Variational method

2021/5/24

Ritz variational principle

- consider a Hamiltonian H and arbitrary normalized state

$$\langle \psi | \psi \rangle = 1$$

- The ground state energy has a upperbound

$$E_0 \leq \langle \psi | H | \psi \rangle$$

Proof

- Expand the wavefunction with eigenstates

$$|\psi\rangle = \sum_m C_m |m\rangle \qquad \sum_m |C_m|^2 = 1$$

- Calculate the expectation value of E

$$\langle\psi|H|\psi\rangle = \sum_{nm} C_n^* C_m \langle n|H|m\rangle = \sum_{nm} C_n^* C_m E_m \langle n|m\rangle$$

$$= \sum_m |C_m|^2 E_m$$

$$\geq E_0 \sum_m |C_m|^2 = E_0$$

SHO energy

- Consider SHO $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$

- Trial wavefunction: Gaussian function

$$\psi(x) = Ae^{-bx^2}$$

- normalization constant

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = A \int_{-\infty}^{\infty} e^{-2bx^2} dx = 1 \qquad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

SHO energy

- Calculate kinetic energy

$$\psi(x) = Ae^{-bx^2}$$

$$\langle T \rangle = \frac{\hbar^2}{2m}\int \psi^*(x)\frac{d^2}{dx^2}\psi(x)dx = \frac{\hbar^2}{2m}A^2(2b)^2\int x^2 e^{-2bx^2}dx$$

$$= \frac{\hbar^2}{2m}(2b)^2A^2\int \frac{1}{4b}e^{-2bx^2}dx = \frac{\hbar^2 b}{2m}$$

- potential energy

$$\langle V \rangle = \frac{m\omega^2}{2}\int \psi^*(x)x^2\psi(x)dx = \frac{m\omega^2}{2}A^2\int x^2 e^{-2bx^2}dx$$

$$= \frac{m\omega^2}{2}A^2\frac{1}{4b}\int e^{-2bx^2}dx = \frac{m\omega^2}{8b}$$

SHO energy

- Expectation energy

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

- Minimize energy in respect to b

$$\frac{d\langle H \rangle}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \qquad b = \frac{m\omega}{2\hbar}$$

- Minimum energy

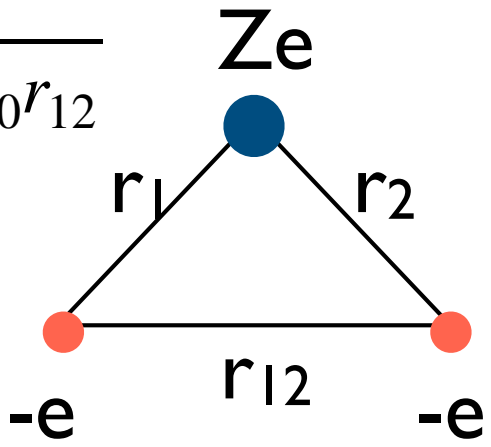
$$\langle H \rangle_{min} = \left(\frac{\hbar^2}{2m}\right)\left(\frac{m\omega}{2\hbar}\right) + \left(\frac{m\omega^2}{8}\right)\left(\frac{2\hbar}{m\omega}\right) = \frac{1}{2}\hbar\omega$$

It is an exact result!

Ground state of He

- The 2-particle Hamiltonian

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$



- 2-particle trial wavefunction

$$\psi(r_1, r_2) = \psi_{100}(r_1)\,\psi_{100}(r_2)$$

- single particle wavefunction(effective nuclear charge)

$$H\psi_{100} = \left[\frac{p^2}{2m} - \frac{Z^* e^2}{4\pi\varepsilon_0 r}\right]\psi_{100} = E\psi_{100}$$

$$E = -Z^{*2}\left(\frac{1}{2}mc^2\alpha^2\right) = -13.6Z^{*2}\text{eV}$$

Electron repulsion energy

- Trial wavefunction

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \qquad \psi(r_1, r_2) = \frac{Z^3}{\pi a_0^3} e^{-Z\frac{r_1 + r_2}{a_0}}$$

- Repulsion energy

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0} \int \Psi^* \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \Psi d^3 r_1 d^3 r_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int \frac{e^{-2Z(r_1+r_2)/a_0}}{|\mathbf{r_1} - \mathbf{r_2}|} d^3 r_1 d^3 r_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int \frac{e^{-2Z(r_1+r_2)/a_0}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} d^3 r_1 d^3 r_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int dr_1\, dr_2\, d\Omega_1\, d\Omega_2 \frac{r_1^2 r_2^2 e^{-2Z(r_1+r_2)/a_0}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}$$

dΩ solid angle

$$d^3 r = r^2 dr d\Omega$$

- angular part

$$\int \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}} d\Omega_2 d\Omega_1 = \int d\Omega_1 \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}}$$

$$= \int d\Omega_1 2\pi \frac{1}{r_1 r_2} \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}\Big|_{-1}^{1}$$

$$= \frac{8\pi^2}{r_1 r_2}\left(r_1 + r_2 - \left|r_1 - r_2\right|\right)$$

- radial part

$$8\pi^2 \int dr_1 \int dr_2 r_1^2 r_2^2 \frac{1}{r_1 r_2} e^{-2Z(r_1+r_2)/a_0}\left(r_1 + r_2 - \left|r_1 - r_2\right|\right)$$

$$= 16\pi^2 \int_0^{\infty} dr_1 e^{-2Zr_1/a_0}\left(r_1 \int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2/a_0} - r_1^2 \int_{r_1}^{\infty} dr_2 r_2 e^{-2Zr_2/a_0}\right)$$

$$= 16\pi^2 \int_0^{\infty} dr_1 r_1 e^{-2Zr_1/a_0}\left(2\left(\frac{a_0}{2Z}\right)^3\left(e^{-2Zr_1/a_0}-1\right) + r_1\left(\frac{a_0}{2Z}\right)^2 e^{-2Zr_1/a_0}\right)$$

$$= 32\pi^2\left(\frac{a_0}{2Z}\right)^3 \int_0^{\infty} dr_1 r_1 e^{-2Zr_1/a_0}\left[1-\left(1+\frac{Zr_1}{a_0}\right)e^{-2Zr_1/a_0}\right]$$

$$= 32\pi^2\left(\frac{a_0}{2Z}\right)^3\left[\left(\frac{a_0}{2Z}\right)^2 - \left(\frac{a_0}{4Z}\right)^2 - 2\left(\frac{a_0}{4Z}\right)^3\frac{Z}{a_0}\right]$$

$$= 32\pi^2\left(\frac{a_0}{2Z}\right)^5\left[1-\frac{1}{4}-\frac{1}{8}\right] = 20\pi^2\left(\frac{a_0}{2Z}\right)^5$$

Estimated energy for Z*=2

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z^3}{\pi a_0^3}\right)^2 \times 20\pi^2 \left(\frac{a_0}{2Z}\right)^5 = \frac{e^2}{4\pi\varepsilon_0}\frac{5}{8}\frac{Z}{a_0}$$

- Replace Z by Z*

$$\rightarrow \frac{e^2}{4\pi\varepsilon_0}\frac{5}{8}\frac{Z^*}{a_0} = \frac{5}{4}Z^*\left(\frac{1}{2}mc^2\alpha^2\right)$$

- If $Z^*=2, V_{ee}=34$ eV
- $Z^*=2$, 2E= 8 x (-13.6 eV)= -109 eV, total energy=$2E+V_{ee}$ =-109 eV+ 34 eV= -75 eV
- Exact He energy = -78.975 eV

Z* <> 2

- Rewrite the Hamiltonian

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Z^* e^2}{4\pi\varepsilon_0 r_1} - \frac{Z^* e^2}{4\pi\varepsilon_0 r_2} - \frac{\Delta Z e^2}{4\pi\varepsilon_0 r_1} - \frac{\Delta Z e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |r_{12}|}$$

$$\Delta Z = Z - Z^*$$

- For the first 4- terms the energy is

$$\left\langle \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Z^* e^2}{4\pi\varepsilon r_1} - \frac{Z^* e^2}{4\pi\varepsilon r_2} \right\rangle = -2Z^{*2}\left(\frac{1}{2}mc^2\alpha^2\right)$$

- For the last term is

$$\langle V_{ee} \rangle = \frac{5}{4} Z^* \left(\frac{1}{2}mc^2\alpha^2\right)$$

estimated energy for $Z^* \neq 2$

- Additional potential term

$$\left\langle -\frac{\Delta Z e^2}{4\pi\varepsilon_0 r_1} - \frac{\Delta Z e^2}{4\pi\varepsilon_0 r_2} \right\rangle = -2\frac{\Delta Z e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle = -2\frac{\Delta Z e^2}{4\pi\varepsilon_0}\frac{Z^*}{a_0}$$

$$= 4\Delta Z Z^* \left(\frac{1}{2} mc^2\alpha^2\right)$$

- total energy

$$\langle H \rangle = \left[-2Z^{*2} - 4(Z - Z^*)Z^* + \frac{5}{4}Z^*\right]\left(\frac{1}{2} mc^2\alpha^2\right)$$

$$= \left(2Z^{*2} - 4ZZ^* + \frac{5}{4}Z^*\right)\left(\frac{1}{2} mc^2\alpha^2\right)$$

minimize energy

- minimize E

$$\frac{d\langle H\rangle}{dZ^*} = \left(4Z^* - 4Z + \frac{5}{4}\right)\left(\frac{1}{2}mc^2\alpha^2\right) = 0$$

$$Z^* = Z - \frac{5}{16}$$

- minimum energy

$$\langle H\rangle_{min} = -2\left(Z - \frac{5}{16}\right)^2\left(\frac{1}{2}mc^2\alpha^2\right) = -77.38\text{eV}$$

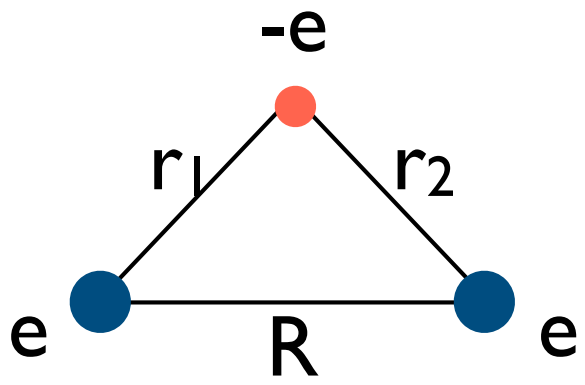
- Exact He energy = -78.975 eV

H_2^+ ion

- Hamiltonian

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 R}$$

R is bond length



- Trial wavefunction: Linear combination of atomic orbitals(LCAO)

$$\Psi_{\pm} = A\left[\psi_0(r_1) \pm \psi_0(r_2)\right]$$

$$\psi_0(r_1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

- For simplicity, we only consider even wavefunction.(bonding mode)

overlap integral

- normalization constant

$$1 = \langle \psi | \psi \rangle = A^2 \left[\langle \psi_0(r_1) | \psi_0(r_1) \rangle + \langle \psi_0(r_2) | \psi_0(r_2) \rangle + 2 \langle \psi_0(r_1) | \psi_0(r_2) \rangle \right]$$

$$= 2A^2 \left[1 + \langle \psi_0(r_1) | \psi_0(r_2) \rangle \right]$$

$$A^2 = \frac{1}{2} \frac{1}{1 + \langle \psi_0(r_1) | \psi_0(r_2) \rangle}$$

- Overlap integral

$$I = \langle \psi_0(r_1) | \psi_0(r_2) \rangle = \int \psi_0(r_1) \psi_0(r_2) d^3 r$$

$$= \frac{1}{\pi a_0^3} \int d^3 r_1 e^{-r_1/a_0} e^{-|r_1 - R|/a_0}$$

$$= \frac{1}{\pi a_0^3} \int_0^{\infty} dr_1 \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) r_1^2 e^{-r_1/a_0} e^{-\sqrt{r_1^2 + R^2 - 2 r_1 R \cos\theta}/a_0}$$

$$= e^{-R/a_0} \left[\frac{R^2}{3a_0^2} + \frac{R}{a_0} + 1 \right] = \left(1 + x + \frac{x^2}{3} \right) e^{-x} \qquad x = \frac{R}{a_0}$$

$$\int \psi_0(r_1)\psi_0(r_2)d^3r = \frac{1}{\pi a_0^3}\int_0^\infty dr \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) r_1^2 e^{-r_1/a_0} e^{-\sqrt{r_1^2+R^2-2r_1R\cos\theta}/a_0}$$

$$= -\frac{1}{\pi a_0^3}\int_0^\infty dr \int_0^{2\pi} d\phi \int_{|r_1-R|}^{r_1+R} dy \frac{r_1 y}{R} e^{-r_1/a_0} e^{-y/a_0} \qquad y = \sqrt{r_1^2+R^2-2r_1R\cos\theta}$$

$$= -\frac{2}{a_0^2 R}\int_0^\infty dr_1 r_1 e^{-r_1/a_0}\left(\left(r_1+R+a_0\right)e^{-(r_1+R)/a_0} - \left(\left|r_1-R\right|+a_0\right)e^{-|r_1-R|/a_0}\right)$$

$$= -\frac{2}{a_0^2 R}\left\{\begin{array}{l} e^{-R/a_0}\displaystyle\int_0^\infty dr r_1\left(r_1+R+a_0\right)e^{-2r_1/a_0} - e^{-R/a_0}\int_0^R dr_1 r_1\left(R-r_1+a_0\right) \\ -e^{R/a_0}\displaystyle\int_R^\infty dr_1 r_1\left(r_1-R+a_0\right)e^{-2r_1/a_0} \end{array}\right\}$$

$$= -\frac{2}{a_0^2 R}e^{-R/a_0}\left\{\begin{array}{l} 2\left(\frac{a_0}{2}\right)^3 + \left(\frac{a_0}{2}\right)^2\left(R+a_0\right) - \frac{R^3}{6} - \frac{R^2 a_0}{2} \\ -\frac{a_0}{2}R^2 - 2\left(\frac{a_0}{2}\right)^2 R - 2\left(\frac{a_0}{2}\right)^3 + \left(R-a_0\right)\left(\frac{a_0}{2}\right)\left(R+\frac{a_0}{2}\right) \end{array}\right\}$$

$$= \frac{2}{a_0^2 R}e^{-R/a_0}\left[\frac{R^3}{6} + \left(\frac{a_0}{2}\right)R^2 + 2\left(\frac{a_0}{2}\right)^2 R\right] \qquad \mathbf{r}_1 = \mathbf{r} - \frac{\mathbf{R}}{2}$$

$$= e^{-R/a_0}\left[\frac{R^2}{3a_0^2} + \frac{R}{a_0} + 1\right] \qquad \mathbf{r}_2 = \mathbf{r} + \frac{\mathbf{R}}{2}$$

Expectation energy

- The expectation value of energy

$$\langle H\rangle = A^2\left[\langle\psi_0(r_1)\,|\,H\,|\,\psi_0(r_1)\rangle + \langle\psi_0(r_2)\,|\,H\,|\,\psi_0(r_2)\rangle + 2\langle\psi_0(r_1)\,|\,H\,|\,\psi_0(r_2)\rangle\right]$$

$$= 2A^2\left[\langle\psi_0(r_1)\,|\,H\,|\,\psi_0(r_1)\rangle + \langle\psi_0(r_1)\,|\,H\,|\,\psi_0(r_2)\rangle\right]$$

$$\langle\psi_0(r_1)\,|\,H\,|\,\psi_0(r_1)\rangle = \langle\psi_0(r_2)\,|\,H\,|\,\psi_0(r_2)\rangle$$ **why?**

- H is invariant if $1 \leftrightarrow 2$

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 R}$$

Expectation energy

- The matrix elements

$$\langle\psi_0(r_1)|H|\psi_0(r_1)\rangle = \left\langle \psi_0(r_1) \left| \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 R} \right| \psi_0(r_1) \right\rangle$$

$$= E_1 + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{e^2}{4\pi\varepsilon_0} \left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle$$

$$\langle\psi_0(r_1)|H|\psi_0(r_2)\rangle = \left\langle \psi_0(r_1) \left| \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 R} \right| \psi_0(r_2) \right\rangle$$

$$= \left(E_1 + \frac{e^2}{4\pi\varepsilon_0 R} \right) \langle\psi_0(r_1)|\psi_0(r_2)\rangle - \frac{e^2}{4\pi\varepsilon_0} \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle$$

Expectation energy

$$\langle H \rangle = 2A^2 \left[\langle \psi_0 | H | \psi_0 \rangle + \langle \psi_0(r_1) | H | \psi_0(r_2) \rangle \right]$$

$$= 2A^2 \left[\left(E_1 + \frac{e^2}{4\pi\varepsilon_0 R} \right) \left(1 + \left\langle \psi_0(r_1) | \psi_0(r_2) \right\rangle \right) \right]$$

$$-2A^2 \frac{e^2}{4\pi\varepsilon_0} \left[\left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle + \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle \right]$$

$$= E_1 + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{e^2}{4\pi\varepsilon_0 a_0} \left(\frac{D + X}{1 + I} \right)$$

$$= E_1 \left(1 - 2\frac{a_0}{R} + 2\frac{D + X}{1 + I} \right)$$

$$A^2 = \frac{1}{2} \frac{1}{1 + \langle \psi_0(r_1) | \psi_0(r_2) \rangle}$$

$$E_1 = -\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 a_0}$$

Direct integral

- Direct integral

$$D = a_0 \left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle = \frac{a_0}{R} - \left(1 + \frac{a_0}{R}\right) e^{-2R/a_0} = \frac{1}{x}\left[1 - (1+x)e^{-2x}\right]$$

$$x = \frac{R}{a_0}$$

- Exchange integral

$$X = a_0 \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle = \left(1 + \frac{R}{a_0}\right) e^{-R/a_0} = (1+x)e^{-x}$$

optimization

- Express the <E> with x

$$\langle H \rangle = E_1 \left(1 - 2\frac{a_0}{R} + 2\frac{D+X}{1+I} \right)$$

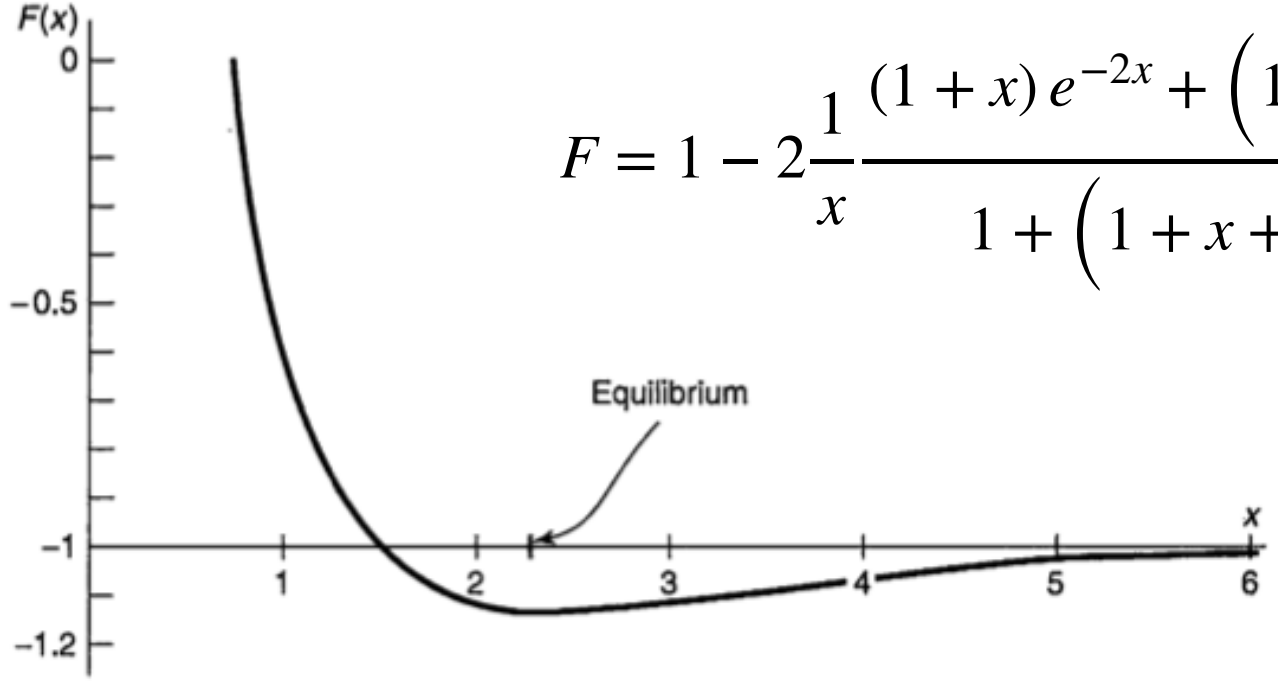
$$= E_1 \left(1 - 2\frac{1}{x} + 2\frac{\frac{1}{x}\left[1-(1+x)e^{-2x}\right] + (1+x)e^{-x}}{1+\left(1+x+\frac{x^2}{3}\right)e^{-x}} \right)$$

$$= E_1 \left(1 - 2\frac{1}{x}\frac{(1+x)\,e^{-2x} + \left(1-\frac{2}{3}x^2\right)e^{-x}}{1+\left(1+x+\frac{x^2}{3}\right)e^{-x}} \right) = FE_1$$

- To minimize <E> with respect to x

H_2 bonding

- optimum distance R~2.4 a_0 (~0.13 nm)
- optimum energy change ~ -1.76 eV



$$F = 1 - 2\frac{1}{x}\frac{(1+x)\,e^{-2x} + \left(1 - \frac{2}{3}x^2\right)e^{-x}}{1 + \left(1 + x + \frac{x^2}{3}\right)e^{-x}}$$

- experimental R~0.106 nm
- optimum energy change ~ -2.8 eV

Scalable Quantum Simulation of Molecular Energies

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We report the first electronic structure calculation performed on a quantum computer without exponentially costly precompilation. We use a programmable array of superconducting qubits to compute the energy surface of molecular hydrogen using two distinct quantum algorithms. First, we experimentally execute the unitary coupled cluster method using the variational quantum eigensolver. Our efficient implementation predicts the correct dissociation energy to within chemical accuracy of the numerically exact result. Second, we experimentally demonstrate the canonical quantum algorithm for chemistry, which consists of Trotterization and quantum phase estimation. We compare the experimental performance of these approaches to show clear evidence that the variational quantum eigensolver is robust to certain errors. This error tolerance inspires hope that variational quantum simulations of classically intractable molecules may be viable in the near future.

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Subject Areas: Condensed Matter Physics, Quantum Information

Variational eigensolver

- We want to optimize the energy

$$\langle \psi(\theta) | H | \psi(\theta) \rangle$$

- For computation, the hamiltonian is scalable using "local hamiltonians"

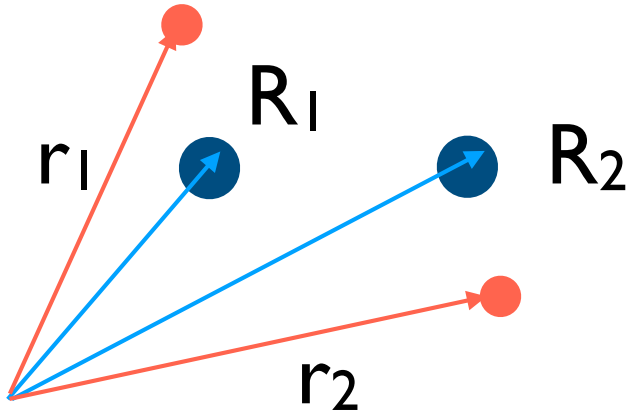
$$H = \sum_{\gamma} h_{\gamma} H_{\gamma}$$

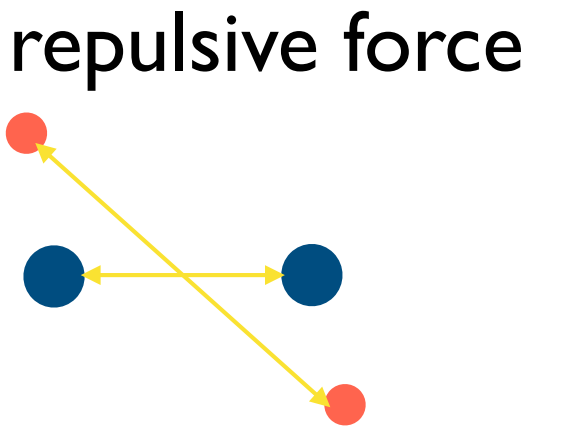
$H_{\gamma} = \{1, X_i, Y_i, Z_i\}$ and their combinations

2nd quantization method

- Original version of H

$$H = \sum_i \frac{p_i^2}{2m} - \frac{Z_j e^2}{4\pi\varepsilon_0 |r_i - R_j|} + \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |R_i - R_j|} + \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}$$





2nd quantization method

- 2nd quantization formulation

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

a_p are fermionic operators

$$h_{pq} = \int dr \phi_p^*(r) \left(\frac{p^2}{2m} - \sum_j \frac{Z_j e^2}{4\pi\varepsilon_0 |r - R_j|} \right) \phi_q(r)$$

$$h_{pqrs} = \frac{e^2}{4\pi\varepsilon_0} \int dr_1 dr_2 \phi_p^*(r_1) \phi_q^*(r_2) \frac{1}{|r_1 - r_2|} \phi_r(r_1) \phi_s(r_2)$$

Local hamiltonians

- For H_2 molecules (4-qubit H for p, q, r and s)

$$
\begin{aligned}
H = {} & f_0\mathbb{1} + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 \\
& + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 \boldsymbol{X_0} Z_1 \boldsymbol{X_2} + f_6 \boldsymbol{Y_0} Z_1 \boldsymbol{Y_2} \\
& + f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 \\
& + f_6 \boldsymbol{X_0} Z_1 \boldsymbol{X_2} Z_3 + f_6 \boldsymbol{Y_0} Z_1 \boldsymbol{Y_2} Z_3 + f_7 Z_0 Z_1 Z_2 Z_3,
\end{aligned}
$$

- q1 and q3 do not flip. Can be simplified to 2-qubit H

$$
\tilde{H} = g_0\mathbb{1} + g_1 Z_0 + g_2 Z_1 + g_3 Z_0 Z_1 + g_4 X_0 X_1 + g_5 Y_0 Y_1,
$$

Variational eigensolver

- Input state is parametrized by a shallow quantum circuit

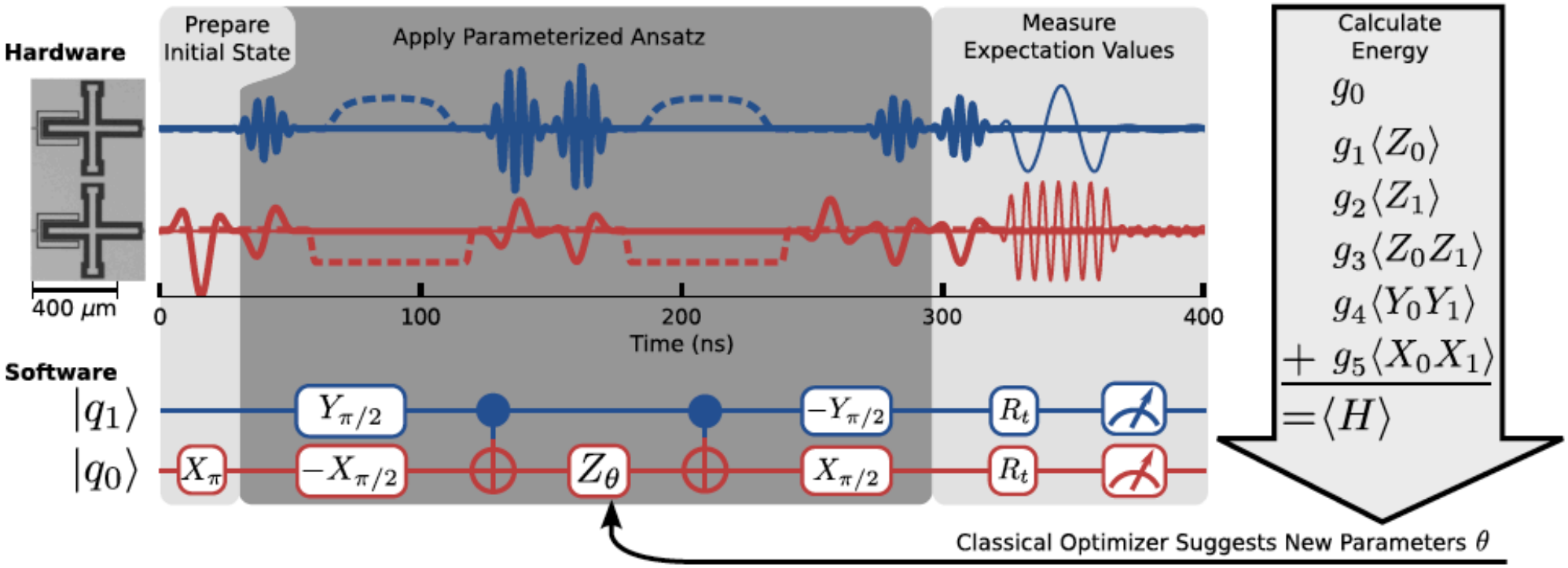
$$|\psi(\theta)\rangle = U(\theta)\,|\phi\rangle$$

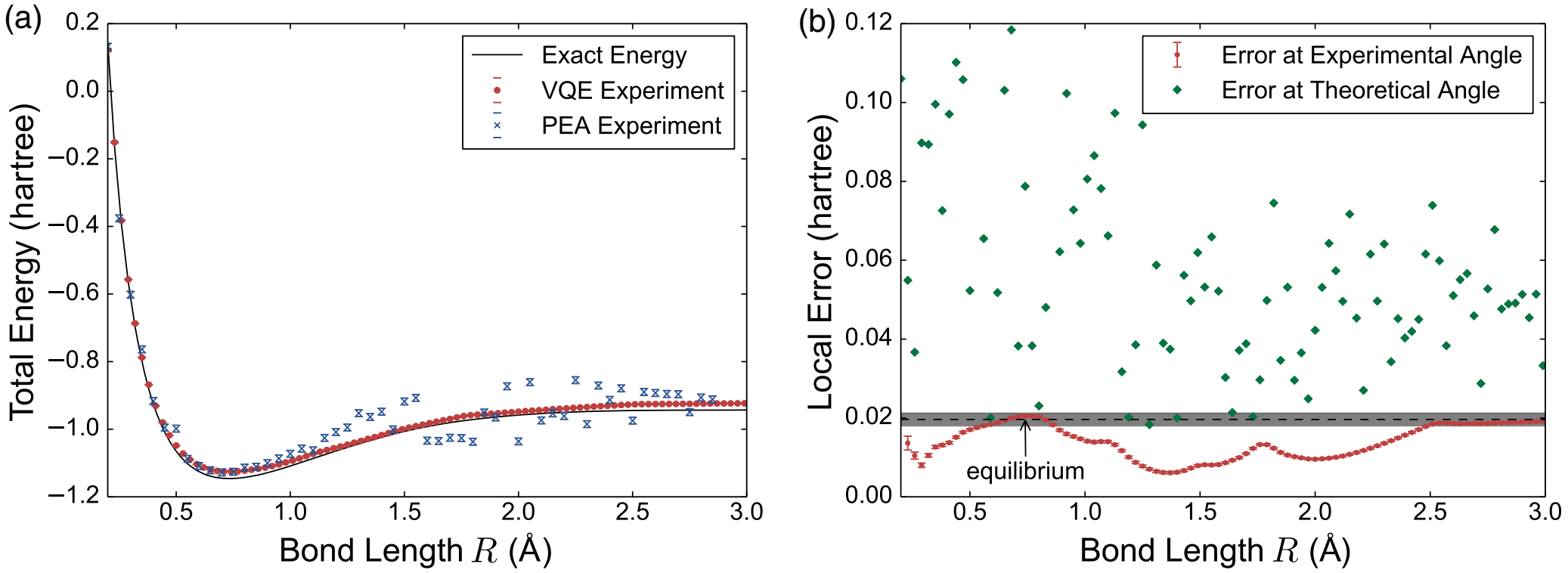
$|\phi\rangle$ is a product state

θ is a list of parameters

- In practice, U can be expressed as

$$U(\theta) = U_1(\theta_1)U_2(\theta_2)\cdots U_n(\theta_n)$$


Hardware
400 μm
Prepare
Initial State
Apply Parameterized Ansatz
Measure
Expectation Values
0
100
200
300
400
Time (ns)
Software
$|q_1\rangle$
$|q_0\rangle$
X_π
$Y_{\pi/2}$
$-X_{\pi/2}$
Z_θ
$-Y_{\pi/2}$
$X_{\pi/2}$
R_t
R_t
Calculate
Energy
g_0
$g_1\langle Z_0\rangle$
$g_2\langle Z_1\rangle$
$g_3\langle Z_0 Z_1\rangle$
$g_4\langle Y_0 Y_1\rangle$
$+ g_5\langle X_0 X_1\rangle$
$=\langle H\rangle$
Classical Optimizer Suggests New Parameters θ


(a)
Exact Energy
VQE Experiment
PEA Experiment
Total Energy (hartree)
Bond Length R (Å)
(b)
Error at Experimental Angle
Error at Theoretical Angle
equilibrium
Local Error (hartree)
Bond Length R (Å)