

Quantum Chemistry:

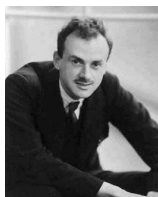
A Branch of Applied Mathematics

Yihan Shao

University of Oklahoma

November 29, 2017

Quantum Chemistry



Paul Dirac

Quote:

“The underlying physical laws necessary for the mathematical theory of **a large part of physics and the whole of chemistry** are thus completely known, and the difficulty is only that the exact application of these laws leads to **equations much too complicated to be soluble**. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. ”

Dirac, Proc. R. Soc. London A, 123, 714 (1929).

- 1 Matrix Diagonalizations in Quantum Chemistry
 - Hückel Molecular Orbital Calculations of Fullerenes
 - Excited State Calculations
 - Response Kernel Calculations
- 2 Electron Integrals and Fast Multipole Method
 - Integrals Over Gaussian Functions
 - Fast Multipole Method
- 3 Technical Challenges

Hückel Theory for π -electrons



Erich Hückel



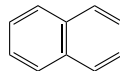
C₄H₄
cyclobutadiene



C₆H₆
benzene



C₈H₈
cyclooctatetraene



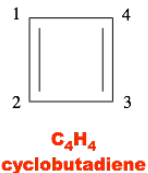
C₁₀H₈
Naphthalene

- Separation of π and σ electrons
- $(4n + 2)$ -rule

Hückel, Z. Phys. 70, 204 (1931); 72, 310 (1931); 76, 628 (1932); 83, 632 (1933).

Hückel Theory for π -electrons

Molecule



Hamiltonian (H)

$$\alpha + \beta \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}$$

$$H\psi = \lambda\psi$$

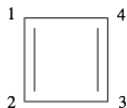
$$\lambda = \begin{cases} \alpha - 2\beta \\ \alpha, \alpha \\ \alpha + 2\beta \end{cases}$$

Hückel Theory for π -electrons

Molecule

Hamiltonian (H)

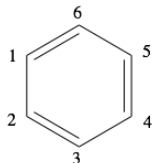
$$H\psi = \lambda\psi$$



C₄H₄
cyclobutadiene

$$\alpha + \beta \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}$$

$$\lambda = \begin{cases} \alpha - 2\beta \\ \alpha, \alpha \\ \alpha + 2\beta \end{cases}$$

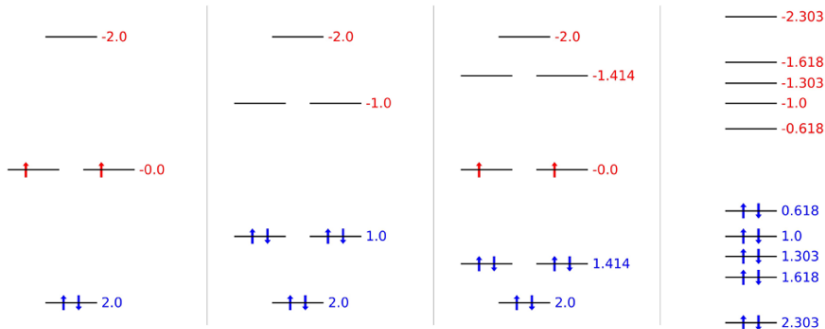


C₆H₆
benzene

$$\alpha + \beta \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\lambda = \begin{cases} \alpha - 2\beta \\ \alpha - \beta, \alpha - \beta \\ \alpha + \beta, \alpha + \beta \\ \alpha + 2\beta \end{cases}$$

Hückel Theory for π -electrons



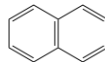
C_4H_4
cyclobutadiene



C_6H_6
benzene

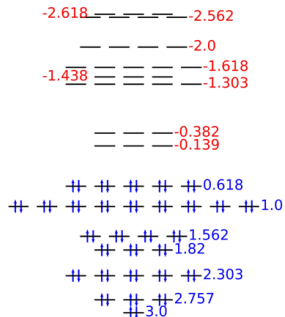
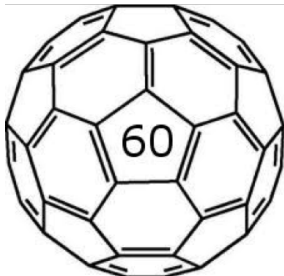


C_8H_8
cyclooctatetraene



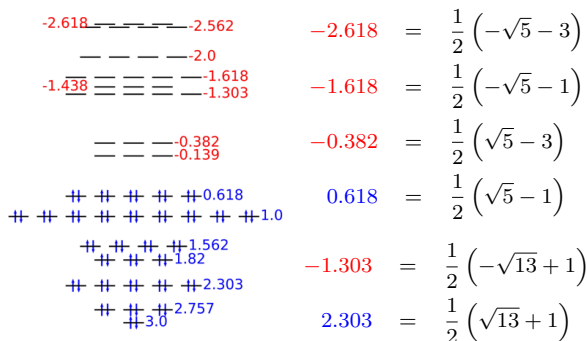
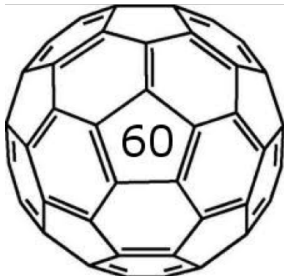
$C_{10}H_8$
Naphthalene

Hückel Calculations of C₆₀



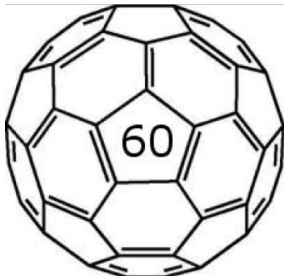
Liu, Shao and Jiang, Chem. Phys. Lett. 210, 149 (1993); 228, 131 (1994).

Hückel Calculations of C₆₀



Liu, Shao and Jiang, Chem. Phys. Lett. 210, 149 (1993); 228, 131 (1994).

Hückel Calculations of C₆₀

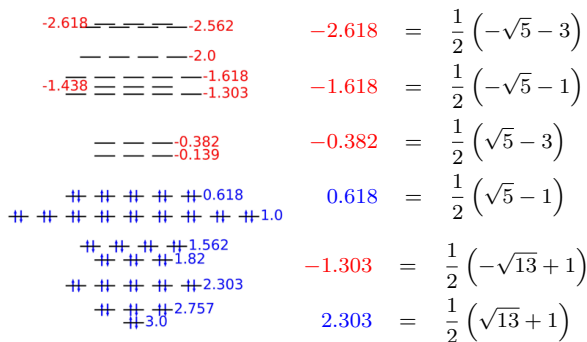


$$\begin{array}{rcl}
 \text{---} & -2.618 & \text{---} & -2.562 & -2.618 & = & \frac{1}{2}(-\sqrt{5}-3) \\
 \text{---} & & \text{---} & -2.0 & & & \\
 \text{---} & -1.438 & \text{---} & -1.618 & -1.618 & = & \frac{1}{2}(-\sqrt{5}-1) \\
 & & & & & & \\
 & & \text{---} & -0.382 & -0.382 & = & \frac{1}{2}(\sqrt{5}-3) \\
 & & & & & & \\
 \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & 0.618 & 0.618 & = & \frac{1}{2}(\sqrt{5}-1) \\
 \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & 1.0 & \\
 & \text{++} & \text{++} & \text{++} & \text{++} & 1.562 & & & & \\
 & & \text{++} & \text{++} & \text{++} & 1.82 & & & & \\
 \text{++} & \text{++} & \text{++} & \text{++} & \text{++} & 2.303 & -1.303 & = & \frac{1}{2}(-\sqrt{13}+1) \\
 & \text{++} & \text{++} & \text{++} & \text{++} & 2.757 & & & & \\
 & & \text{++} & \text{++} & \text{++} & 3.0 & 2.303 & = & \frac{1}{2}(\sqrt{13}+1)
 \end{array}$$

$$-2.562 = \frac{1}{2}(-\sqrt{17}-1)$$

$$1.562 = \frac{1}{2}(\sqrt{17}-1)$$

Liu, Shao and Jiang, Chem. Phys. Lett. 210, 149 (1993); 228, 131 (1994).



$$-2.562 = \frac{1}{2} \left(-\sqrt{17} - 1 \right)$$

$$1.562 = \frac{1}{2} (\sqrt{17} - 1)$$

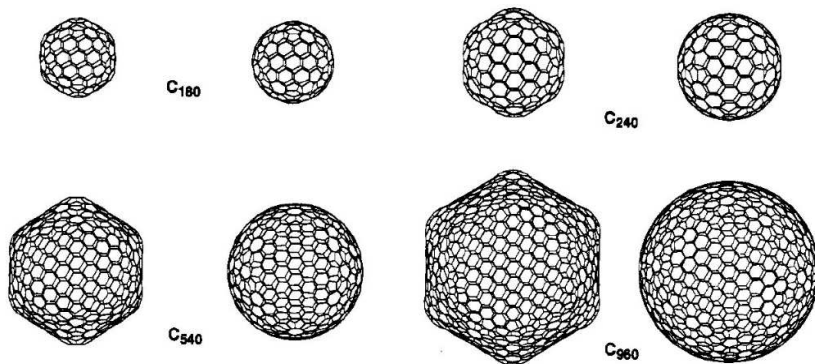
$$\textcolor{red}{-1.438}, \textcolor{blue}{1.820} = \frac{1}{4} \left(3 - \sqrt{5} \mp \sqrt{38 + 2\sqrt{5}} \right)$$

$$-0.139, 2.757 = \frac{1}{4} \left(3 + \sqrt{5} \mp \sqrt{38 - 2\sqrt{5}} \right)$$

Liu, Shao and Jiang, Chem. Phys. Lett. 210, 149 (1993); 228, 131 (1994).

Hückel Calculations of Larger Fullerenes

- To solve the Hückel energy spectrum of larger fullerenes
 - group theory
 - Lanczos method for iterative diagonalization



Liu, Wang, Shao and Jiang, Phys. Lett. A 196, 120 (1994). Liu, Shao and Jiang, Croat. Chem. Acta, 69, 201 (1996).

Application of Lanczos Method in HMO Calculations

Goal: $\mathbf{H}\psi = \lambda\psi$

- \mathbf{H} is a very sparse matrix. Do not want to save it explicitly.

Application of Lanczos Method in HMO Calculations

Goal: $\mathbf{H}\psi = \lambda\psi$

- \mathbf{H} is a very sparse matrix. Do not want to save it explicitly.

Lanczos Steps

- 1: Obtain an initial vector, \mathbf{u}_1
- 2: Obtain the second vector,

$$\begin{aligned}\mathbf{u}_2 &= \mathbf{H}\mathbf{u}_1 - a_1\mathbf{u}_1 \\ a_1 &= \langle \mathbf{u}_1 | \mathbf{H} | \mathbf{u}_1 \rangle / \langle \mathbf{u}_1 | \mathbf{u}_1 \rangle\end{aligned}$$

- 3. Add basis vectors till residual is zero.

$$\begin{aligned}\mathbf{u}_k &= \mathbf{H}\mathbf{u}_{k-1} - a_{k-1}\mathbf{u}_{k-1} - b_{k-1}\mathbf{u}_{k-2} \\ a_{k-1} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_{k-1} \rangle / \langle \mathbf{u}_{k-1} | \mathbf{u}_{k-1} \rangle \\ b_{k-1} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_{k-2} \rangle / \langle \mathbf{u}_{k-2} | \mathbf{u}_{k-2} \rangle\end{aligned}$$

- 4. Diagonalize the final tridiagonal matrix

C. Lanczos, J. Res. Nat. Bur. Std. 45, 255 (1950).

Application of Lanczos Method in HMO Calculations

Goal: $\mathbf{H}\psi = \lambda\psi$

- \mathbf{H} is a very sparse matrix. Do not want to save it explicitly.

Lanczos Steps

- 1: Obtain an initial vector, \mathbf{u}_1
- 2: Obtain the second vector,

$$\begin{aligned}\mathbf{u}_2 &= \mathbf{H}\mathbf{u}_1 - a_1\mathbf{u}_1 \\ a_1 &= \langle \mathbf{u}_1 | \mathbf{H} | \mathbf{u}_1 \rangle / \langle \mathbf{u}_1 | \mathbf{u}_1 \rangle\end{aligned}$$

- 3. Add basis vectors till residual is zero.

$$\begin{aligned}\mathbf{u}_k &= \mathbf{H}\mathbf{u}_{k-1} - a_{k-1}\mathbf{u}_{k-1} - b_{k-1}\mathbf{u}_{k-2} \\ a_{k-1} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_{k-1} \rangle / \langle \mathbf{u}_{k-1} | \mathbf{u}_{k-1} \rangle \\ b_{k-1} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_{k-2} \rangle / \langle \mathbf{u}_{k-2} | \mathbf{u}_{k-2} \rangle\end{aligned}$$

- 4. Diagonalize the final tridiagonal matrix

$$\begin{pmatrix} a_1 & b_2 & & & & 0 \\ b_2 & a_2 & b_3 & & & \\ & b_3 & a_3 & \ddots & & \\ & & \ddots & \ddots & & \\ & & & b_{m-1} & a_{m-1} & b_m \\ 0 & & & & b_m & a_m \end{pmatrix}$$

C. Lanczos, J. Res. Nat. Bur. Std. 45, 255 (1950).

Iterative Method for Obtaining Lowest Excited States

Goal: $\mathbf{H}\Psi = \lambda\Psi$

- To obtain the lowest excited states of **diradicals**.
- Using the Spin-Flip Time-Dependent Density Functional Theory.
- **Cannot afford** the explicit computation of \mathbf{H} matrix elements.

Iterative Method for Obtaining Lowest Excited States

Goal: $\mathbf{H}\Psi = \lambda\Psi$

- To obtain the lowest excited states of **diradicals**.
- Using the Spin-Flip Time-Dependent Density Functional Theory.
- **Cannot afford** the explicit computation of \mathbf{H} matrix elements.

Computational Steps

- 1: Obtain an initial vector, \mathbf{u}_1
- 2: Obtain the second vector,

$$\begin{aligned}\mathbf{u}_2 &= \mathbf{H}\mathbf{u}_1 - a_1\mathbf{u}_1 \\ a_1 &= \langle \mathbf{u}_1 | \mathbf{H} | \mathbf{u}_1 \rangle / \langle \mathbf{u}_1 | \mathbf{u}_1 \rangle\end{aligned}$$

- 3. Add basis vectors till residual is zero.

$$\begin{aligned}\mathbf{u}_k &= \mathbf{H}\mathbf{u}_{k-1} - \sum_{m=1}^{k-1} a_{k-1,m}\mathbf{u}_m \\ a_{k-1,m} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_m \rangle / \langle \mathbf{u}_m | \mathbf{u}_m \rangle\end{aligned}$$

- 4. Diagonalize the matrix

Y. Shao, Yves Bernard, M. Head-Gordon, A. I. Krylov, J. Chem. Phys. 118, 4807 (2003); 136, 204103 (2012).

Iterative Method for Obtaining Lowest Excited States

Goal: $\mathbf{H}\Psi = \lambda\Psi$

- To obtain the lowest excited states of **diradicals**.
- Using the Spin-Flip Time-Dependent Density Functional Theory.
- **Cannot afford** the explicit computation of \mathbf{H} matrix elements.

Computational Steps

- 1: Obtain an initial vector, \mathbf{u}_1
- 2: Obtain the second vector,

$$\begin{aligned}\mathbf{u}_2 &= \mathbf{H}\mathbf{u}_1 - a_1\mathbf{u}_1 \\ a_1 &= \langle \mathbf{u}_1 | \mathbf{H} | \mathbf{u}_1 \rangle / \langle \mathbf{u}_1 | \mathbf{u}_1 \rangle\end{aligned}$$

- 3. Add basis vectors till residual is zero.

$$\begin{aligned}\mathbf{u}_k &= \mathbf{H}\mathbf{u}_{k-1} - \sum_{m=1}^{k-1} a_{k-1,m}\mathbf{u}_m \\ a_{k-1,m} &= \langle \mathbf{u}_{k-1} | \mathbf{H} | \mathbf{u}_m \rangle / \langle \mathbf{u}_m | \mathbf{u}_m \rangle\end{aligned}$$

- 4. Diagonalize the matrix

Technical Challenges

- **Is this the most efficient way?**
- Need to request more states than necessary, because it can miss high-energy states.
How to make it more robust?

Y. Shao, Yves Bernard, M. Head-Gordon, A. I. Krylov, J. Chem. Phys. 118, 4807 (2003); 136, 204103 (2012).

Iterative Method for Obtaining the Response Kernel

Goal: Obtaining the response kernel (inverse Hessian), \mathbf{H}^{-1}

- The same Hamiltonian for excited state calculations: $\mathbf{H}\Psi = \lambda\Psi$
- Solve for a large number of excited states, and invert the matrix

Y. Shao et al, J. Phys. Chem. A 119, 1511 (2015); J. Chem. Theory Comput. 12, 332 (2016); 13, 679 (2017).

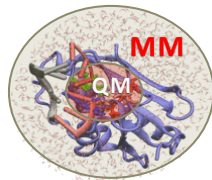
Iterative Method for Obtaining the Response Kernel

Goal: Obtaining the response kernel (inverse Hessian), \mathbf{H}^{-1}

- The same Hamiltonian for excited state calculations: $\mathbf{H}\Psi = \lambda\Psi$
- Solve for a large number of excited states, and invert the matrix

Why do we want the response kernel?

- How QM electronic structure changes with the environment?
- Parameterization of molecular mechanics (MM) force fields
- Newton's method: faster multi-scale (QM/MM) simulations
 - molecular solvation
 - enzymatic reactions
 - ligand-receptor binding



Y. Shao et al, J. Phys. Chem. A 119, 1511 (2015); J. Chem. Theory Comput. 12, 332 (2016); 13, 679 (2017).

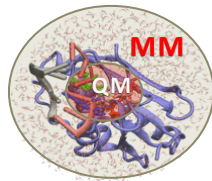
Iterative Method for Obtaining the Response Kernel

Goal: Obtaining the response kernel (inverse Hessian), \mathbf{H}^{-1}

- The same Hamiltonian for excited state calculations: $\mathbf{H}\Psi = \lambda\Psi$
- Solve for a large number of excited states, and invert the matrix

Why do we want the response kernel?

- How QM electronic structure changes with the environment?
- Parameterization of molecular mechanics (MM) force fields
- Newton's method: faster multi-scale (QM/MM) simulations
 - molecular solvation
 - enzymatic reactions
 - ligand-receptor binding



Technical Challenge:

- How to more quickly obtain the response kernel?

Y. Shao et al, J. Phys. Chem. A 119, 1511 (2015); J. Chem. Theory Comput. 12, 332 (2016); 13, 679 (2017).

- 1 Matrix Diagonalizations in Quantum Chemistry
 - Hückel Molecular Orbital Calculations of Fullerenes
 - Excited State Calculations
 - Response Kernel Calculations
- 2 Electron Integrals and Fast Multipole Method
 - Integrals Over Gaussian Functions
 - Fast Multipole Method
- 3 Technical Challenges

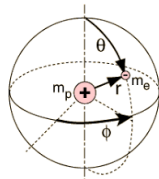
Atomic Orbitals Are Exponential Functions

- The Schrödinger equation for hydrogen atom is

$$\hat{H}\psi(r, \theta, \phi) = \left[-\frac{1}{2} \nabla^2 - \frac{1}{r} \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where the Laplacian is

$$\begin{aligned} \nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \end{aligned}$$



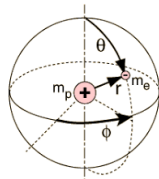
Atomic Orbitals Are Exponential Functions

- The Schrödinger equation for hydrogen atom is

$$\hat{H}\psi(r, \theta, \phi) = \left[-\frac{1}{2} \nabla^2 - \frac{1}{r} \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where the Laplacian is

$$\begin{aligned} \nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \end{aligned}$$



- The first few solutions (**atomic orbitals**) are **Slater exponential functions**

$$\begin{aligned} \psi_{1s} &\sim e^{-r} \\ \psi_{2s} &\sim (2 - r)e^{-r/2} \\ \psi_{2p_z} &\sim [r \cos \theta] e^{-r/2} \\ \psi_{2p_x} &\sim [r \sin \theta \cos \phi] e^{-r/2} \\ \psi_{2p_y} &\sim [r \sin \theta \sin \phi] e^{-r/2} \end{aligned}$$

Switch to Gaussian Functions

- However, in quantum chemistry calculations, we need to compute

$$(ab|cd) = \iint d\vec{r}_1 d\vec{r}_2 \psi_a^*(\vec{r}_1) \psi_b(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_c^*(\vec{r}_2) \psi_d(\vec{r}_2)$$

where $\psi_a, \psi_b, \psi_c, \psi_d$ are “atomic” orbitals on **different atoms**.

- It is hard to evaluate 4-center 2-electron integrals over Slater exponential functions.

Switch to Gaussian Functions

- However, in quantum chemistry calculations, we need to compute

$$(ab|cd) = \iint d\vec{r}_1 d\vec{r}_2 \psi_a^*(\vec{r}_1) \psi_b(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_c^*(\vec{r}_2) \psi_d(\vec{r}_2)$$

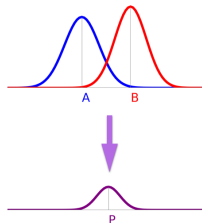
where $\psi_a, \psi_b, \psi_c, \psi_d$ are “atomic” orbitals on **different atoms**.

- It is hard to evaluate 4-center 2-electron integrals over Slater exponential functions.**
- Gaussian functions are better, thanks to Gaussian product theorem

$$\begin{aligned} e^{-\alpha(\vec{r}-\vec{A})^2} e^{-\beta(\vec{r}-\vec{B})^2} &= e^{-\alpha[(x-A_x)^2+(y-A_y)^2+(z-A_z)^2]} \\ &\quad \times e^{-\beta[(x-B_x)^2+(y-B_y)^2+(z-B_z)^2]} \\ &= e^{-(\alpha+\beta)|\vec{r}-\vec{P}|^2} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{A}-\vec{B}|^2} \end{aligned}$$

$$\text{where } \vec{P} = \frac{\alpha\vec{A} + \beta\vec{B}}{\alpha + \beta}.$$

- This allows 4-center 2-electron integrals $(ab|cd)$ to be easily converted into 2-center 2-electron integrals $(p|q)$.



Fast Electrostatics Calculations in Quantum Chemistry

Near Field: Overlapping Gaussians

- Electron integrals over s -type Gaussians (exponents: α_p and α_q)^a

$$(p|q) = \frac{1}{R} \operatorname{erf} \left(\sqrt{\frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q}} R \right)$$

$$\text{where } R = |\vec{P} - \vec{Q}|.$$

Far Field: Non-overlapping Gaussians

Gaussian Integrals: ^aS. Boys, Proc. Roy. Soc. A 200, 542 (1950); ^bP. Gill, Adv. Quantum Chem. 25, 141 (1994).

FMM: L. Greengard and V. Rocklin, J. Comput. Phys. 60, 187 (1985); L. Greengard, Science, 165, 909 (1994).

^c**CFMM:** C. White, B. Johnson, P. Gill, M. Head-Gordon, Chem.Phys.Lett. 230, 8 (1994); J. Chem. Phys. 101, 6593 (1994).

^d**Coulomb Engine:** Y. Shao, C. White, M. Head-Gordon, Chem. Phys. Lett. 323, 425 (2000); J. Chem. Phys. 114, 6572 (2001).

Fast Electrostatics Calculations in Quantum Chemistry

Near Field: Overlapping Gaussians

- Electron integrals over s -type Gaussians (exponents: α_p and α_q)^a

$$(p|q) = \frac{1}{R} \operatorname{erf} \left(\sqrt{\frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q}} R \right)$$

where $R = |\vec{P} - \vec{Q}|$.

- For integrals over higher angular momentum Gaussians, several recurrence relations^b can be used.

Far Field: Non-overlapping Gaussians

Gaussian Integrals: ^aS. Boys, Proc. Roy. Soc. A 200, 542 (1950); ^bP. Gill, Adv. Quantum Chem. 25, 141 (1994).

FMM: L. Greengard and V. Rocklin, J. Comput. Phys. 60, 187 (1985); L. Greengard, Science, 165, 909 (1994).

^c**CFMM:** C. White, B. Johnson, P. Gill, M. Head-Gordon, Chem.Phys.Lett. 230, 8 (1994); J. Chem. Phys. 101, 6593 (1994).

^d**Coulomb Engine:** Y. Shao, C. White, M. Head-Gordon, Chem. Phys. Lett. 323, 425 (2000); J. Chem. Phys. 114, 6572 (2001).

Fast Electrostatics Calculations in Quantum Chemistry

Near Field: Overlapping Gaussians

- Electron integrals over s -type Gaussians (exponents: α_p and α_q)^a

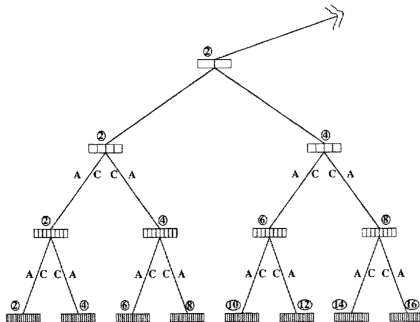
$$(p|q) = \frac{1}{R} \operatorname{erf} \left(\sqrt{\frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q}} R \right)$$

where $R = |\vec{P} - \vec{Q}|$.

- For integrals over higher angular momentum Gaussians, several recurrence relations^b can be used.

Far Field: Non-overlapping Gaussians

- Continuous Fast Multipole Method (CFMM)^c



Gaussian Integrals: ^aS. Boys, Proc. Roy. Soc. A 200, 542 (1950); ^bP. Gill, Adv. Quantum Chem. 25, 141 (1994).

FMM: L. Greengard and V. Rocklin, J. Comput. Phys. 60, 187 (1985); L. Greengard, Science, 165, 909 (1994).

^c**CFMM:** C. White, B. Johnson, P. Gill, M. Head-Gordon, Chem.Phys.Lett. 230, 8 (1994); J. Chem. Phys. 101, 6593 (1994).

^d**Coulomb Engine:** Y. Shao, C. White, M. Head-Gordon, Chem. Phys. Lett. 323, 425 (2000); J. Chem. Phys. 114, 6572 (2001).

Fast Electrostatics Calculations in Quantum Chemistry

Near Field: Overlapping Gaussians

- Electron integrals over s -type Gaussians (exponents: α_p and α_q)^a

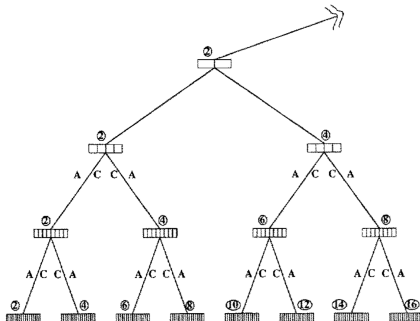
$$(p|q) = \frac{1}{R} \operatorname{erf} \left(\sqrt{\frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q}} R \right)$$

where $R = |\vec{P} - \vec{Q}|$.

- For integrals over higher angular momentum Gaussians, several recurrence relations^b can be used.
- Accelerated by the **Coulomb Engine method**,^d which shifts the electron density to centers **P** and **Q**.

Far Field: Non-overlapping Gaussians

- Continuous Fast Multipole Method (CFMM)^c



Gaussian Integrals: ^aS. Boys, Proc. Roy. Soc. A 200, 542 (1950); ^bP. Gill, Adv. Quantum Chem. 25, 141 (1994).

FMM: L. Greengard and V. Rocklin, J. Comput. Phys. 60, 187 (1985); L. Greengard, Science, 165, 909 (1994).

^c**CFMM:** C. White, B. Johnson, P. Gill, M. Head-Gordon, Chem.Phys.Lett. 230, 8 (1994); J. Chem. Phys. 101, 6593 (1994).

^d**Coulomb Engine:** Y. Shao, C. White, M. Head-Gordon, Chem. Phys. Lett. 323, 425 (2000); J. Chem. Phys. 114, 6572 (2001).

- 1 Matrix Diagonalizations in Quantum Chemistry
 - Hückel Molecular Orbital Calculations of Fullerenes
 - Excited State Calculations
 - Response Kernel Calculations
- 2 Electron Integrals and Fast Multipole Method
 - Integrals Over Gaussian Functions
 - Fast Multipole Method
- 3 **Technical Challenges**

Many Technical Challenges in Computational Quantum Chemistry

Excited-state and response-kernel calculations

- Given a positive-definite symmetric matrix, how to (a) quickly, robustly, and iteratively solve for its lowest eigenvalues? and (b) quickly obtain its inverse?

Many Technical Challenges in Computational Quantum Chemistry

Excited-state and response-kernel calculations

- Given a positive-definite symmetric matrix, how to (a) quickly, robustly, and iteratively solve for its lowest eigenvalues? and (b) quickly obtain its inverse?

Global optimization

- How to quickly converge the electronic wavefunction?
- How to quickly optimize parameters (e.g. molecular mechanical force field and semi-empirical quantum chemistry models)?

Many Technical Challenges in Computational Quantum Chemistry

Excited-state and response-kernel calculations

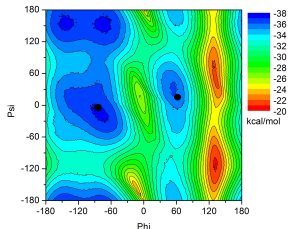
- Given a positive-definite symmetric matrix, how to (a) quickly, robustly, and iteratively solve for its lowest eigenvalues? and (b) quickly obtain its inverse?

Global optimization

- How to quickly converge the electronic wavefunction?
- How to quickly optimize parameters (e.g. molecular mechanical force field and semi-empirical quantum chemistry models)?

Optimization and sampling on the 3N-6 dimensional potential energy surface

- In a basin, how to quickly reach the local minimum?
- From a minimum, how to quickly reach the closest saddle points and nearby minima?
- Given a pair of minima, how to obtain a connecting pathway with the lowest saddle point(s)?
- How to sample the saddle point region?
- How to efficiently sample all the important regions?
- How can we (or machines) **learn** on the fly?



Acknowledgements



Yuansheng Jiang
(Nanjing University)



Martin Head-Gordon
(UC Berkeley)



Bernard Brooks
(NIH)



Chungen Liu
(Nanjing University)



Anna Krylov
(U South Calif)

Acknowledgements



Yuansheng Jiang
(Nanjing University)



Martin Head-Gordon
(UC Berkeley)



Bernard Brooks
(NIH)



Chungen Liu
(Nanjing University)



Anna Krylov
(U South Calif)



John Pople
(Northwestern University)

Acknowledgements

