Study Session on Quantum Computation of Quantum Chemistry

Yuan-Chung Cheng

鄭原忠

Department of Chemistry

National Taiwan University

NTU Chemistry Building, Room 215

September 13, 2018

Information

- Study session on quantum computation of quantum chemistry – originally meant to be for my group only…
- Location: Chemistry Building Room 215
- Time: 12:30 PM – 2:00 PM (Welcome to bring your lunch!)
- CEIBA: https://ceiba.ntu.edu.tw/course/d0bc36/index.htm
- Lectures will be recorded and posted on Youtube

Information

- We will study the following four papers:
  1. I. Kassal *et al.*, Annu. Rev. Phys. Chem. 62, 185 (2011).
  2. P. J. J. O'Malley *et al.*, Phys. Rev. X 6, 361 (2016).
  3. R. Babbush *et al.*, Phys. Rev. X 8, 011044 (2018).
  4. I. D. Kivlichan *et al.*, Phys. Rev. Lett. 120, 110501 (2018).
- The goal is to thoroughly examine the state-of-art theories for quantum computing in Chemistry – *true quantum advantage or not?* – and to promote research in this direction
- Why these four papers?

Paper #1

Simulating Chemistry Using Quantum Computers

Ivan Kassal,* James D. Whitfield,* Alejandro Perdomo-Ortiz, Man-Hong Yung, and Alán Aspuru-Guzik

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138; email: aspuru@chemistry.harvard.edu

- A review for physical chemists! (Aspuru-Guzik)
- Basics of quantum computing, and overview of the problem and basic algorithms (up to 2010)
- Qubits/quantum circuit/QFT/PEA/electronic Hamiltonian in second-quantized form

Paper #2

PHYSICAL REVIEW X 6, 031007 (2016)

Scalable Quantum Simulation of Molecular Energies

P. J. J. O'Malley,[1,*] R. Babbush,[2,†] I. D. Kivlichan,[3] J. Romero,[3] J. R. McClean,[4] R. Barends,[5] J. Kelly,[5] P. Roushan,[5] A. Tranter,[6,7] N. Ding,[2] B. Campbell,[1] Y. Chen,[5] Z. Chen,[1] B. Chiaro,[1] A. Dunsworth,[1] A. G. Fowler,[5] E. Jeffrey,[5] E. Lucero,[5] A. Megrant,[5] J. Y. Mutus,[5] M. Neeley,[5] C. Neill,[1] C. Quintana,[1] D. Sank,[5] A. Vainsencher,[1] J. Wenner,[1] T. C. White,[5] P. V. Coveney,[7] P. J. Love,[6] H. Neven,[2] A. Aspuru-Guzik,[3] and J. M. Martinis[5,1,‡]

- Algorithms and experiments on the simulation of H_2 dissociation curve (John Martinis, Josephson Junction Quantum Computing, UCSB & Google)
- Read-outs based on variational quantum eigensolver & phase estimation algorithm are both tested
- Jordan-Wigner transformation/Bravyi-Kitaev transformation/Trotterization/VQE/iterative PEA/CI space reduction/unitary coupled cluster

Paper #3

PHYSICAL REVIEW X **8,** 011044 (2018)

Low-Depth Quantum Simulation of Materials

Ryan Babbush,[1,*] Nathan Wiebe,[2] Jarrod McClean,[1] James McClain,[3] Hartmut Neven,[1] and Garnet Kin-Lic Chan[3,†]
[1]*Google Inc., Venice, California 90291, USA*
[2]*Microsoft Research, Redmond, Washington 98052, USA*
[3]*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

- "Linear-scaling" algorithms for solving electronic structures in planewave dual basis – simulation of materials, i.e. quantum VASP!!
- Basic solid-state physics/FFFT/linear depth quantum simulation/computation on planar architecture/Taylor-series algorithm

Paper #4

PHYSICAL REVIEW LETTERS **120,** 110501 (2018)

Quantum Simulation of Electronic Structure with Linear Depth and Connectivity

Ian D. Kivlichan,[1,2] Jarrod McClean,[1] Nathan Wiebe,[3] Craig Gidney,[4] Alán Aspuru-Guzik,[2]
Garnet Kin-Lic Chan,[5,*] and Ryan Babbush[1,†]
[1]*Google Inc., Venice, California 90291, USA*
[2]*Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA*
[3]*Microsoft Research, Redmond, Washington 98052, USA*
[4]*Google Inc., Santa Barbara, California 93117, USA*
[5]*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

- "Linear-scaling" algorithms for Trotter propagation -- FFFT replaced by fermonic swap gates
- Fermonic swap network/linear depth Trotter/linear depth preparation of Slater determinants.

- We hope that in the end the 4 papers would provide a unified view of QC in Q. Chem.

Electronic Structure Problem

- Solving the electronic structure problem is a major challenge in quantum chemistry.
- For more details, see https://ceiba.ntu.edu.tw/course/0d5091/index.htm

量子化學計算軟體 Gaussian 簡介與實務應用

，歡迎進入 Ceiba 系統

課程資訊
教師資訊
公佈欄
課程內容
討論看板
資源分享
登出

語言 Language:
中文(Chinese)

更新：2018-09-12
訪客：222

課程內容

課程進度			
週次	日期	單元主題	內容檔案
第1-1週		第一天: Gaussian 簡介 - 量子計算化學原理簡介 - 基本 Unix 系統指令介紹 - Gaussian 計算化學軟體 、台大計資中心 Gaussian 計算環境簡介 - Avogadro 圖形介面程式: 輸入檔製作以及計算結果分析	Foresman _ Frisch-Ch1-3.pdf NTUCC-GauLectures-01.pdf Syllabus.pdf fwunixref.pdf g09-examples.zip ntucc-g09_lab.pdf ntucc-grading.pdf virefcard.pdf
第1-2週		第二天: 用 Gaussian 了解化學反應 - 反應位能平面簡介 - 化學反應路徑計算與中間體分析 - 活化能分析與反應速率常數	NTUCC-GauLectures-02.pdf papers-dft-performance.zip
第1-3週		第三天: 用 Gaussian 研究分子激發態性質 - 分子激發態理論簡介 - 分子激發態性質計算 - 溶劑效應計算以及分子螢光效應	NTUCC-GauLectures-03.pdf papers-tddft-performance.zip

Schrödinger Equation

$$\mathbf{H} = \mathbf{T}_n + \mathbf{T}_e + \mathbf{V}_{nn} + \mathbf{V}_{ee} + \mathbf{V}_{ne}$$

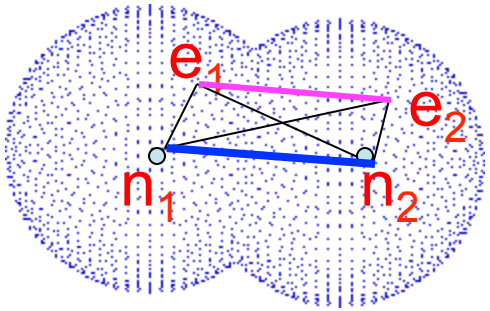
$$H\Psi = E\Psi$$

$$\mathbf{T}_n = -\sum_a^{N_n} \frac{1}{2M_a} \nabla_a^2$$

Kinetic energy of nuclei

$$\mathbf{T}_e = -\sum_i^{N_e} \frac{1}{2m_e} \nabla_i^2$$

Kinetic energy of electrons



$$\mathbf{V}_{nn} = \sum_a^{N_n} \sum_{b>a}^{N_n} \frac{Z_a Z_b}{r_{ab}}$$

Coulombic energy between nuclei

$$\mathbf{V}_{ee} = \sum_i^{N_e} \sum_{i>j}^{N_e} \frac{1}{r_{ij}}$$

Coulombic energy between electrons

$$\mathbf{V}_{ne} = \sum_a^{N_n} \sum_i^{N_e} \frac{Z_a}{r_{ai}}$$

Coulombic energy between nuclei and electrons

Courtesy of Hai Lin

Approximations

To solve the Schrödinger equation approximately, assumptions are made to simplify the equation:

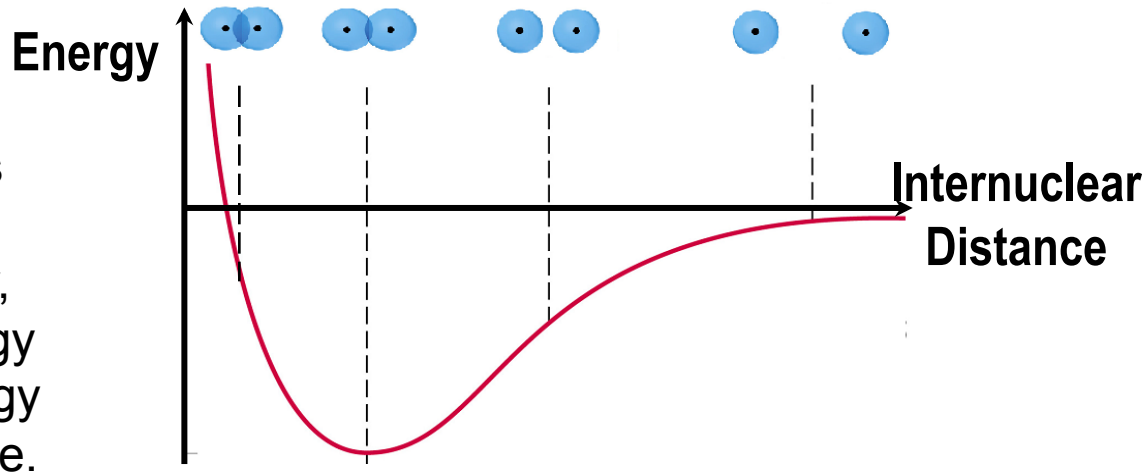
- **Born-Oppenheimer approximation** allows separate treatment of nuclei and electrons. ($m_a >> m_e$)
- **Hartree-Fock independent electron approximation** allows each electron to be considered as being affected by the sum (field) of all other electrons.
- **LCAO Approximation** represents molecular orbitals as linear combinations of atomic orbitals (basis functions).

Courtesy of Hai Lin

Born-Oppenheimer Approximation

- Nuclei are much heavier than electrons ($m_a / m_e > 1836$) and move much slower.
- Effectively, electrons adjust themselves instantaneously to nuclear configurations.
- Electron and nuclear motions are uncoupled, thus the energies of the two are separable.

1. For a given nuclear configuration, one calculates electronic energy.
2. As nuclei move continuously, the points of electronic energy joint to form a potential energy surface on which nuclei move.



Elec. Schrodinger equation: $H(R)\Psi(R) = E(R)\Psi(R)$

Basic Quantum Mechanics

Schrodinger equation: $H\Psi = E\Psi$

Variational principle: $E = \left\langle \Psi \middle| \hat{\mathbf{H}} \middle| \Psi \right\rangle \geq E_{\text{exact}}$

$$\Psi = \Psi(x_1, x_2 \ldots, x_N)$$

The N-electron wave function is a function with 3N dimensions, this is too complicated to even "think about" practically for systems with > 3 electrons → must simplify the functional form of the wave function.

Many-electron Wave function

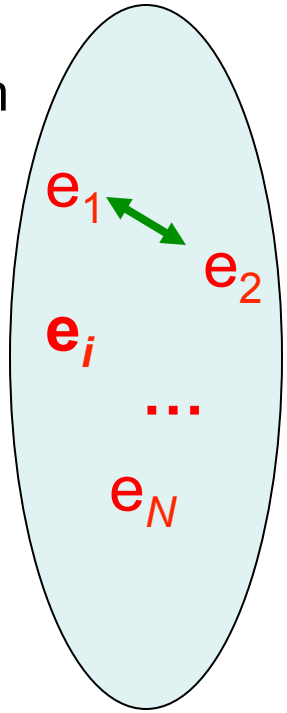
Hartree product: All electrons are independent, each in its own orbital.

$$\psi^{HP}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) = f_1(\mathbf{x}_1)f_2(\mathbf{x}_2)\cdots f_N(\mathbf{x}_N)$$

Pauli principle: Two electrons can not have all quantum number equal.

This requires that the total (many-electron) wave function is anti-symmetric whenever one exchanges two electrons' coordinates.

$$\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) = -\psi(\mathbf{x}_2,\mathbf{x}_1,\ldots,\mathbf{x}_N)$$



Slater determinant satisfies the Pauli exclusion principle.

$$\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} f_1(\mathbf{x}_1) & f_2(\mathbf{x}_1) & \cdots & f_N(\mathbf{x}_1) \\ f_1(\mathbf{x}_2) & f_2(\mathbf{x}_2) & \cdots & f_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ f_1(\mathbf{x}_N) & f_2(\mathbf{x}_N) & \cdots & f_N(\mathbf{x}_N) \end{vmatrix}$$

Courtesy of Hai Lin

Many-electron Wave function (2)

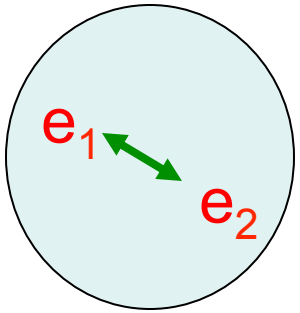
Example: A two-electron system.

Hartree product: Both electrons are independent.

$$\psi^{HP}(\mathbf{x}_1,\mathbf{x}_2) = f_1(\mathbf{x}_1) f_2(\mathbf{x}_2)$$

Slater determinant satisfies the Pauli principle.

$$\psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} f_1(\mathbf{x}_1) & f_2(\mathbf{x}_1) \\ f_1(\mathbf{x}_2) & f_2(\mathbf{x}_2) \end{vmatrix}$$



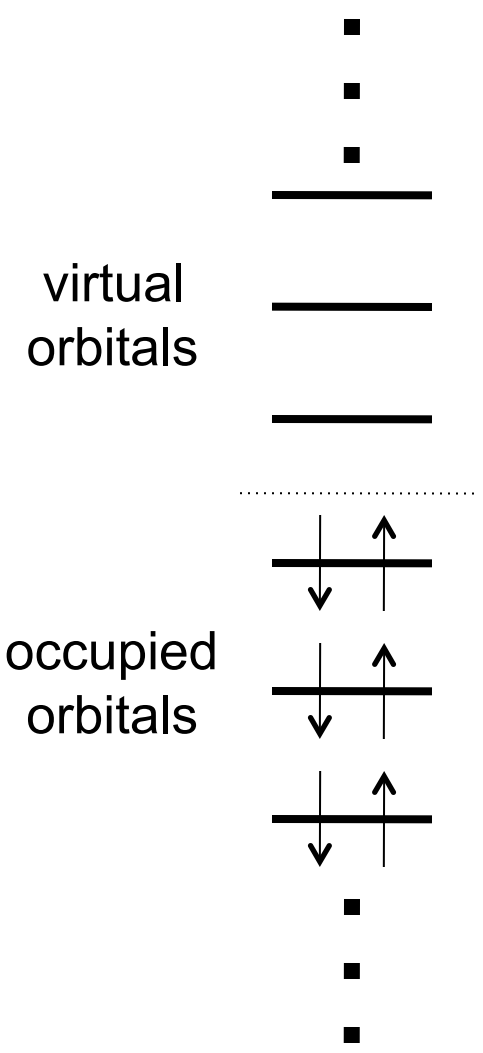
$$\psi(\mathbf{x}_1,\mathbf{x}_2) = (1/2)^{1/2}\left[f_1(\mathbf{x}_1) f_2(\mathbf{x}_2) - f_2(\mathbf{x}_1) f_1(\mathbf{x}_2)\right]$$

$$\psi(\mathbf{x}_2,\mathbf{x}_1) = (1/2)^{1/2}\left[f_1(\mathbf{x}_2) f_2(\mathbf{x}_1) - f_2(\mathbf{x}_2) f_1(\mathbf{x}_1)\right] = -\psi(\mathbf{x}_1,\mathbf{x}_2)$$

The total (many-electron) wavefuntion is anti-symmetric when one exchanges two electrons' coordinates $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$.

Courtesy of Hai Lin

Molecular Orbital & Slater Determinant



Single-electron wavefunction (orbital!!):

$\chi_i(\mathrm{x}_1)$: spin orbital

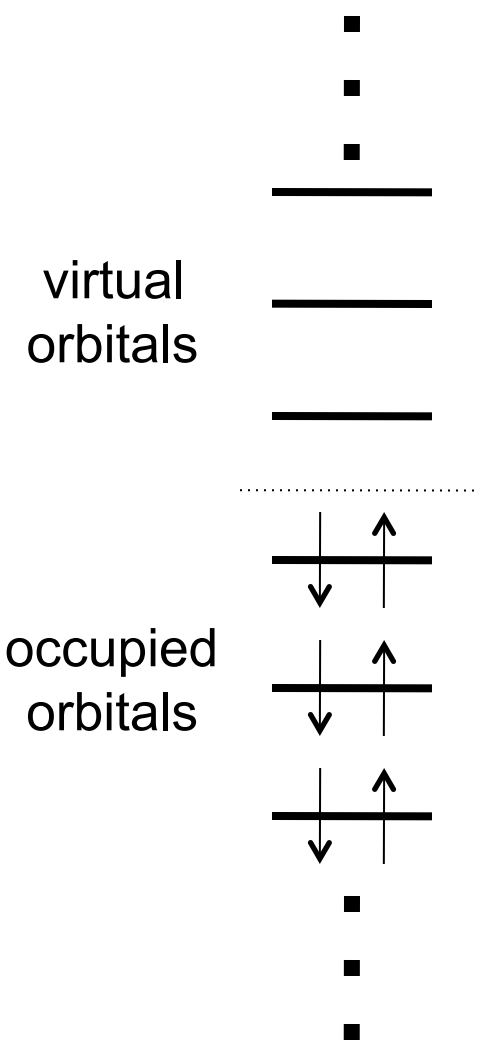
x_1 : electron variable

N-electron wavefunction: Slater determinants

$$\Psi(\mathrm{x}_1,\ldots,\mathrm{x}_N) = (N!)^{1/2}\begin{vmatrix} \chi_i(\mathrm{x}_1) & \chi_j(\mathrm{x}_1) & \cdots & \chi_k(\mathrm{x}_1) \\ \chi_i(\mathrm{x}_2) & \chi_j(\mathrm{x}_2) & \cdots & \chi_k(\mathrm{x}_N) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathrm{x}_N) & \chi_j(\mathrm{x}_N) & \cdots & \chi_k(\mathrm{x}_N) \end{vmatrix}$$

Given a basis, **Hartree-Fock theory** provides a variational groundstate & molecular orbitals within the single determinant approximation ➔ mean-field, no electron correlations

Molecular Orbital & Slater Determinant



Single-electron wavefunction (orbital!!):

$\chi_i(\mathrm{x}_1)$: spin orbital

x_1 : electron variable

N-electron wavefunction: Slater determinants

$$\Psi(\mathrm{x}_1,\ldots,\mathrm{x}_N) = (N!)^{1/2}\begin{vmatrix} \chi_i(\mathrm{x}_1) & \chi_j(\mathrm{x}_1) & \cdots & \chi_k(\mathrm{x}_1) \\ \chi_i(\mathrm{x}_2) & \chi_j(\mathrm{x}_2) & \cdots & \chi_k(\mathrm{x}_N) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathrm{x}_N) & \chi_j(\mathrm{x}_N) & \cdots & \chi_k(\mathrm{x}_N) \end{vmatrix}$$

Electron configuration: a many-electron wave function constructed from a single slater determinant

LCAO ➔ Basis Functions

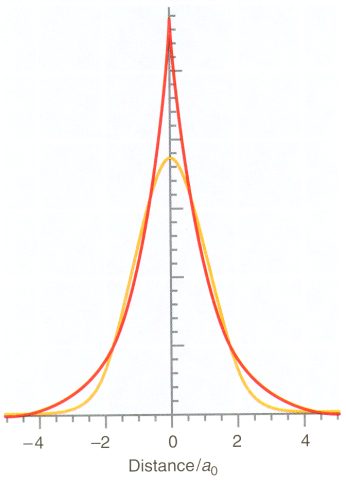
- Use a form that describes hydrogenic orbitals well
  - Slater functions (STO): physical, but difficult to calculate two-electron integrals
  - Gaussians (GTO): analytical two-electron integrals, but wrong behavior at nucleus and decays too fast with r

$$\phi_{1s}(\vec{r};\zeta_1) = \sqrt{\frac{\zeta_1^3}{\pi}}\exp(-\zeta_1\vec{r})$$

Slater function

$$g_s(\vec{r};\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\exp(-\alpha\vec{r}^{\,2})$$

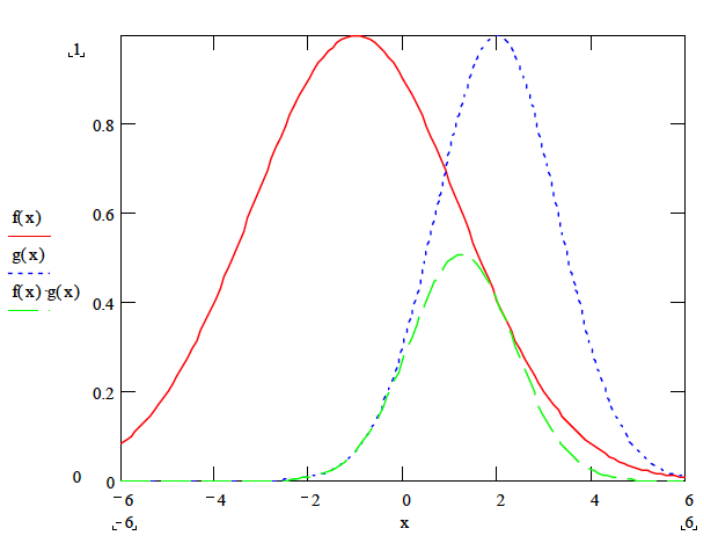
Gaussian



Gaussian Basis Functions

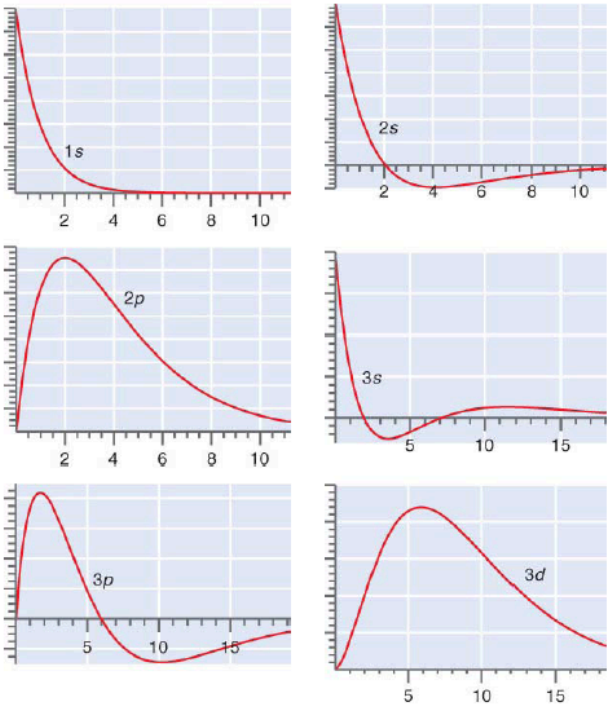
- GTOs have many advantages, most importantly, product of two Gaussians remains a Gaussian – analytical integrals

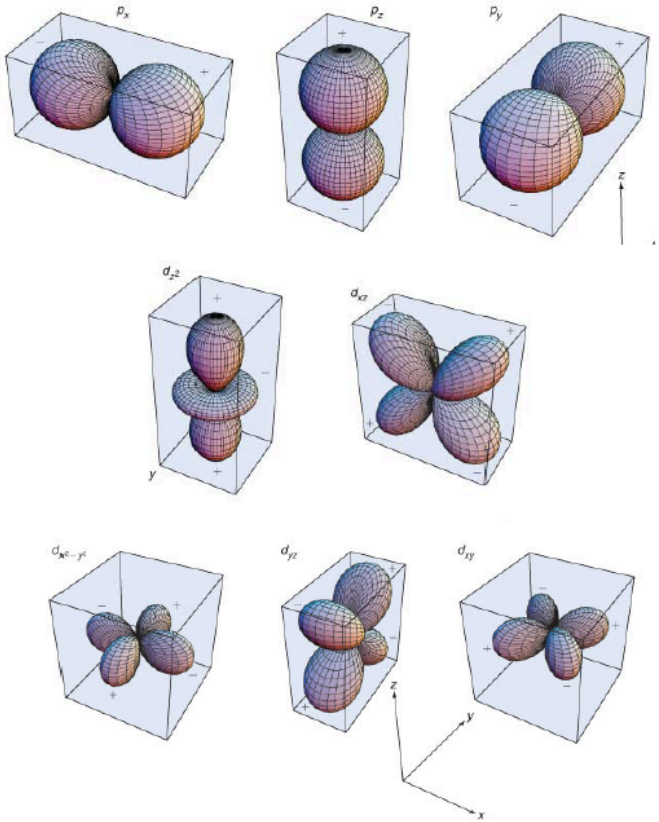
$$e^{-a_m r_m^2} e^{-a_n r_n^2} = e^{-\frac{a_m a_n}{a_m + a_n} r_{mn}^2} e^{-a r_c^2}$$

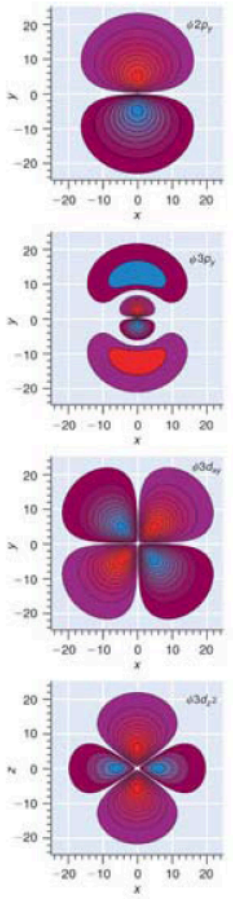


Basis Functions

Hydroden-like atomic orbitals

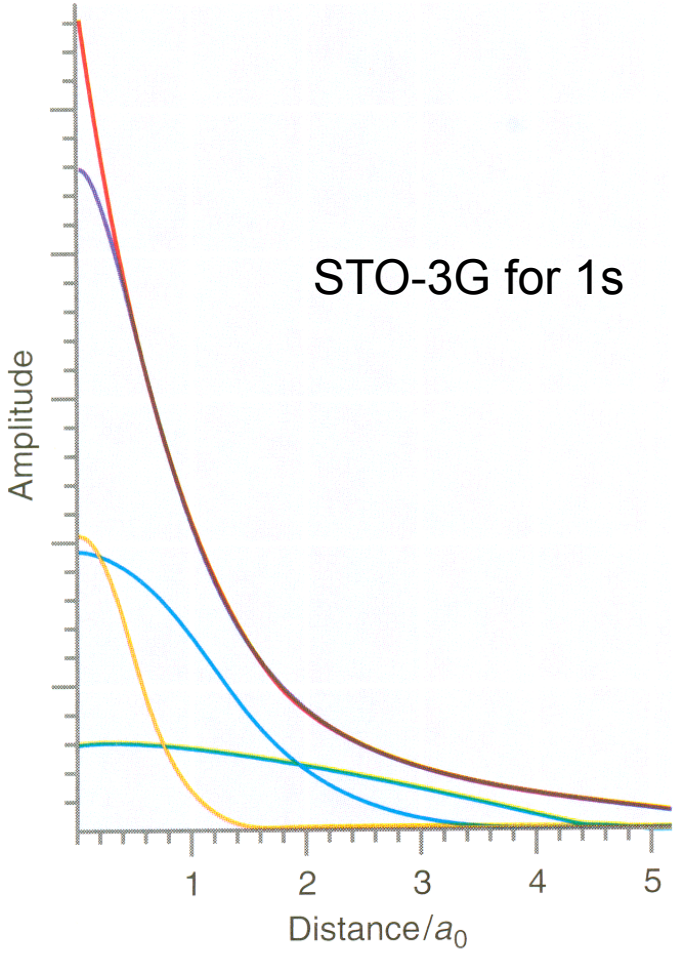






Ab initio Jargons: Basis Set

- STO-nG: use n Gaussians to approach a Slater-type orbital (**minimal basis set**)
- Many basis sets with different sizes and characteristics: STO-nG, 3-21G, 4-31G, 6-31G*, 6-311G**, cc-pVDZ, cc-pVTZ, aug-cc-pVDZ…
- Choose wisely according to the problem at hand



Limitations of HF-SCF

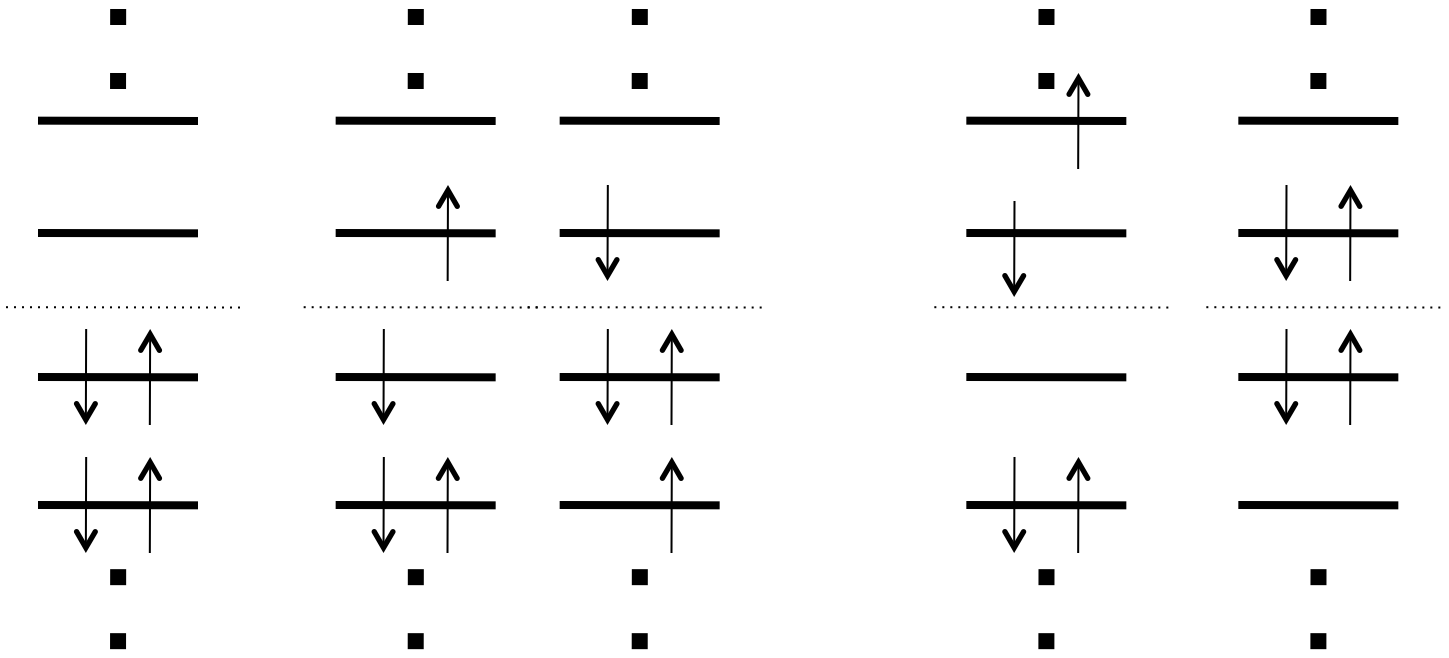
- The Hartree-Fock SCF method is limited by the single Slater determinant approximation
- HF-SCF calculation does not include the effects of electron correlation

$$E_{corr} = E_{exact} - E_{HF}$$

E_{corr}: correlation energy

Excited Configurations

Hartree-Fock groundstate is a good reference state that generates excited determinants (excited configurations)



➔ More!!

HF GS

$|\psi_0\rangle$

Single excitations

$|\psi_a^r\rangle$

Double excitations

$|\psi_{ab}^{rs}\rangle$

Configuration Interaction

Since the HF method yields the best single determinant wavefunction and provides about 99% of the total electronic energy, it is commonly used as the reference on which subsequent improvements are based.
As a starting point, consider as a trial function a linear combination of Slater determinants:

$$\Psi = a_0 \Phi_{HF} + \sum_{i=1} a_i \Phi_i$$

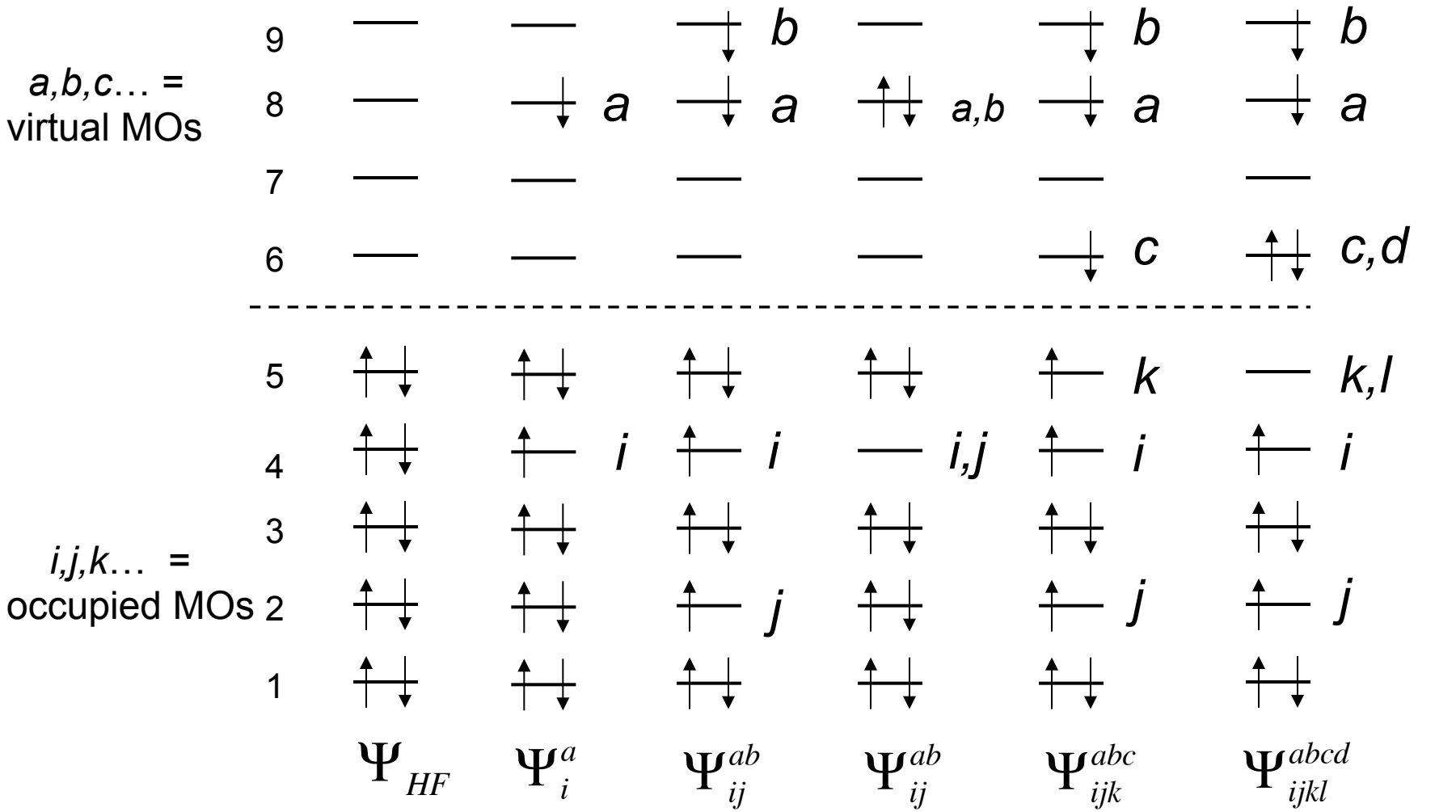
Multi-determinant wavefunction

a_0 is usually close to 1 (~0.9).

- M basis functions yield M molecular orbitals.
- For N electrons, N/2 orbitals are occupied in the RHF wavefunction.
- M-N/2 are unoccupied or virtual (anti-bonding) orbitals.

Courtesy of Sourav Pal, National Chemical Laboratory

Generate excited Slater determinants by promoting up to N electrons from the N/2 occupied to M-N/2 virtuals:



Represent the space containing all N-fold excitations by $\Psi(N)$.

Then the COMPLETE CI wavefunction has the form

$$\Psi_{CI} = C_0\Phi_{HF} + \Phi^{(1)} + \Phi^{(2)} + \Phi^{(3)} + \ldots + \Phi^{(N)} + \ldots$$

Where

$$\Phi_{HF} = Hartree - Fock$$

$$\Phi^{(1)} = \sum_{i}^{occ}\sum_{a}^{virt} C_i^a \Psi_i^a$$

Linear combination of Slater determinants with single excitations

$$\Phi^{(2)} = \sum_{i,j}^{occ}\sum_{a,b}^{virt} C_{ij}^{ab} \Psi_{ij}^{ab}$$

Doubly excitations

$$\Phi^{(3)} = \sum_{i,j,k}^{occ}\sum_{a,b,c}^{virt} C_{ijk}^{abc} \Psi_{ijk}^{abc}$$

Triples

$$\Phi^{(N)} = \sum_{i,j,k\ldots}^{occ}\sum_{a,b,c\ldots}^{virt} C_{ijk\ldots}^{abc\ldots} \Psi_{ijk\ldots}^{abc\ldots}$$

N-fold excitation

The complete Ψ_{CI} expanded in an infinite basis yields the exact solution to the Schrödinger eqn. (Non-relativistic, Born-Oppenheimer approx.), often used as benchmark.

The various coefficients, $C_{ijk\ldots}^{abc\ldots}$, may be obtained in a variety of ways.
A straightforward method is to use the Variation Principle.

$$E_{CI} = \frac{\langle \Psi_{CI} | H | \Psi_{CI} \rangle}{\langle \Psi_{CI} | \Psi_{CI} \rangle}$$

Expectation value of H_e.

$$\partial E_{CI} \Big/ \partial C_{ijk\ldots}^{abc\ldots} = 0$$

Energy is minimized wrt coeff

$$H\vec{C}_K = E_K \vec{C}_K$$

In a fashion analogous to the HF eqns, the CI Schrodinger equation can be formulated as a matrix eigenvalue problem.

The elements of the vector, $\vec{C}_K$, are the coefficients, $C_{ijk\ldots}^{abc\ldots}$
And the eigenvalue, E_K, approximates the energy of the K^{th} state.

$E_1 = E_{CI}$ for the lowest state of a given symmetry and spin.
E_2 = 1st excited state of the same symmetry and spin, and so on.

Electron Correlation & Configuration Interaction

All these determinants form a new & complete basis

$$H\Psi = E\Psi$$

	$\lvert\Psi_0\rangle$	$\lvert\Psi_a^r\rangle$	$\lvert\Psi_{ab}^{rs}\rangle$	$\lvert\Psi_{abc}^{rst}\rangle$	$\lvert\Psi_{abcd}^{rstu}\rangle$	$\cdots$
		$\lvert S\rangle$	$\lvert D\rangle$	$\lvert T\rangle$	$\lvert Q\rangle$	$\cdots$
$\langle\Psi_0\rvert$	$\langle\Psi_0\rvert\mathscr{H}\lvert\Psi_0\rangle$	0	$\langle\Psi_0\rvert\mathscr{H}\lvert D\rangle$	0	0	$\cdots$
$\langle S\rvert$		$\langle S\rvert\mathscr{H}\lvert S\rangle$	$\langle S\rvert\mathscr{H}\lvert D\rangle$	$\langle S\rvert\mathscr{H}\lvert T\rangle$	0	$\cdots$
$\langle D\rvert$			$\langle D\rvert\mathscr{H}\lvert D\rangle$	$\langle D\rvert\mathscr{H}\lvert T\rangle$	$\langle D\rvert\mathscr{H}\lvert Q\rangle$	$\cdots$
$\langle T\rvert$				$\langle T\rvert\mathscr{H}\lvert T\rangle$	$\langle T\rvert\mathscr{H}\lvert Q\rangle$	$\cdots$
$\langle Q\rvert$					$\langle Q\rvert\mathscr{H}\lvert Q\rangle$	$\cdots$
$\vdots$						$\vdots$

$$\langle S|\mathscr{H}|T\rangle \leftrightarrow \langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle$$
$$\langle D|\mathscr{H}|D\rangle \leftrightarrow \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cd}^{tu}\rangle$$

full CI matrix

- Eigenfunctions are now superpositions of determinants
- Constructing & diagonalizing the matrix to obtain CI ground & excited-states with electron correlation effects
- Full CI (FCI) is generally impossible, one must truncate at some level → CIS, CISD, CISD(T), …, FCI
- **CIS** describes a large array of low-lying excitations

Szabo & Ostlund

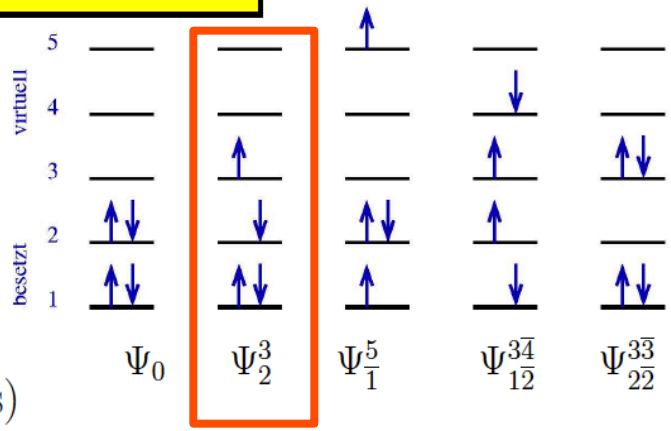
METHODS TO TREAT ELECTRON CORRELATION

- **Form of exact wavefunction and configuration interaction (CI) methods**

$$\Psi = \underbrace{\underbrace{D_0\Psi_0}_{\text{HF}} + \underbrace{\sum_{a=1}^{N}\sum_{r=N+1}^{N_{\text{virt}}} D_a^r \Psi_a^r}_{\text{CI Singles}}}_{\text{CI Singles Doubles}} + \underbrace{\sum_{a<b}^{N}\sum_{r<s}^{N_{\text{virt}}} D_{ab}^{rs}\,\Psi_{ab}^{rs}}_{\text{CI Doubles}} + \underbrace{\ldots \text{N-excitations}}_{\text{Full CI, FCI}}$$

❶ correlation energy

❷ excited states: $\underline{\underline{H}}^{CI}\,\underline{D}_n = E_n\,\underline{D}_n$



- **Variants of CI-type methods**
  - MCSCF and CASSCF (vary amplitudes and orbitals)
  - Coupled Cluster (CC) methods: $\Psi = \underbrace{\underbrace{\exp(\hat{T}_1}_{\text{CCS}} + \hat{T}_2 + \ldots \hat{T}_N)}_{\text{CCSD}}\ \Psi_0$ (Full CI)

HOMO→LUMO transition

- **Non-variational: Møller-Plesset perurbation theory (MP2, MP3, ...)**

Slide of Peter Saalfrank

Cost of Methods in Computational Chemistry

	Quality	Size dependence
• *Ab initio MO Methods*		
– CCSD(T)	quantitative (1~2 kcal/mol) but expensive	~N^6
– MP2	semi-quantitative and doable	~N^4
– HF	qualitative	~N^{2-3}
• *Density Functional Theory*		
– DFT	semi-quantitative and cheap	~N^{2-3}
• *Semi-empirical MO Methods*		
– AM1, PM3, MNDO	semi-qualitative	~N^{2-3}
• Molecular Mechanics Force Field		
– MM3, Amber, Charmm	semi-qualitative (no bond-breaking)	~N^{1-2}

Using a quantum computer??

Hamiltonian in Second Quantization

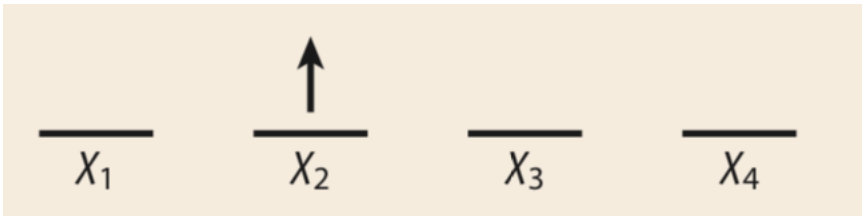
The **CI** Hamiltonian in the second-quantized form is

$$H\Psi = E\Psi$$

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s ,$$

p, q, r, s are **orbital** indecies

CI basis states (Slater determinants) can be compactly encoded in a quantum computer → occupation number states



$|\psi\rangle = |0100\rangle$

M spin orbitals → M qubits → 2^M Fock states (0 - M electrons)

FCI classically requires M choose N determinants for N-electron states

Quantum Advantage?

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s ,$$

- Classical computer: explicitly construct the FCI matrix with exponentially-large number of matrix elements → not possible
- Quantum computer: implement H (N^4 terms) with parameters (h_{pq} & h_{pqrs} provided by a classical HF calculation), then quantum mechanics takes care of the matrix elements → needs only M qubits
- Construction based on "***state and matrix elements***" versus that based on "***operators***"

Quantum Computation of Quantum Chemistry

i.e. FULL CI

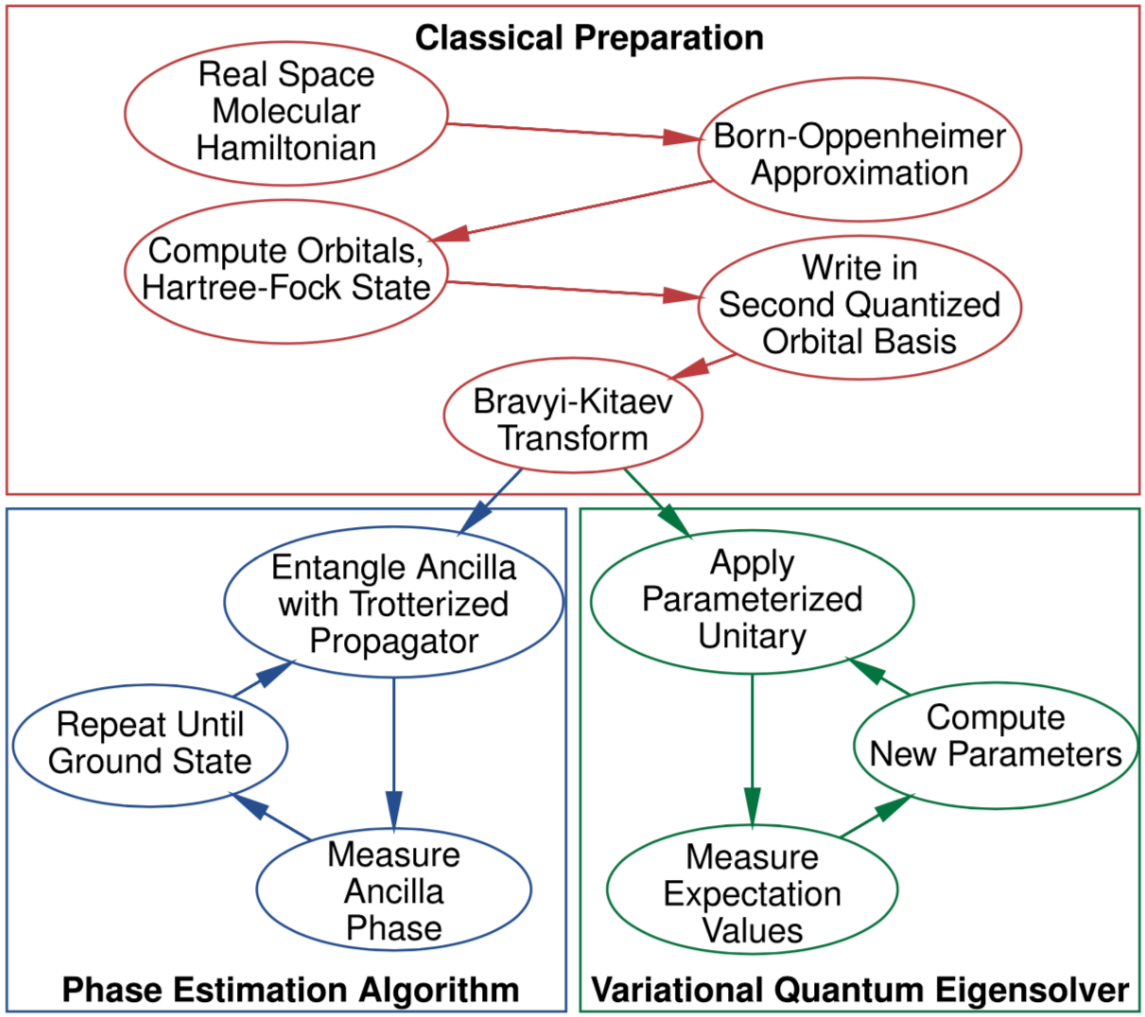
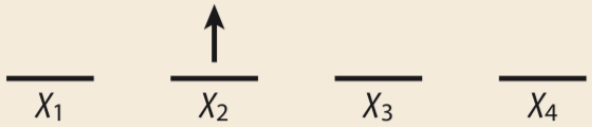
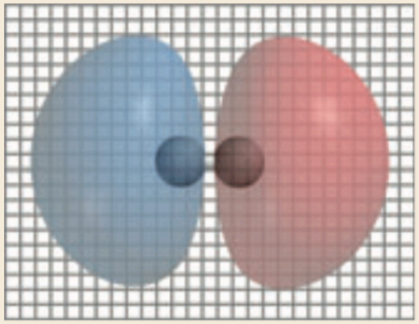


FIG. 5. A flow chart describing steps required to quantum compute molecular energies using both PEA and VQE.

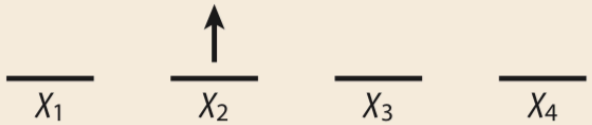
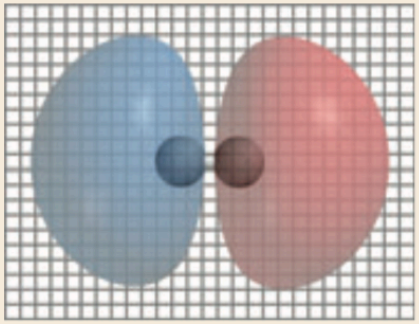
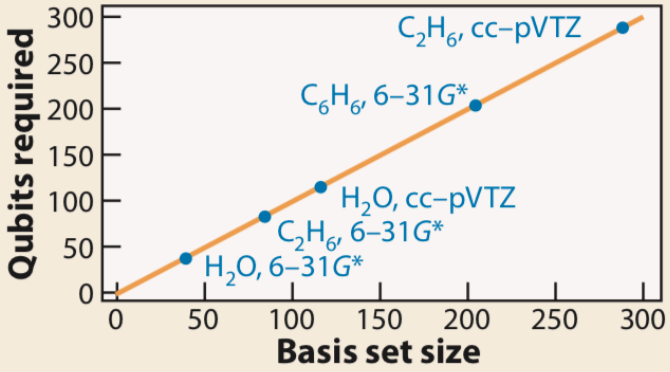
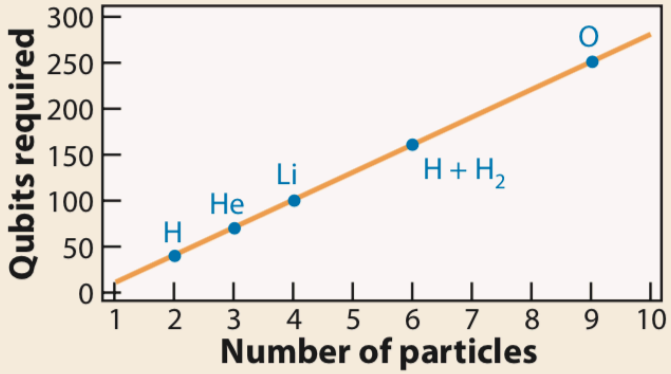
(paper #2)

Table 1 Comparison of second- and first-quantization approaches to quantum simulation

	Second quantized	First quantized
Wave-function encoding	Fock state in a given basis:  $\|\psi\rangle = \|0100\rangle$	On a grid of 2^n sites per dimension: $\|\psi\rangle = \sum_x a_x \|x\rangle$ 
Molecular Hamiltonian	Coefficients precomputed classically: $\sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$	Interaction calculated on the fly: $\sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} \frac{q_i q_j}{r_{ij}}$
Quantum gates required for simulation	$O(M^5)$ with number of basis states	$O(B^2)$ with number of particles
Advantages	• Compact wave-function representation (requires fewer qubits) • Takes advantage of classical electronic-structure theory to improve performance • Already experimentally implemented	• Better asymptotic scaling (requires fewer gates) • Treats dynamics better • Can be used for computing reaction rates or state-to-state transition amplitudes

(paper #1)

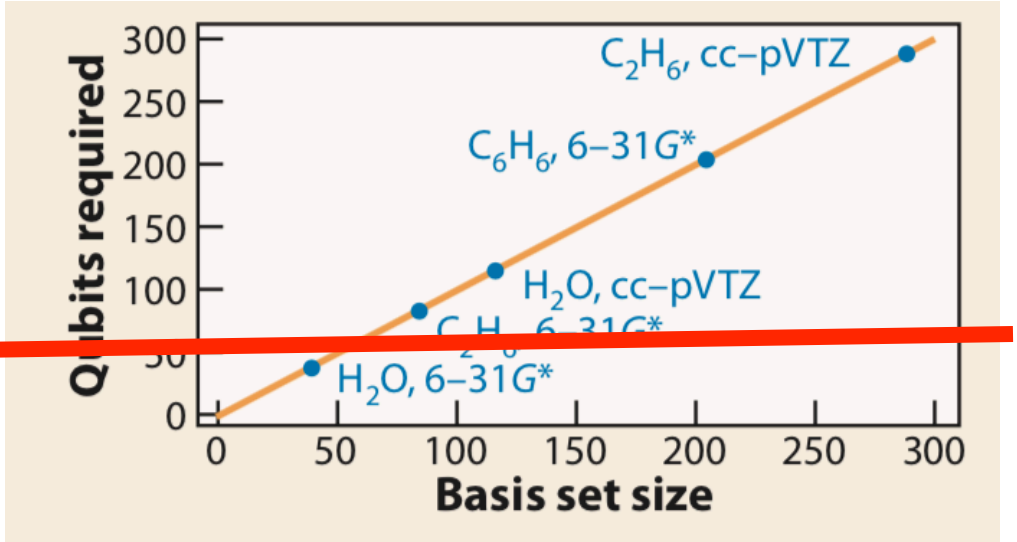
Table 1 Comparison of second- and first-quantization approaches to quantum simulation

	Second quantized	First quantized
Wave-function encoding	Fock state in a given basis:  $\|\psi\rangle = \|0100\rangle$	On a grid of 2^n sites per dimension: $\|\psi\rangle = \sum_x a_x \|x\rangle$ 
Qubits required to represent the wave function	One per basis state (spin-orbital): 	3n per particle (nuclei and electrons): 
Molecular Hamiltonian	Coefficients precomputed classically: $\sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$	Interaction calculated on the fly: $\sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} \frac{q_i q_j}{r_{ij}}$

(paper #1)

Critical Review of QCoQC

- Quantum supremacy?

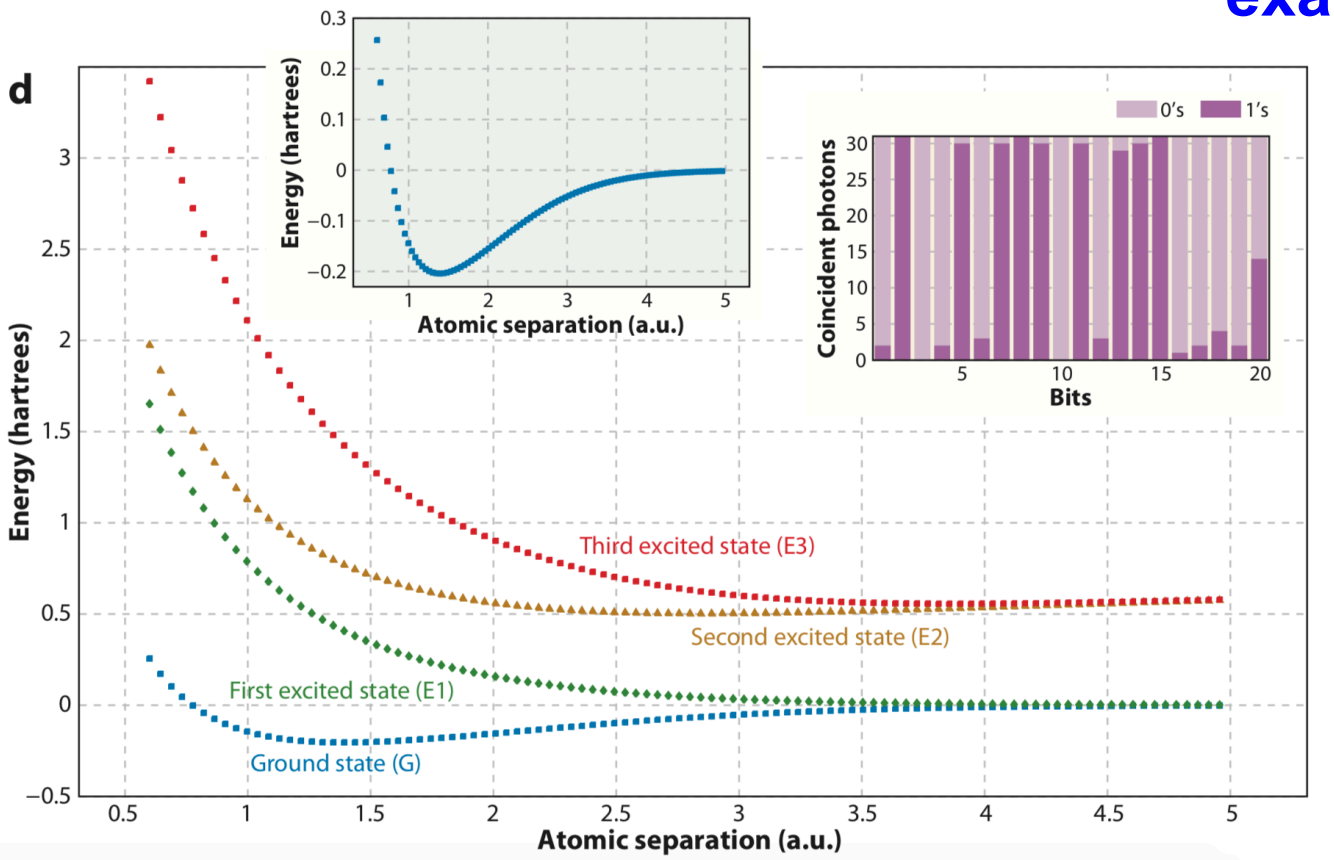


- Doing FCI on 6-31G* water would be (almost) impossible on classical computers… But this does not mean QC has an absolute advantage here
- Very accurate ***classical*** first-principle simulation of C_6H_6 is possible ***with the right approximations***

Critical Review of QCoQC

- Experimental simulation of H_2 energy curve on a linear optical quantum computer:

exact FCI results??

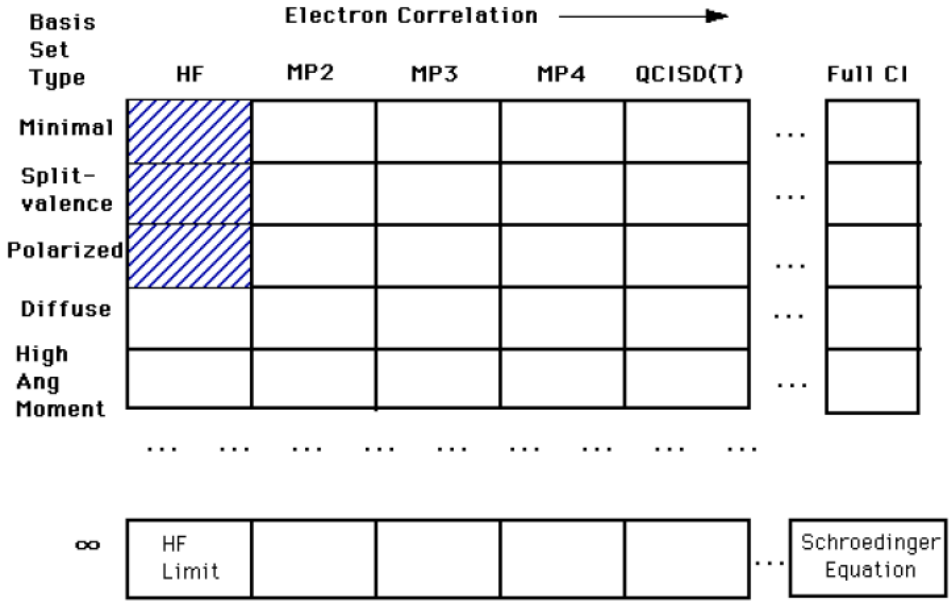


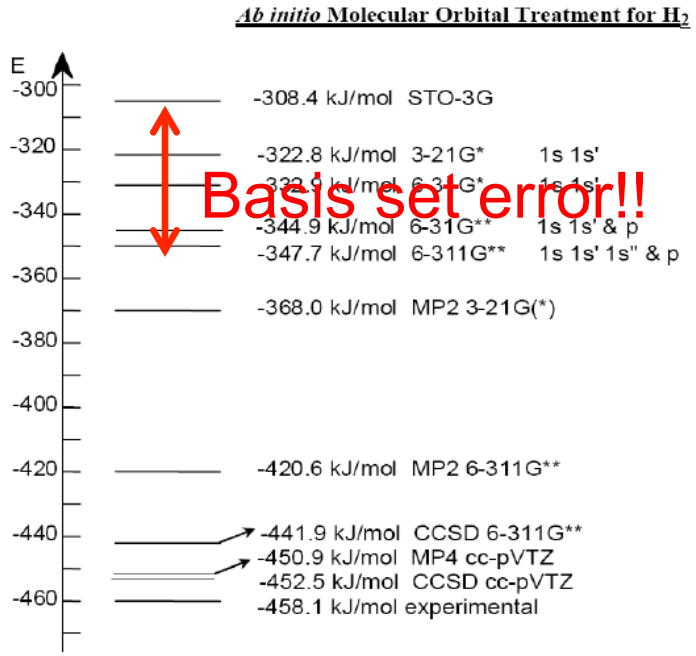
the optical elements used to implement the quantum gates on photonic polarization qubits. (*d*) The computed potential energy surfaces of the H_2 molecule in a minimal-basis set. The results are the exact (in the basis) full-configuration-interaction energies, to 20 bits of precision.

(paper #1)

Exact *assuming* minimal basis set – this is not acceptable!!!

Accuracy of ab initio Quantum Chemistry Methods

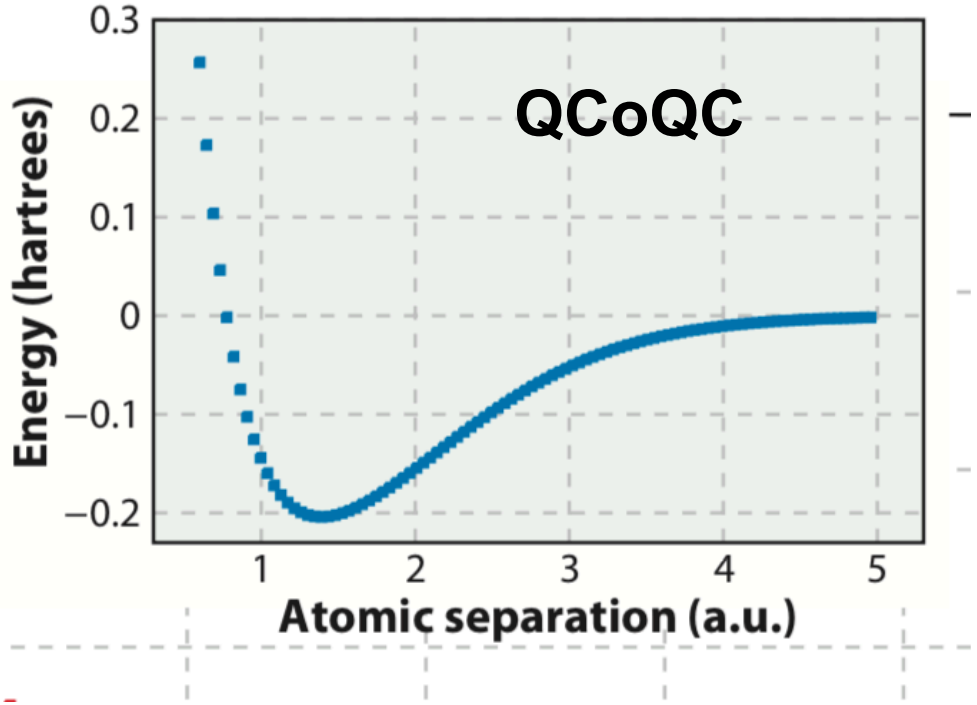




The minimal basis results are not accurate enough to be compared to experiments!!

Critical Review of QCoQC

- Experimental H_2 bond length = 1.4 a.u., bond dissociation energy = 0.1744 a.u.



(paper #1)

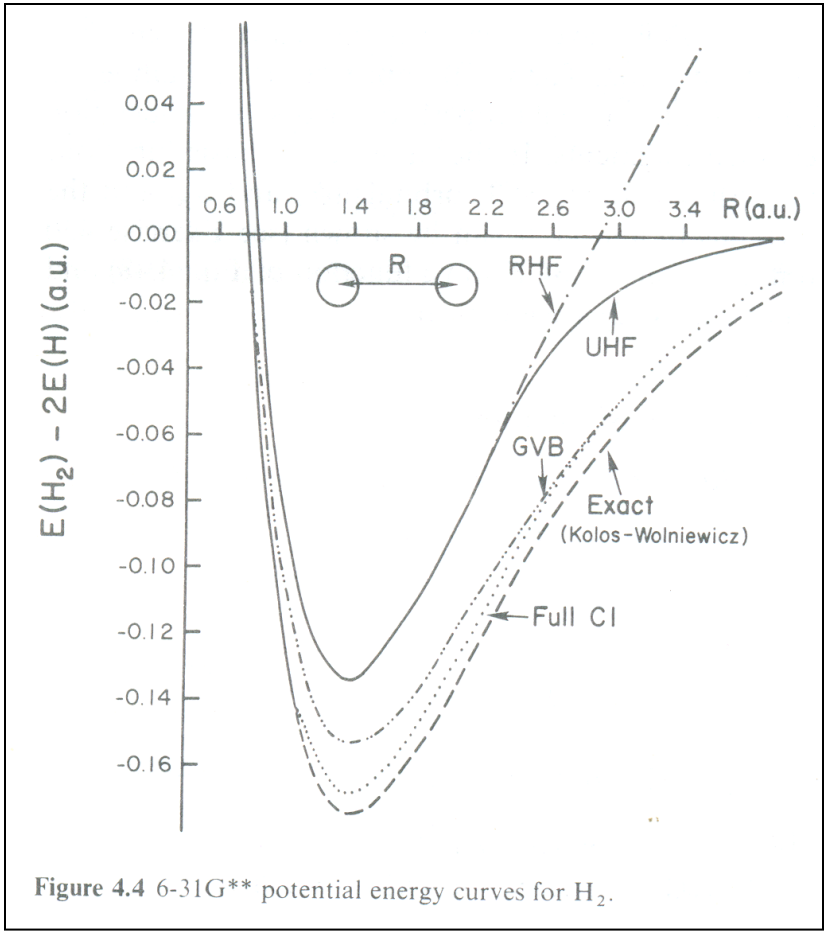
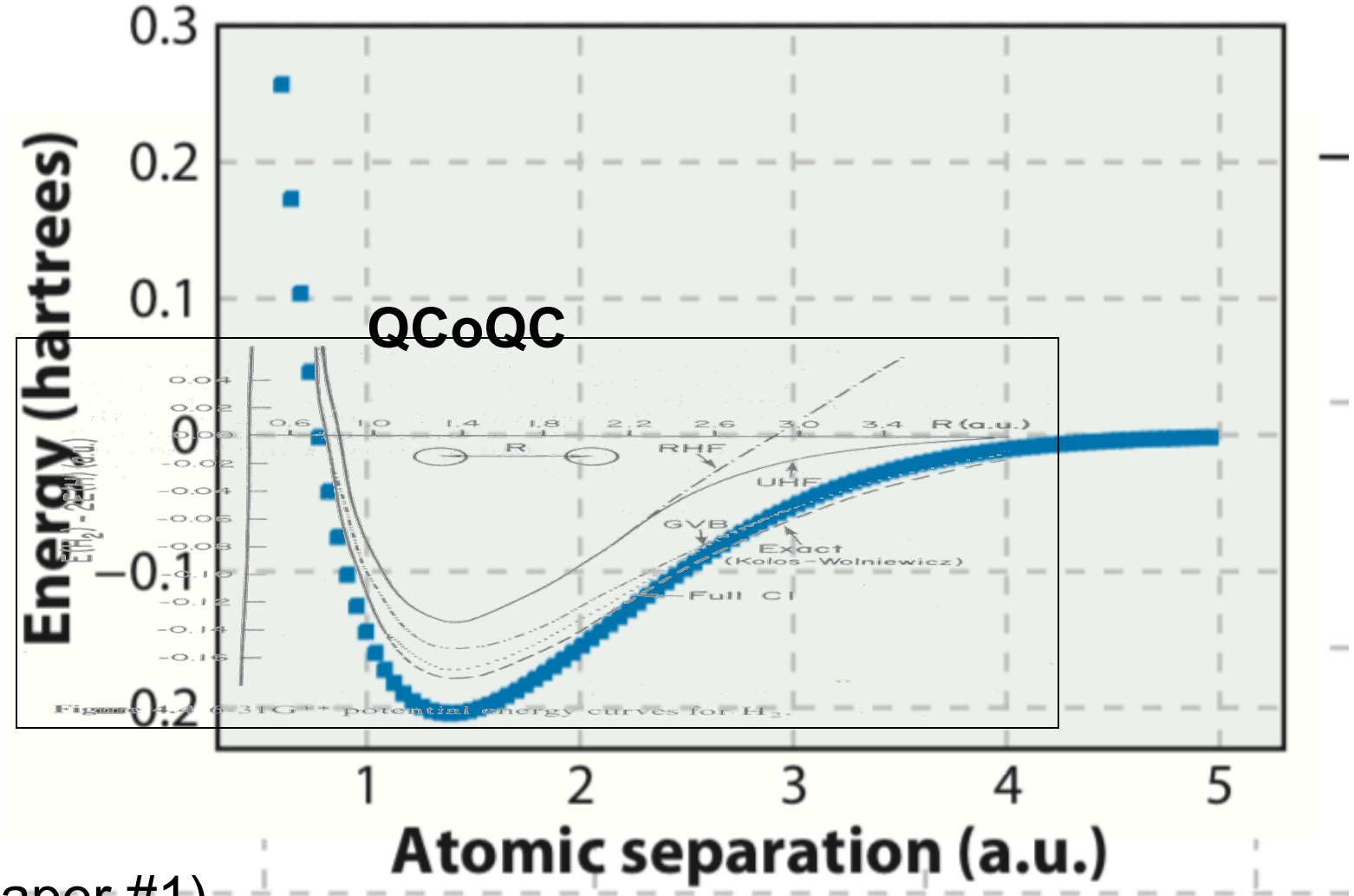


Figure 4.4 6-31G** potential energy curves for H_2.

Critical Review of QCoQC



(paper #1)

Critical Review of the State-of-the-Art

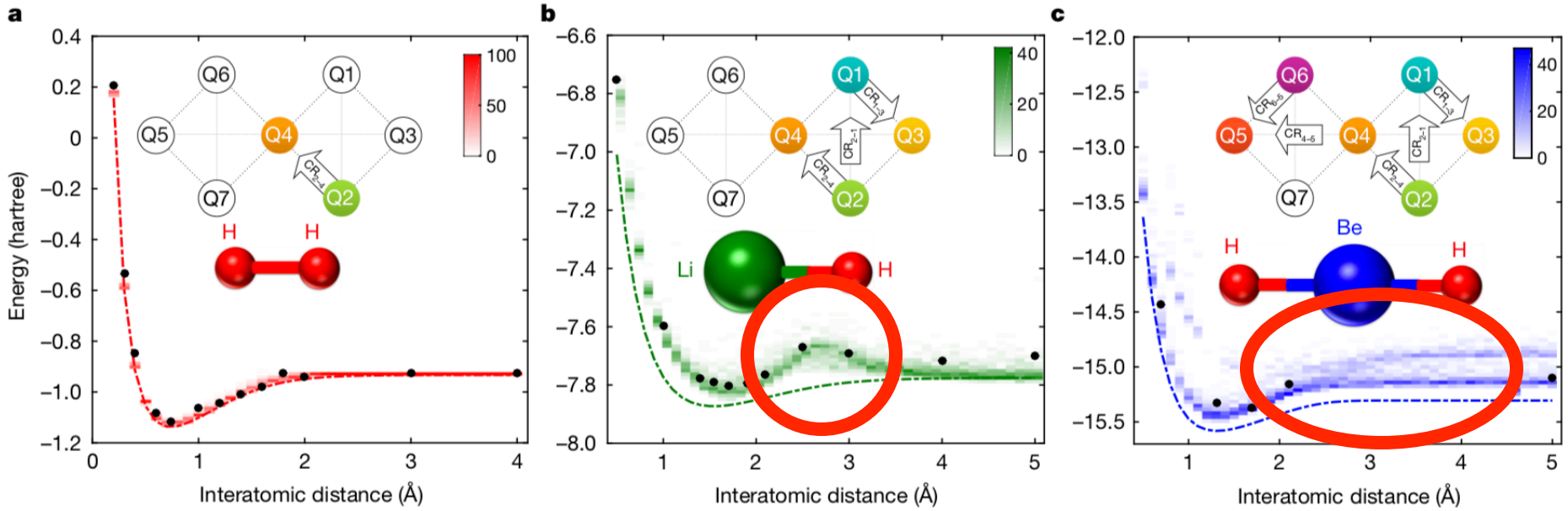


Figure 3 | Application to quantum chemistry. a–c, Experimental results (black filled circles), exact energy surfaces (dotted lines) and density plots (shading; see colour scales) of outcomes from numerical simulations, for several interatomic distances for H_2 (**a**), LiH (**b**) and BeH_2 (**c**). The experimental and numerical results presented are for circuits of depth $d = 1$. The error bars on the experimental data are smaller than the size of the markers. The density plots are obtained from 100 numerical outcomes at each interatomic distance. The top insets in each panel highlight the qubits used for the experiment and the cross-resonance gates (arrows, labelled CR_{c-t}; where 'c' denotes the control qubit and 't' the target qubit) that constitute U_{ENT}. The bottom insets are representations of the molecular geometry (not to scale). For all the three molecules, the deviation of the experimental results from the exact curves is well explained by the stochastic simulations.

- Also minimal basis -→ "exact" not actually "exact"
- Generally speaking, the results are ***qualitatively*** poor⋯

Kandala et al., Nature 549, 242, 2017.

Critical Review of the State-of-the-Art

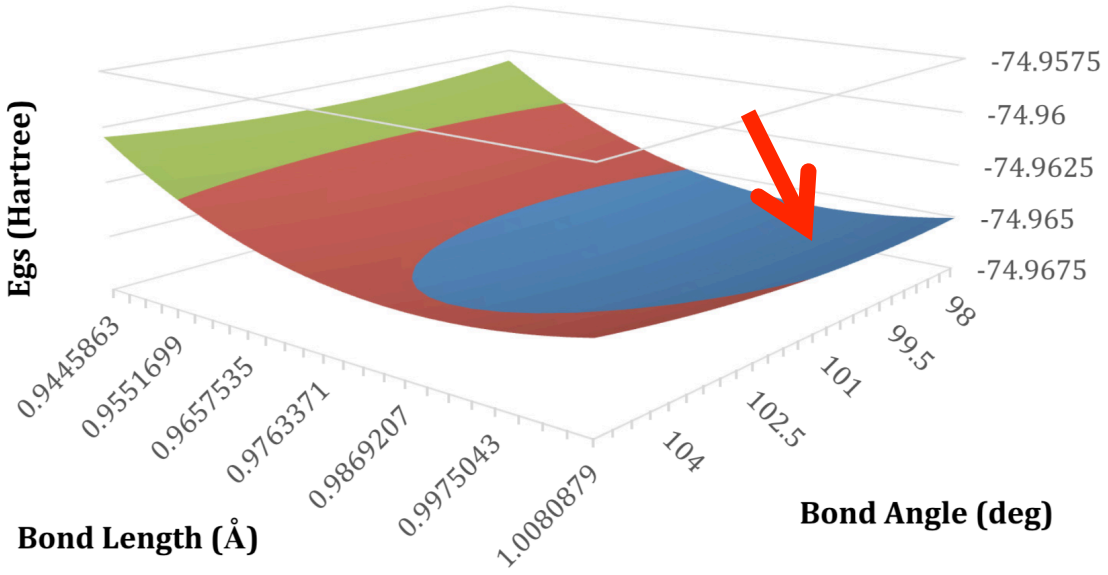


FIG. 1. (Color online) This figure shows the energy of the water molecule as a function of bond angle and bond length for an STO-3G basis obtained from a restricted HF calculation.

- STO-3G basis
- Again, comparison to "exact" results is also claimed
- What will be the equilibrium geometry of this water molecule?

In Fig. 1, we show the energy of a water molecule as a function of bond length and bond angle as obtained from our simulated QFCI calculation. Figure 2 shows the dependence

Wecker et al., PRA 90, 022305, 2014.

Remarks

- Doing quantum chemistry on a quantum computer might be useful, but the current software and hardware must be upgraded → research challenges for innovative ones
- Classical computers still outperform quantum ones, ***significantly***!!
- We need to: increase size, reduce circuit depth, go beyond the minimal basis set model, and utilize classical computers
- Paper #1 & paper #2: check the current status
- Paper #3 & paper #4: ideas for going beyond
- There is still much to learn… but haste is essential!!