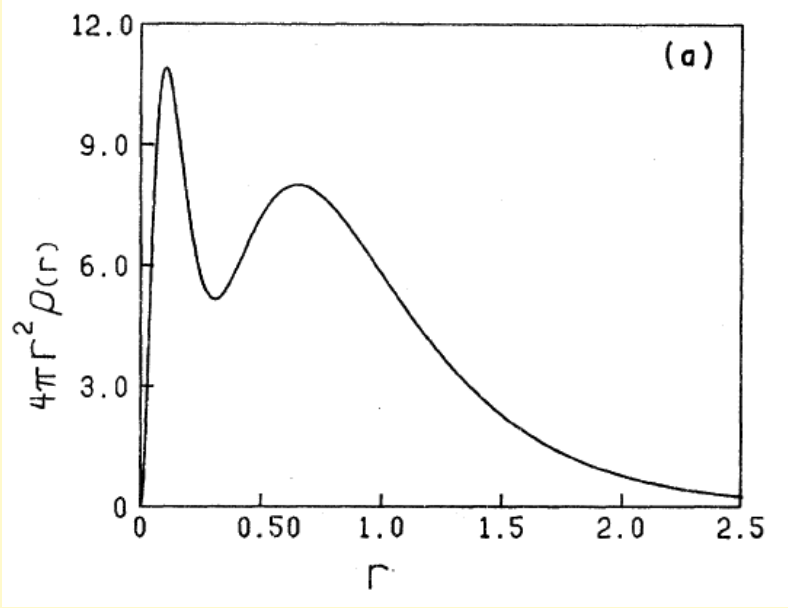
Atomic Hartree-Fock calculations: radial densities of noble gas atoms reveal shell structure

Ref: Wen-Ping Wang and Robert G. Parr, Phys. Rev. A 16 (1977) 891

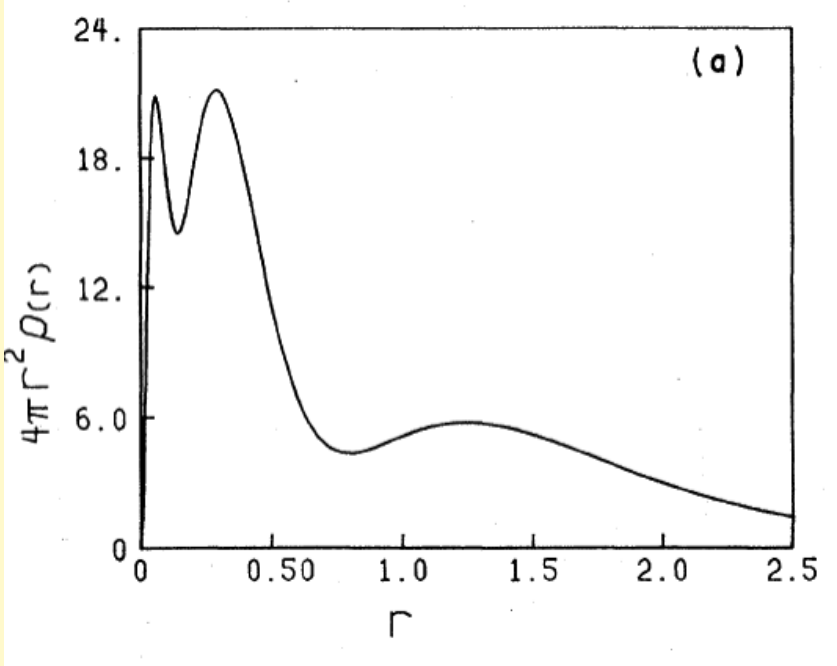


Helium (Z=2)
first shell filled

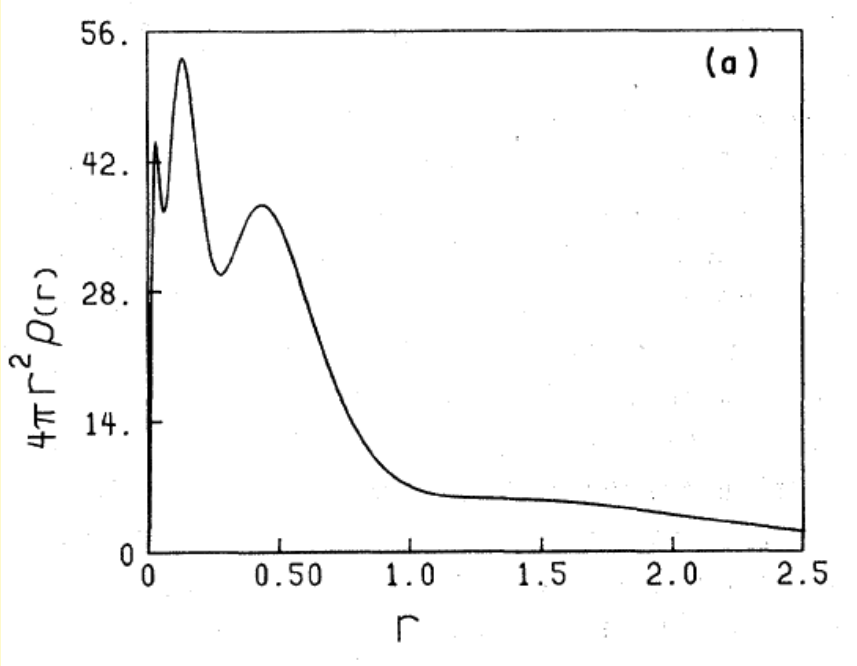


Neon (Z=10)
second shell filled

Atomic HF: radial densities reveal shell structure

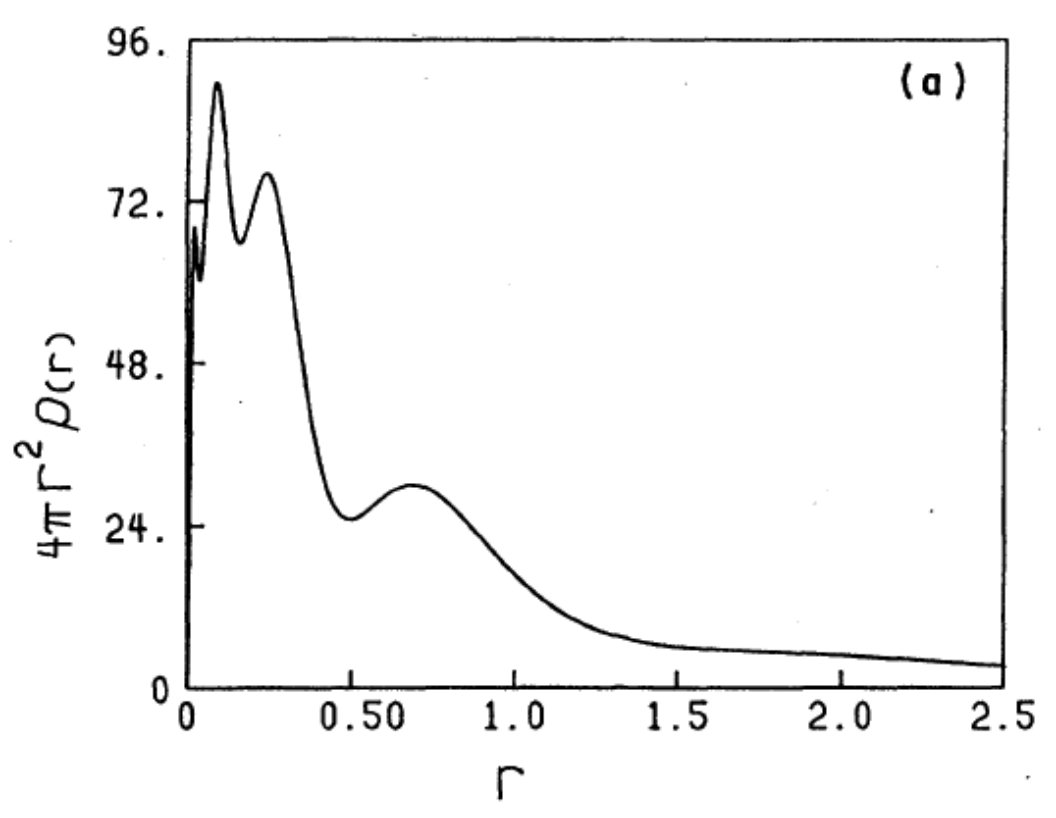


Argon (Z=18)
third shell filled



Krypton (Z=36)
fourth shell filled

Atomic HF: radial densities reveal shell structure



Xenon (Z=54)
fifth shell filled

Improved visualization of atomic shell structure
suggested topic for term paper!

The following paper describes electron localization in atoms and molecules, based on the pair correlation function for fermions:

A. D. Becke and K. E. Edgecombe, J. Chem. Phys., Vol. 92. No.9 (1990), p. 5397-5403

Multiconfiguration Hartree-Fock (MCHF)

Many-body wave function
= superposition of
several hundred
Slater determinants

Textbook:
Computational atomic structure: an MCHF approach

Charlotte Froese Fischer (Vanderbilt University, Prof. Emerita)
Tomas Brage (Lund University, Sweden)
Per Jönsson (Lund University, Sweden)

Atomic physics: relativistic effects
MCDF (multiconfiguration Dirac-Fock)

Instead of solving the many-body non-relativistic Schrödinger equation, one has to solve the many-body Dirac equation for spin-1/2 fermions.

This is important for heavier atoms, because the inner-shell electrons move at relativistic speeds.

Atomic structure calculations (MCHF / MCDF)

Calculate atomic properties

energy levels, binding energies, transition probabilities, lifetimes, hyperfine structure, isotope shifts, and photo-ionization cross sections.

Theoretical and computational approach

- MCHF (multiconfiguration Hartree-Fock): non-relativistic theory, add low-order relativistic corrections
- MCDF (multiconfiguration Dirac-Fock): fully relativistic Dirac-Fock theory including Breit and quantum electrodynamics corrections.
- matrix eigenvalue problem, use Davidson algorithm for finding a few selected eigenvalues of the sparse symmetric interaction matrix. Algorithm relies primarily on matrix-vector multiplication, parallelization using MPI (Message Passing Interface)

Applications

- plasma diagnostics (properties of ionized atoms)
- astrophysics (iron abundance in supernovae → information on nucleosynthesis and galactic chemical evolution).

MCHF for beryllium atom; comparison with experiment

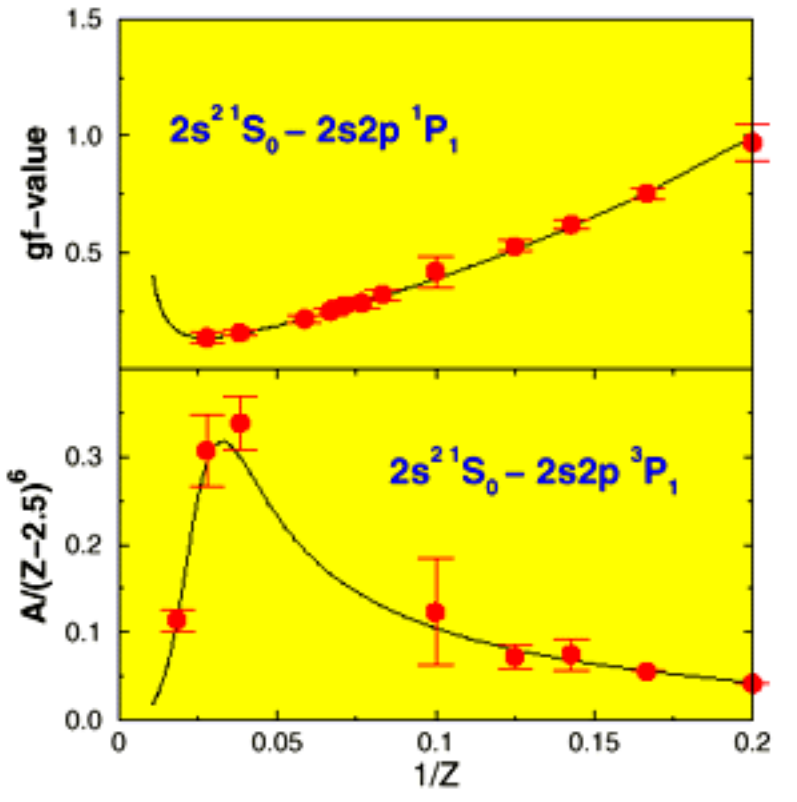
Table 5.9. Frozen-core MCHF results for binding energies (in cm^{-1}) for members of the $2snd\ ^3D$ Rydberg series of beryllium. The limit energy ($E = -14.2773948$ au) is taken as from a Hartree–Fock calculation for $2s\ ^2S$ of Be^+.

	Binding energies			
Term	Hydrogen[a]	HF	MCHF	Experiment
3*d*	12192.1	12453.3	13142.4	13138.35[b]
4*d*	6858.0	6996.9	7251.5	7250.41[b]
5*d*	4389.1	4466.2	4589.0	4588.31[b]
6*d*	3048.0	3094.3	3163.1	3162.57[b]
7*d*	2239.4	2269.1	2311.4	2311.17[c]
8*d*	1714.5	1734.7	1762.8	1762.74[c]
9*d*	1354.7	1369.0	1388.5	1389.5[b]
10*d*	1097.3	1107.8	1121.9	1122.1[b]
11*d*	906.8	914.8	925.4	924.0[b]

[a] Hydrogenic, $1/2n^2$, value.
[b] From Johansson (1962).
[c] From Holmström and Johansson (1969).

Atomic transitions: MCDF theory vs. experiment

Prof. C.F. Fischer (Vanderbilt): NERSC Annual report (1998)



Comparison of computationally predicted atomic transition data with experiment for four electron ions of nuclear charge Z, plotted against 1/Z. For the top graph, relativistic effects are small for $Z < 20$, but they are crucial for all Z in the bottom graph.