Quantum Monte Carlo

solving Schrödinger's equation

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December 14, 2017

Schrödinger's Equation

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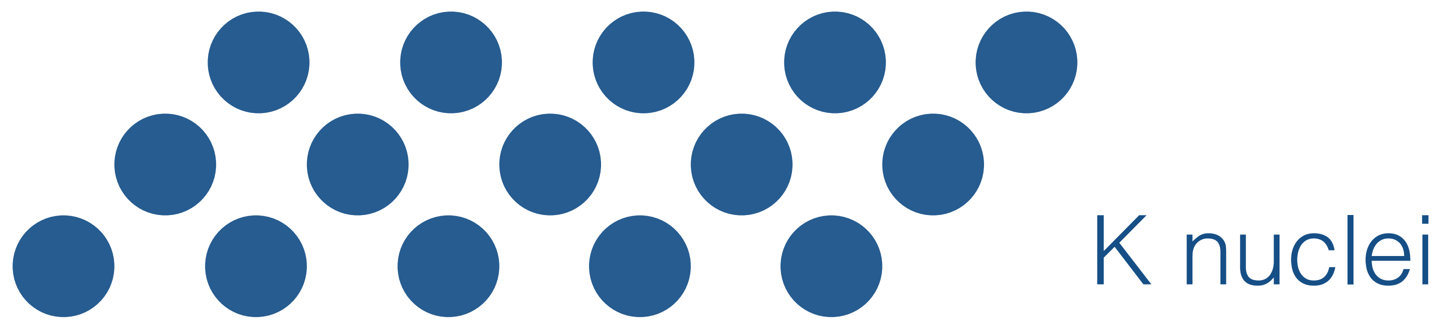
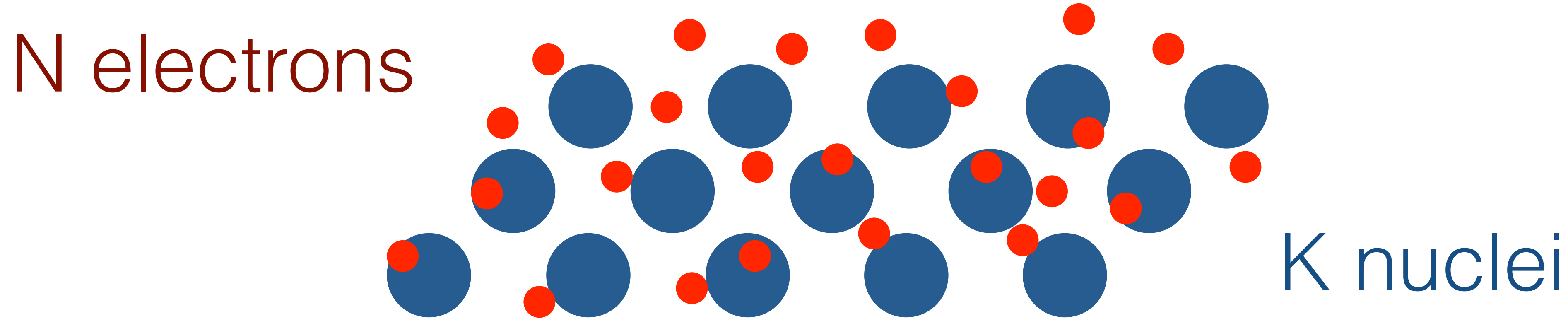


Schrödinger's Equation



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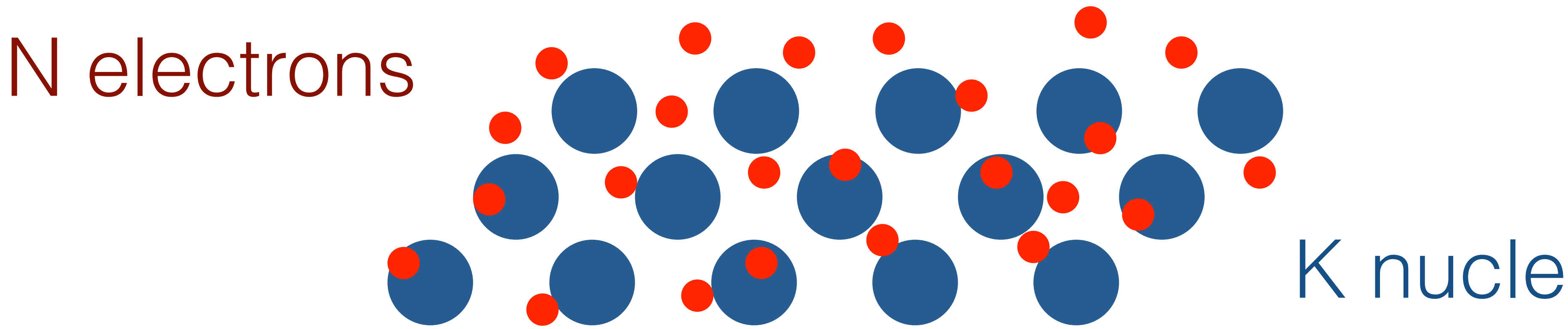
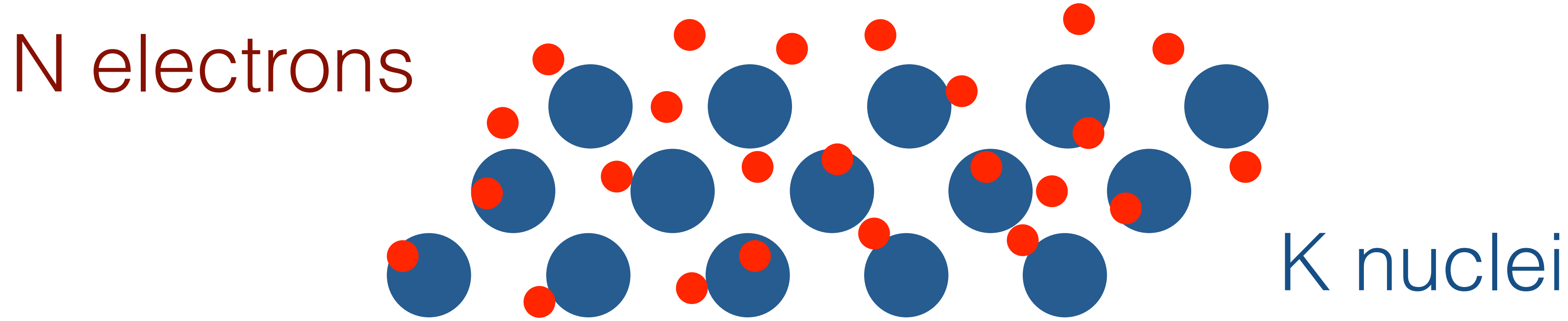


$$\mathcal{H}\Psi = E\Psi$$

Schrödinger’s Equation



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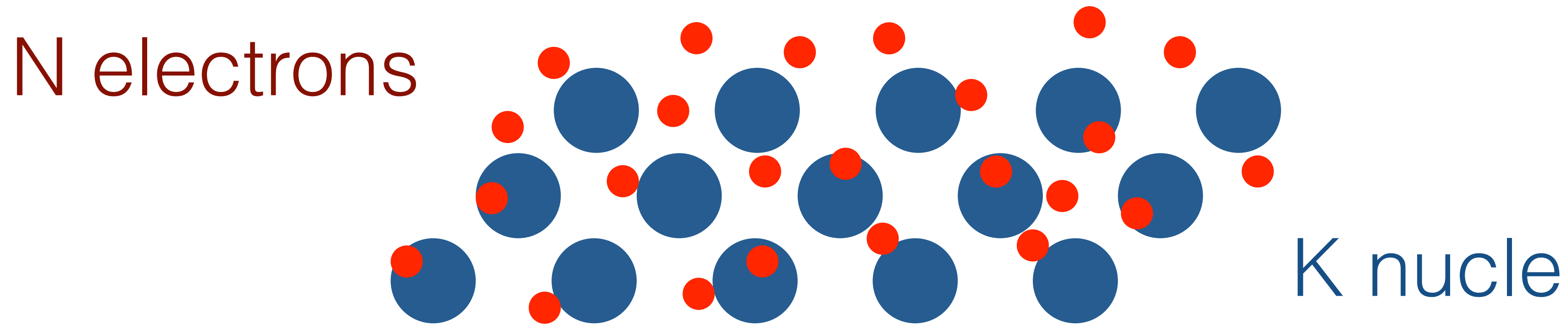

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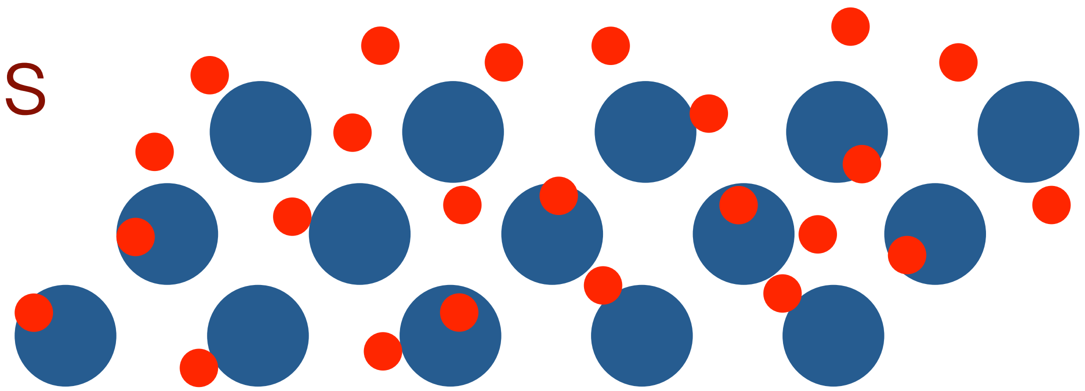
Schrödinger's Equation

N electrons



K nuclei

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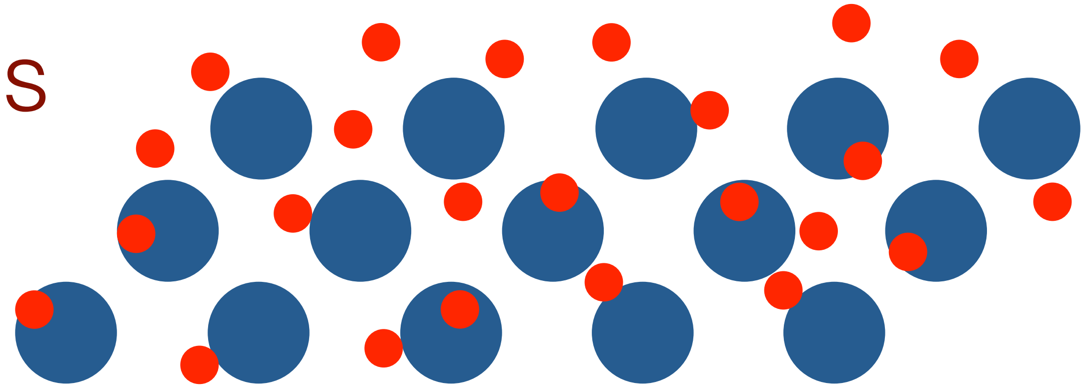

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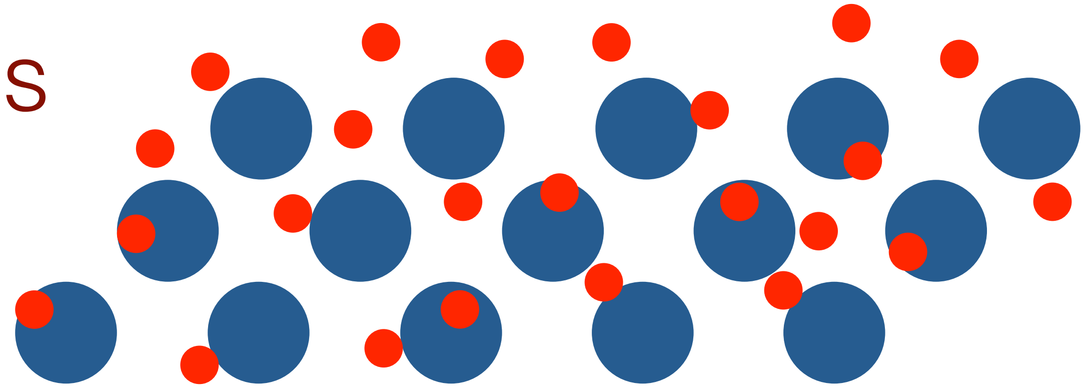

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Born-Oppenheimer Approximation

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Variational Monte Carlo

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2 Evaluate $\langle\mathcal{H}\rangle = \frac{\int \Psi_T^*(\boldsymbol{R})\mathcal{H}\Psi_T(\boldsymbol{R})\,d\boldsymbol{R}}{\int \Psi_T^*(\boldsymbol{R})\Psi_T(\boldsymbol{R})\,d\boldsymbol{R}} \geq E_0$

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3. if $\langle \mathcal{H} \rangle \neq E_0$ Change variational parameters and repeat

Metropolis Algorithm

$$E_L(\boldsymbol{R}, \alpha) = \frac{1}{\Psi_T(\boldsymbol{R}, \alpha)} \mathcal{H} \Psi_T(\boldsymbol{R}, \alpha)$$

Local Energy

$$P(\boldsymbol{R}, \alpha) = \frac{|\Psi_T(\boldsymbol{R})|^2}{\int \Psi_T^*(\boldsymbol{R}) \Psi_T(\boldsymbol{R}) \, d\boldsymbol{R}}$$

PDF

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2. Accept or Reject the move with probability $\min\left(1, \frac{P(\boldsymbol{R}', \alpha)}{P(\boldsymbol{R}, \alpha)}\right)$
3. If accepted $\boldsymbol{R} = \boldsymbol{R}'$ then calculate $E_L(\boldsymbol{R}, \alpha)$ and repeat

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Any wave function that is physical and for which
the value, the gradient and the laplacian of the wave function
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$$\Psi_T(\boldsymbol{R}) = \psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)\cdots\psi(\boldsymbol{r}_N)\prod_{i<j} f(r_{ij})$$

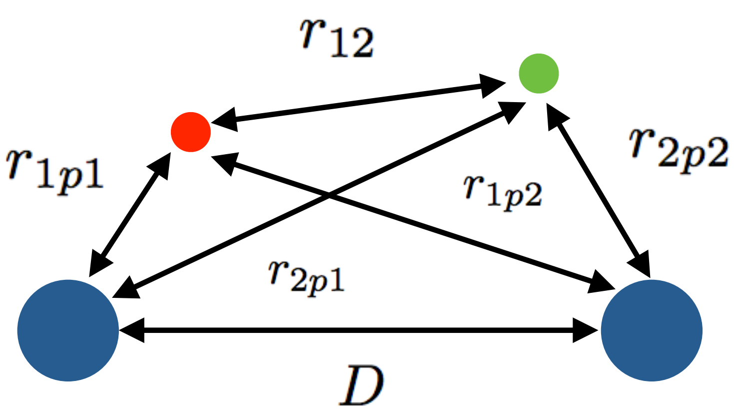
$$\psi(\boldsymbol{r}_i) = \sum_{j=1}^{K} e^{-\alpha|\boldsymbol{r}_i - \boldsymbol{R}_j|}$$

single electron Wavefunction

$$f(r_{ij}) = \left(\frac{r_{ij}}{2(1+\beta r_{ij})}\right)$$

electron-electron correlation

Example: Hydrogen Molecule



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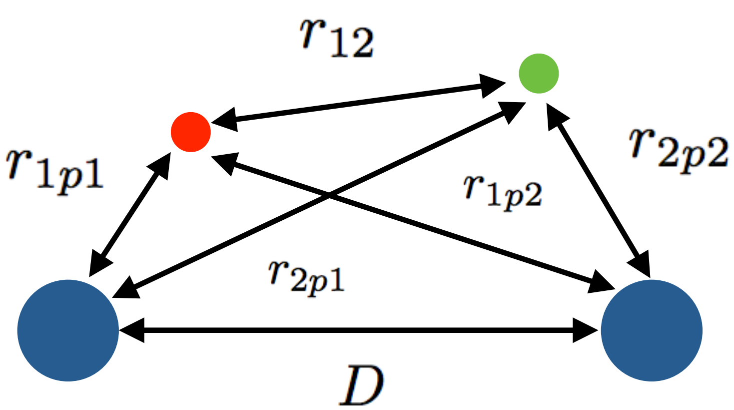

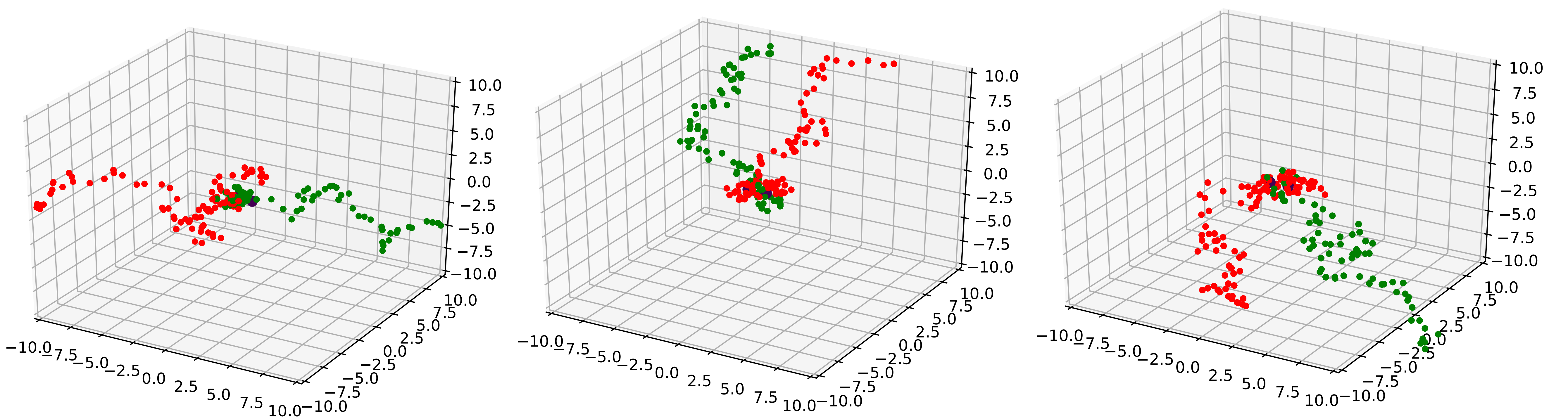

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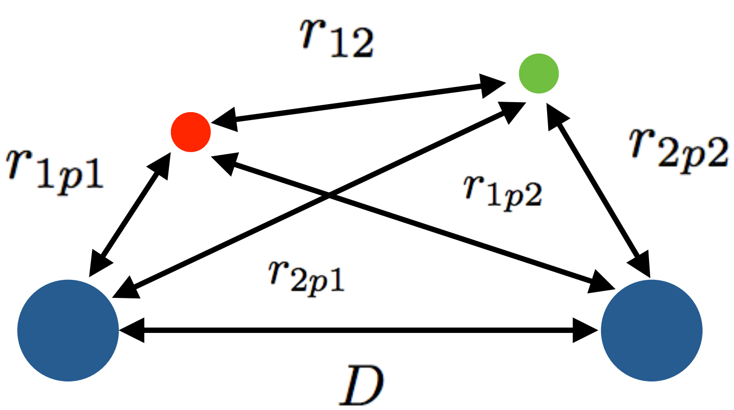

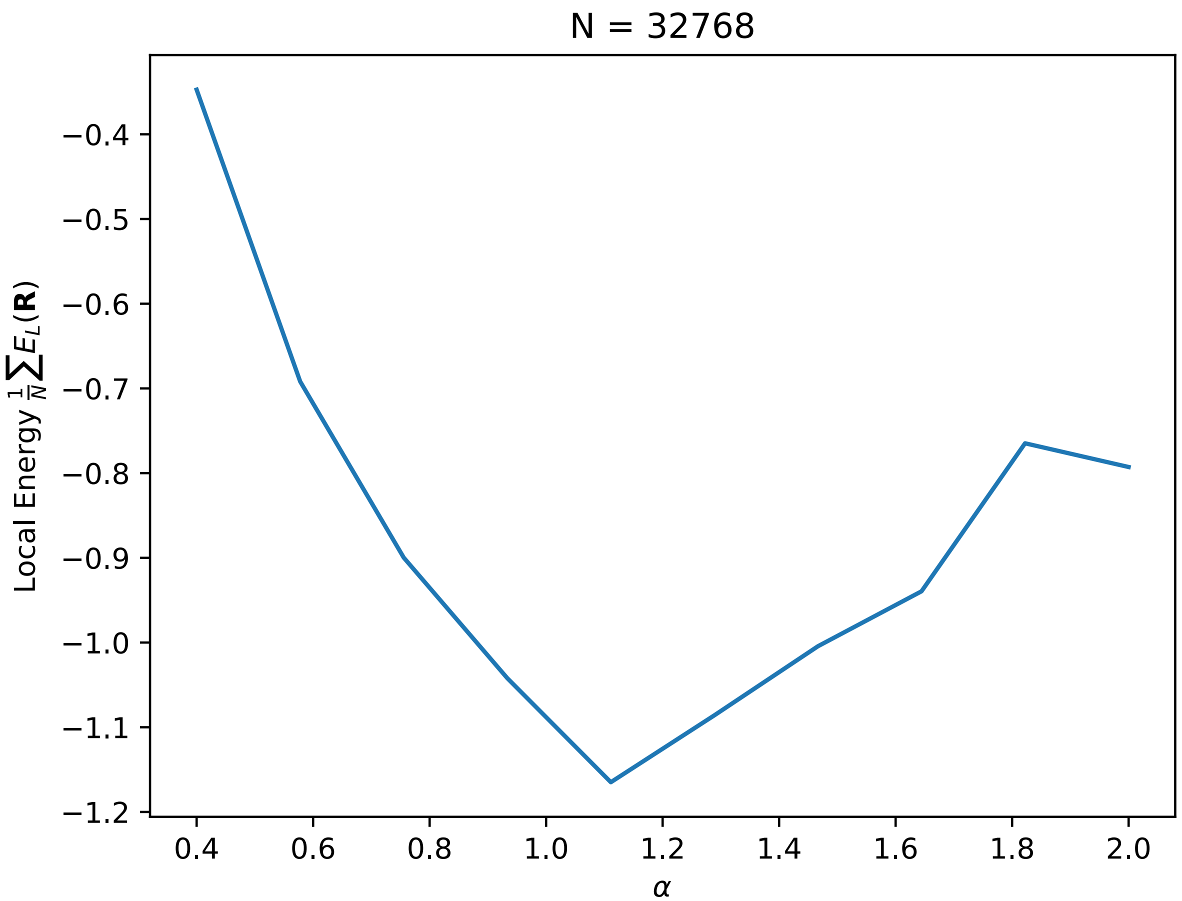

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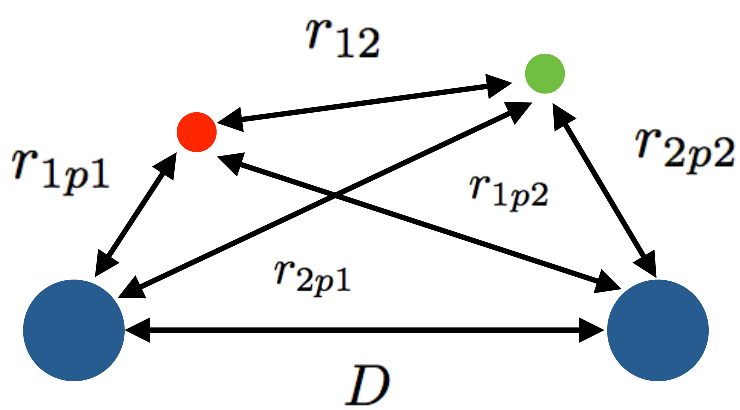

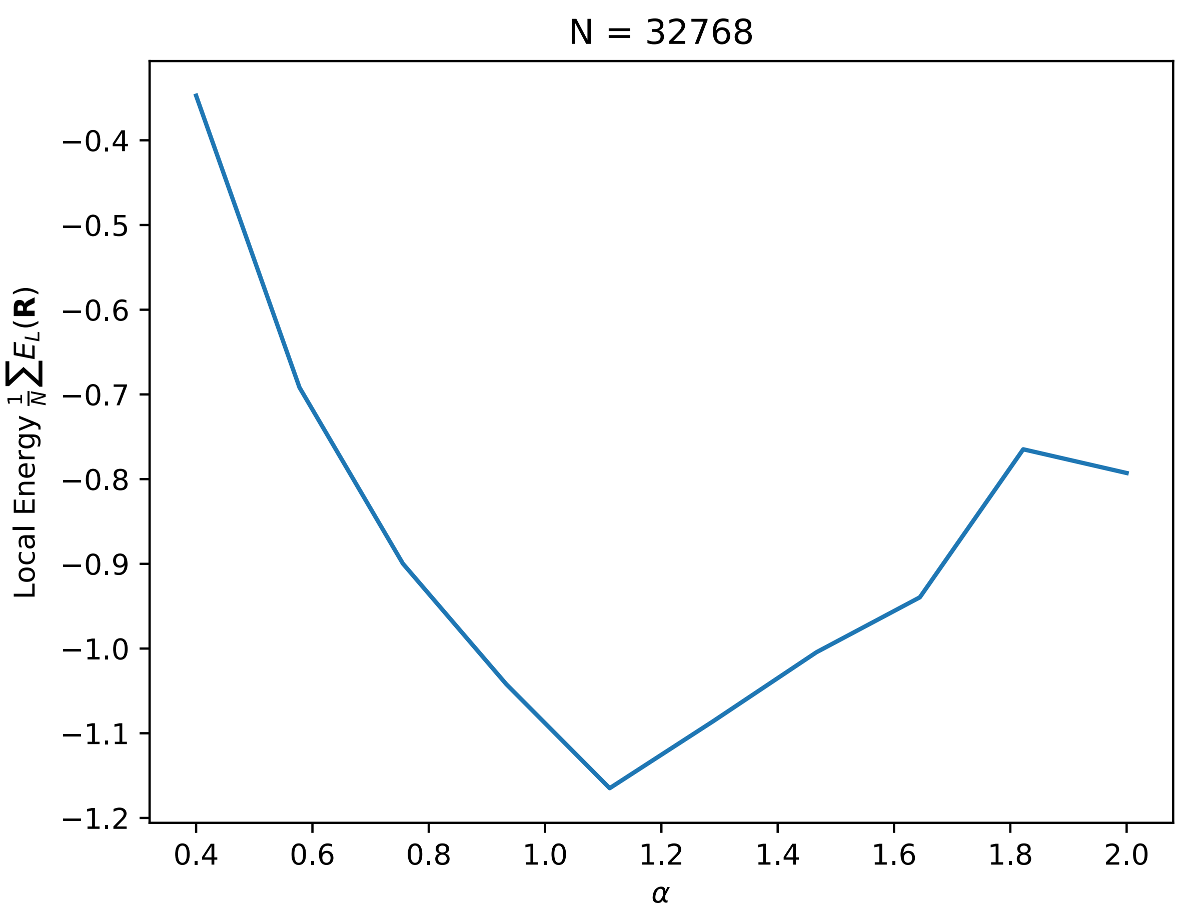

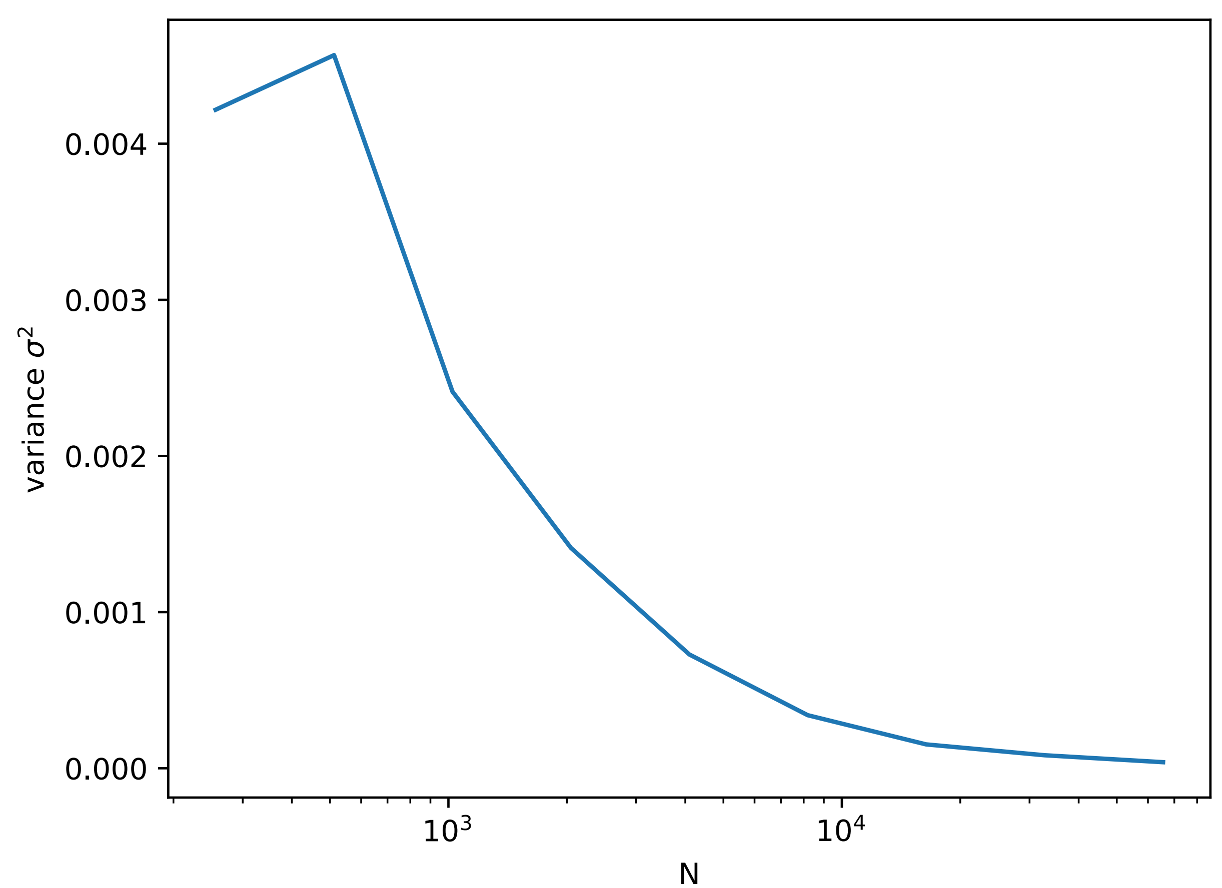

Monte Carlo in Action

Next Steps

- Spin terms in trial wavefunction
- Pseudopotential for heavier atoms
- Parallelization (QMC is very suitable for parallel processing)
- Calculate energy of solids

Any Questions?