All-electron QMC

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Previous work/ motivation

- Many all-electron QMC studies for atoms up to neon (Z=10)
- Very few all-electron QMC studies for heavier atoms
- For heavy atoms, pseudopotentials are used.
- Is all-electron QMC for heavy atoms feasible?

Difficulties

- Presence of core electrons lead to:
  - Shorter length scale variations in the wave funtion near the nucleus
    - require small time step
  - Fluctuations in local energy tend to be large near the nucleus because both kinetic and potential energies are large
    - Fluctuations reduced by accurate trial wave functions

Our work

- Calculate total energies of noble gas atoms up to xenon (Z=54).
- Use VMC and DMC
- Study relativistic corrections to atomic energies using perturbation theory

Trial wave functions

- Trial wave function

$$\Psi(\boldsymbol{R}) = \mathrm{e}^{J(\boldsymbol{R})} D_{\uparrow}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\uparrow}}) D_{\downarrow}(\boldsymbol{r}_{N_{\uparrow}+1}, \ldots, \boldsymbol{r}_N)$$

- The slater determinant is formed from single-particle orbitals from HF calculations:
  - Numerical integration on a radial grid
  - Orbital expanded in a Gaussian basis set

Cusp conditions

- Constraints which have to be satisfied by the wave function when an electron approaches another electron or the nucleus.

$$\hat{H}_{oe} = -1/2\nabla^2 - Z/r$$

- Divergence at $r=0$ for the Coulombic term must be cancelled out
- Manten and Lüchow
  - 1*s* basis function interpolated to $a\exp(-br)+c$ near the nucleus
  - Constants fitted with least squares minimization

CASINO's cusp correction scheme (1)

- Idea: make the one-electron part of the local energy for each orbital finite at the nucleus
  - Inside some radius r_c, replace the orbital by

$$\phi = sgn[\psi(r=0)]e^p$$

where

$$p = \alpha_0 + \alpha_1 r + \alpha_2 r^2 + \alpha_3 r^3 + \alpha_4 r^4$$

  - The local energy is

$$E_L = \phi^{-1}\hat{H}_{oe}\phi = -\frac{p'}{r} - \frac{p''}{2} - \frac{p'^2}{2} - \frac{Z}{r}.$$

CASINO's cusp correction scheme (2)

- Impose constraints:
  - $p(r_c)$, $p'(r_c)$ and $p''(r_c)$ are continuous
  - $p'(0) = -Z$ (cusp condition)
  - $E_L(0) = \frac{-\alpha_1^2}{2} - 3\alpha_2$
- The quantity $E_L(r)/Z^2$ has similar behaviour for different *Z* in the range *r < 1.5/Z*, so an ideal curve is chosen

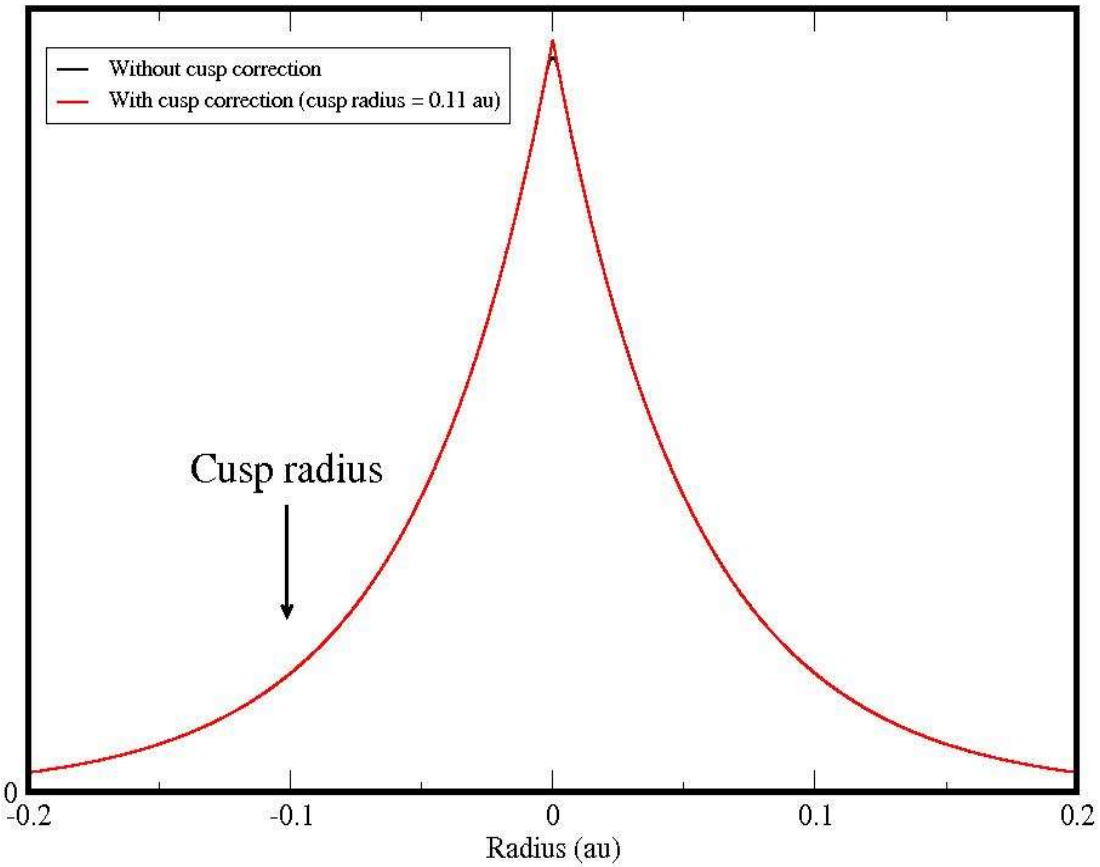
$$\frac{E_L^{\text{ideal}}(r)}{Z^2} = \beta_0 + \beta_1 r^2 + \beta_2 r^3 + \beta_3 r^4 + \beta_4 r^5 + \beta_5 r^6 + \beta_6 6 r^7 + \beta_7 r^8$$

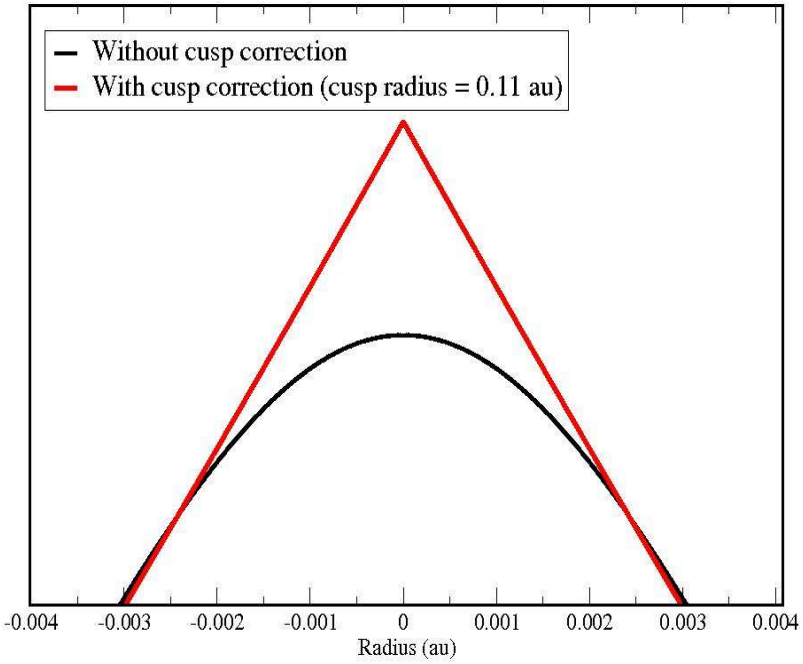
CASINO's cusp correction scheme (3)

- Vales of β's are determined
- β_0 chosen such that local energy is continuous at the cusp correction radius
- Choose cusp correction radius by a keyword, with the maximum radius being

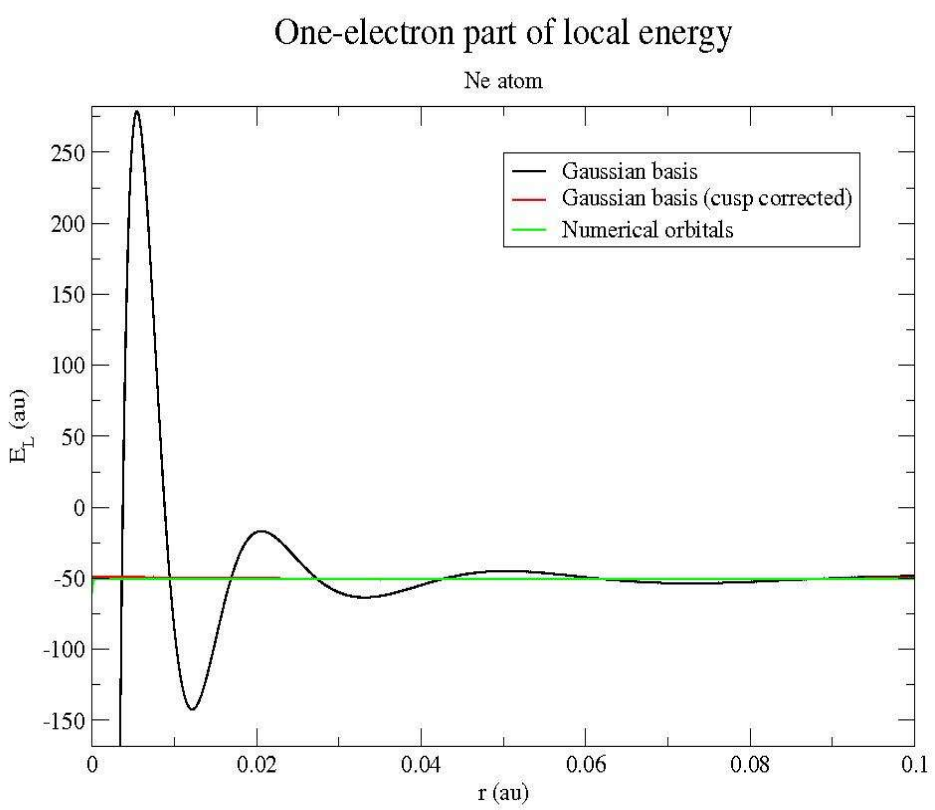
$$r_{c,max} = 1.5/Z$$

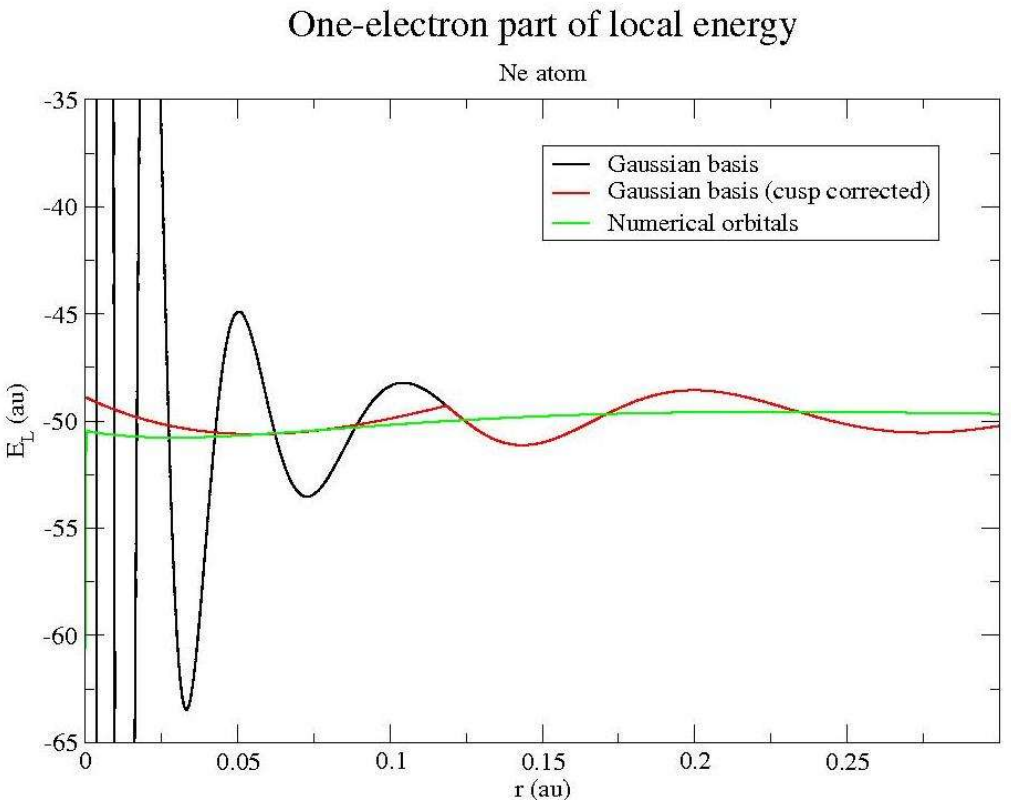
Cusp correction (1)



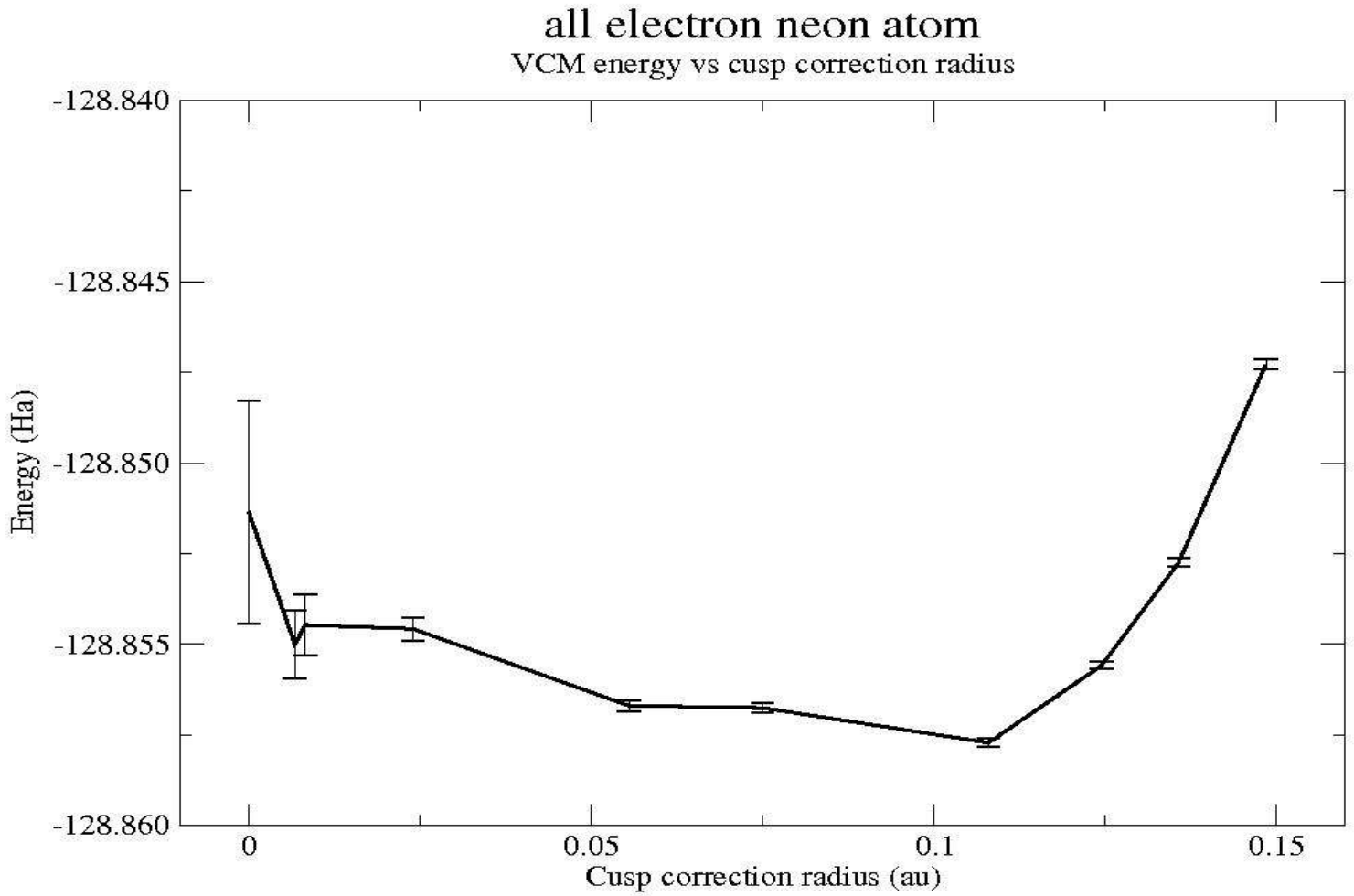


Cusp correction (2)

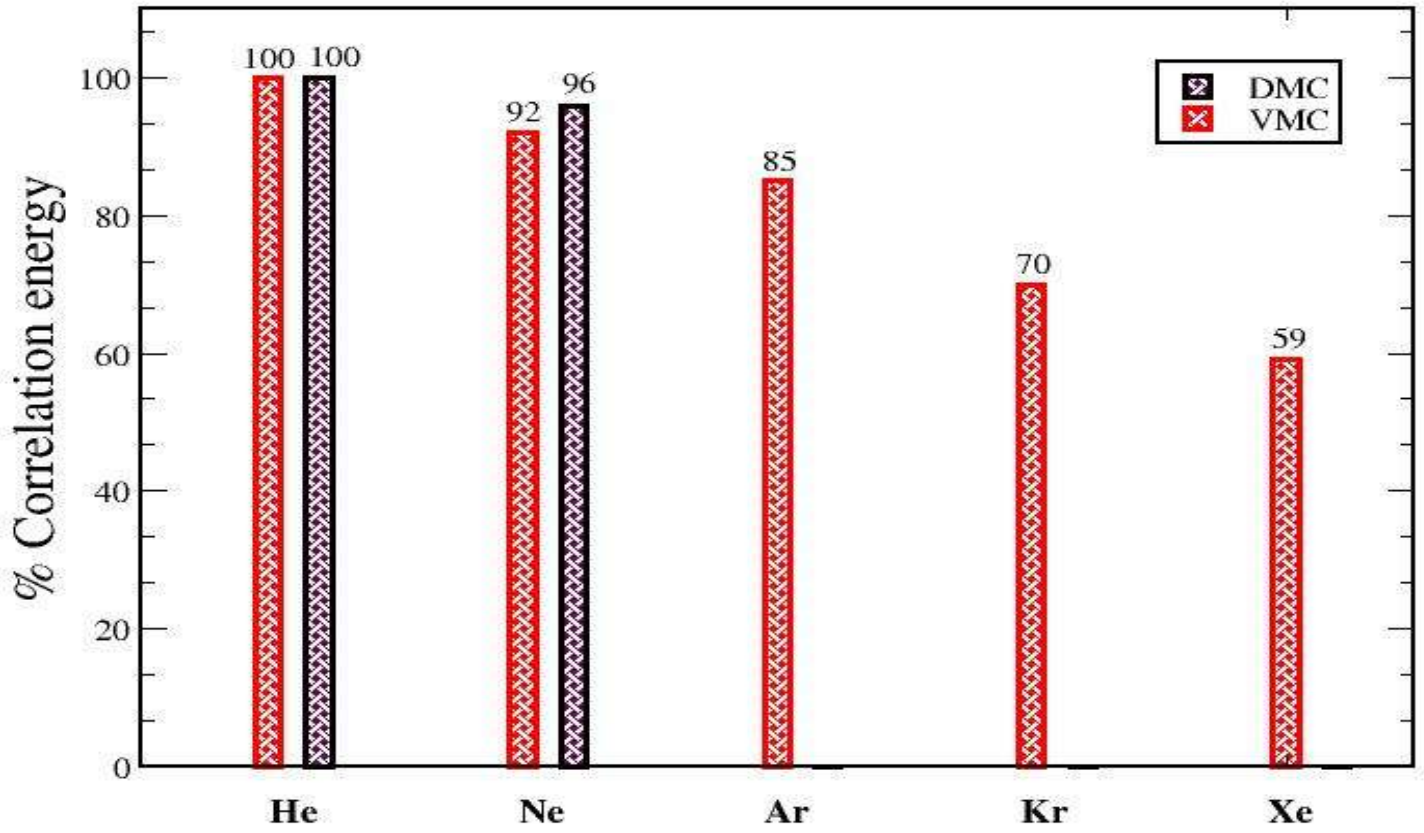




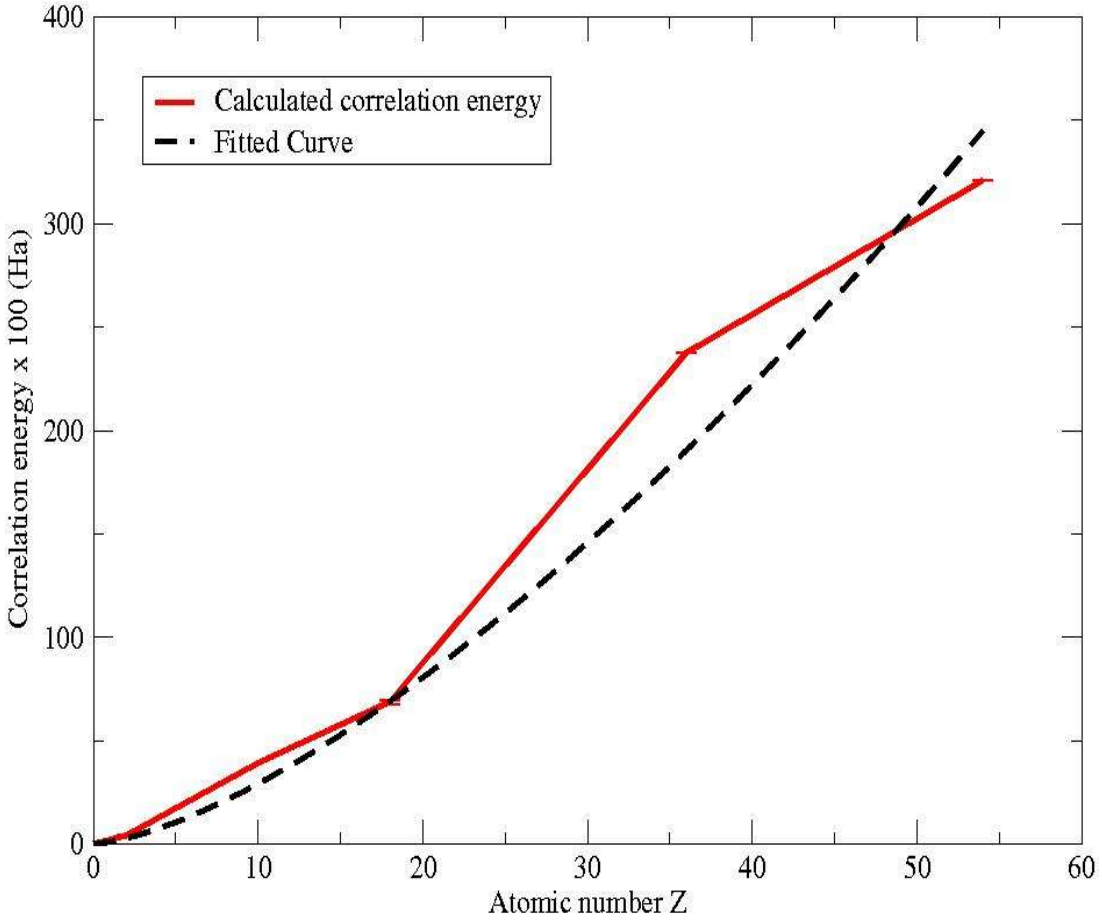
Cusp correction (3)



Correlation energy recovered



How does the correlation energy scale with atomic number Z?



Element	Atomic Number	Correlation Energy (Ha)
He	2	-0.0042(1)
Ne	10	-0.391902(1)
Ar	18	-0.69(1)
Kr	36	-2.376(1)
Xe	54	-3.209(1)

Conclusions

- All-electron QMC calculations for atoms are feasible
- We would like to study how the computer time scales with Z
- To improve results:
  - Acceleration schemes for VMC
  - Use multi-determinant trial wave functions