

# **Basis Sets and Density Functionals**

MERCURY Workshop 2025

# Simplest wavefunction with anti-symmetry

## *Slater Determinant* of single particle functions

$$\Psi_e = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; R)$$

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_n(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_n) & \psi_2(\mathbf{r}_n) & \cdots & \psi_n(\mathbf{r}_n) \end{vmatrix}$$

$$= |\psi_1 \psi_2 \dots \psi_n\rangle = |1, 2 \dots n\rangle$$

**Ground state has all electrons in lowest energy orbitals**

Hartree-Fock:  
Single determinant wavefunction

# In Practice...

- Represent 1 electron orbitals using a *basis set*

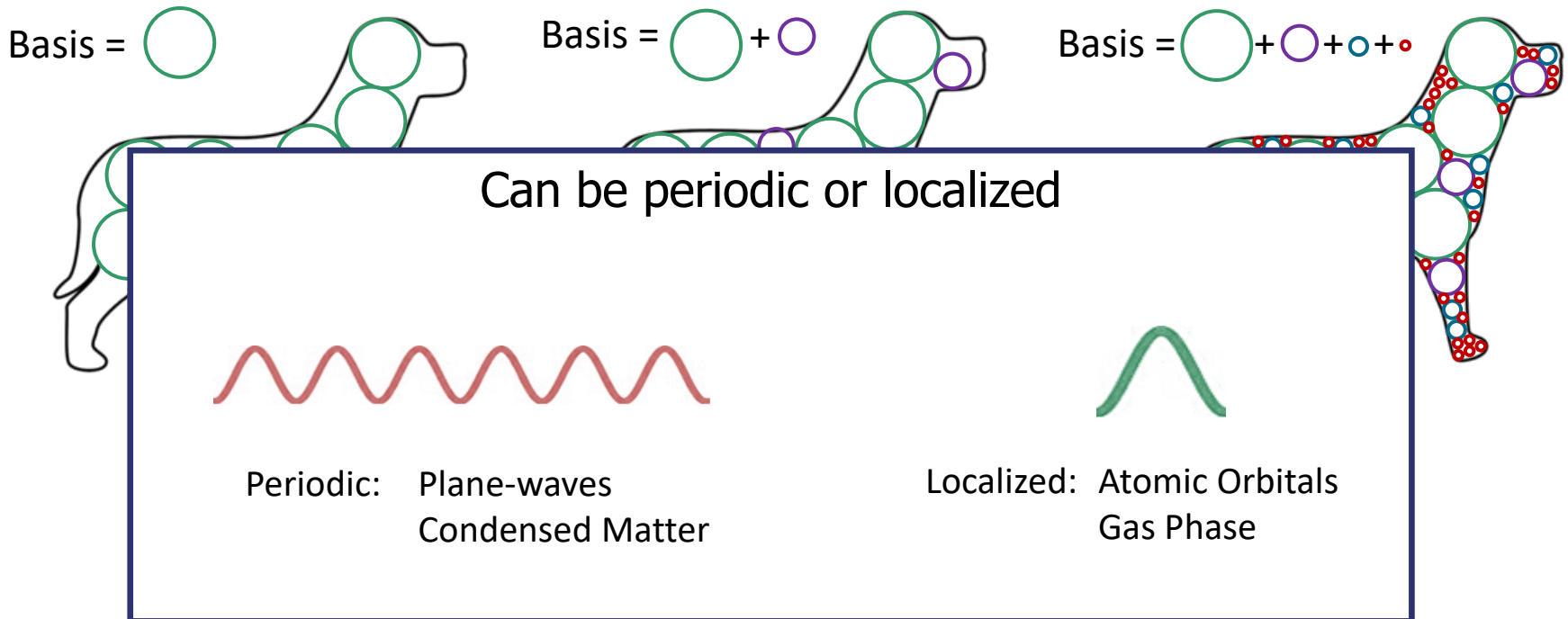
$$\psi_i = \sum_{\mu} c_{\mu}^i \chi_{\mu}$$

- Basis functions are known, optimize coefficients only

# Basis Sets

## Basis Set

Set of known functions used to describe unknown functions (e.g. molecular orbitals)



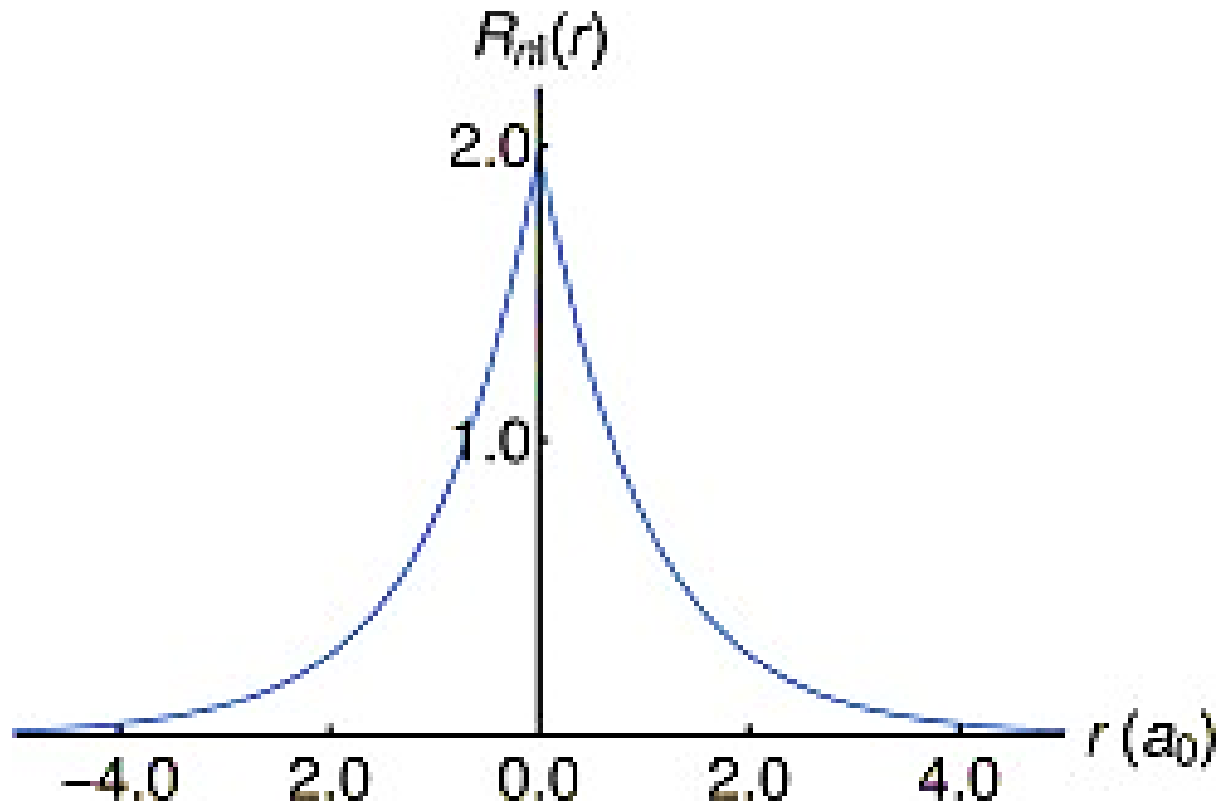
- In principle any sufficiently large basis gives same results
- Requires infinite number of functions to get exact solution

# Basis Functions

Slater type orbitals (STOs)

$$R(r) = N r^{n-1} e^{-\zeta r}$$

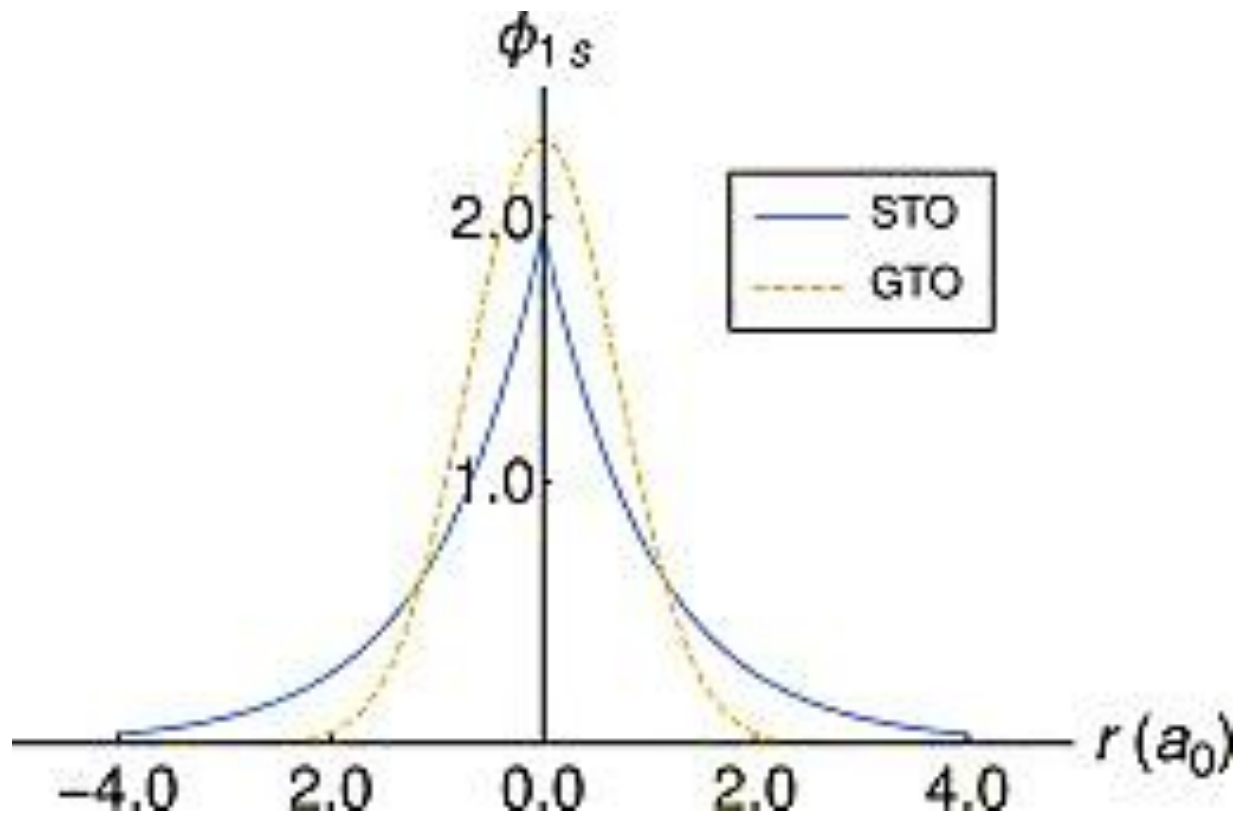
$$\phi_{\zeta,n,l,m}^{STO}(r, \theta, \phi) = R(r) Y_{l,m}(\theta, \phi)$$



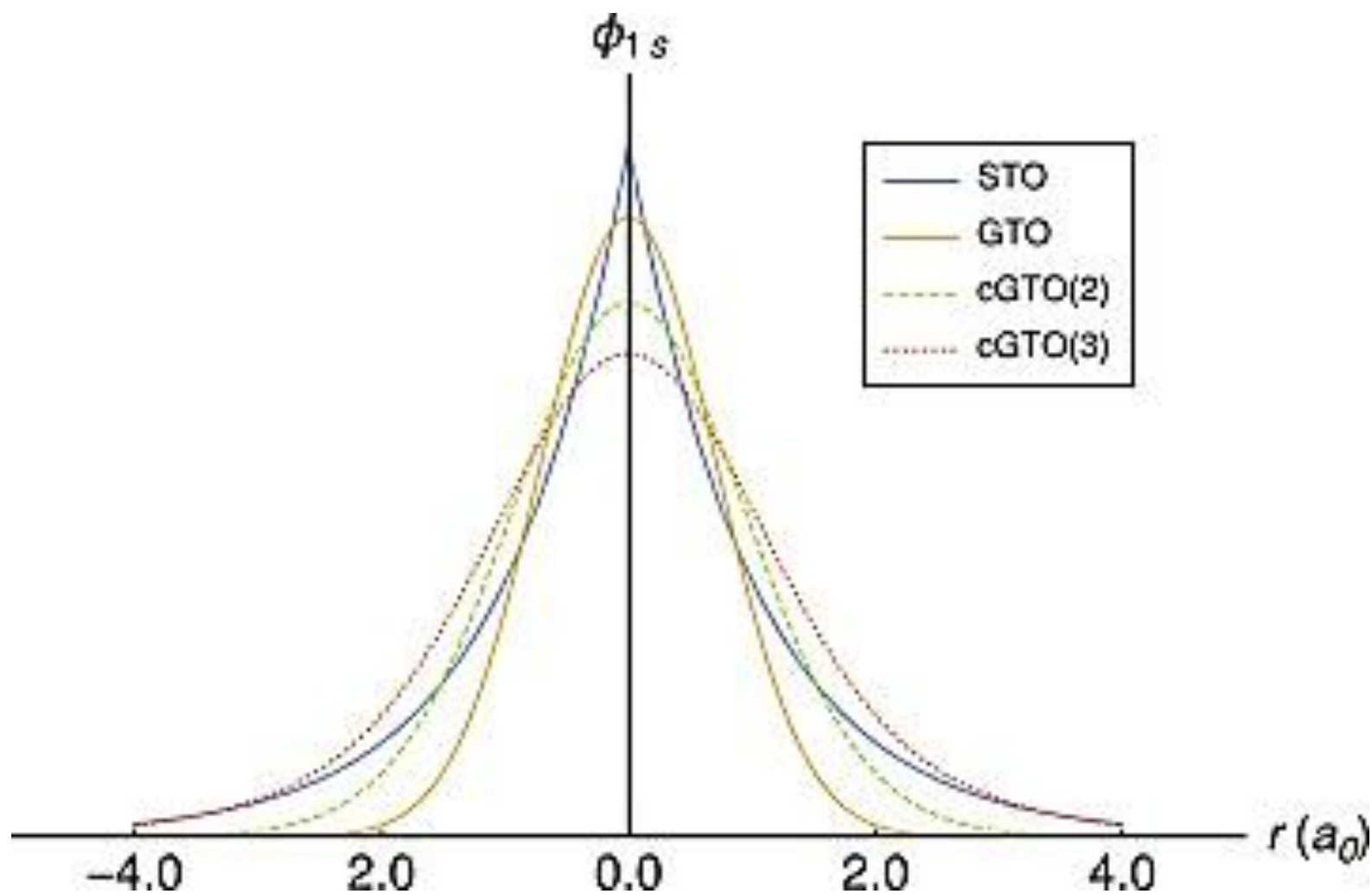
# Basis Functions

Gaussian type orbitals (GTOs)

$$R(r) = N r^{n-1} e^{-\zeta r^2}$$
$$\phi_{\zeta,n,l,m}^{GTO}(r, \theta, \phi) = R(r) Y_{l,m}(\theta, \phi)$$



# Basis Functions



# Basis sets

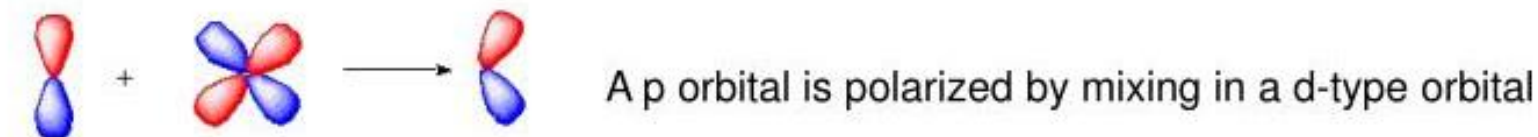
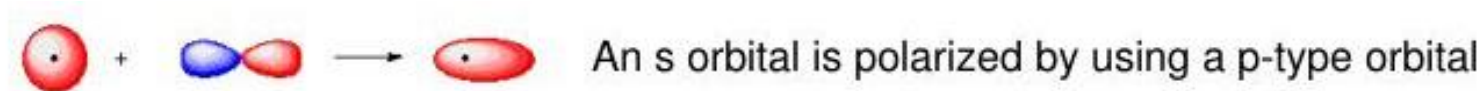
- Minimal Basis: single basis function for each atomic orbital on each atom in the system
  - ⇒ STO-3G, STO-4G, etc.
  - ⇒ Give approximate but not very accurate results
- Double zeta: two basis functions for each atomic orbital on each atom in the system
- Triple zeta: 3 basis functions for each atomic orbital on each atom in the system
- Split-Valence: Treat valence electrons more accurately than core electrons
  - ⇒ 6-31G, cc-pVDZ, etc.



# Basis sets

- Polarization Functions:

⇒ Add extra angular momentum terms to better describe bonding

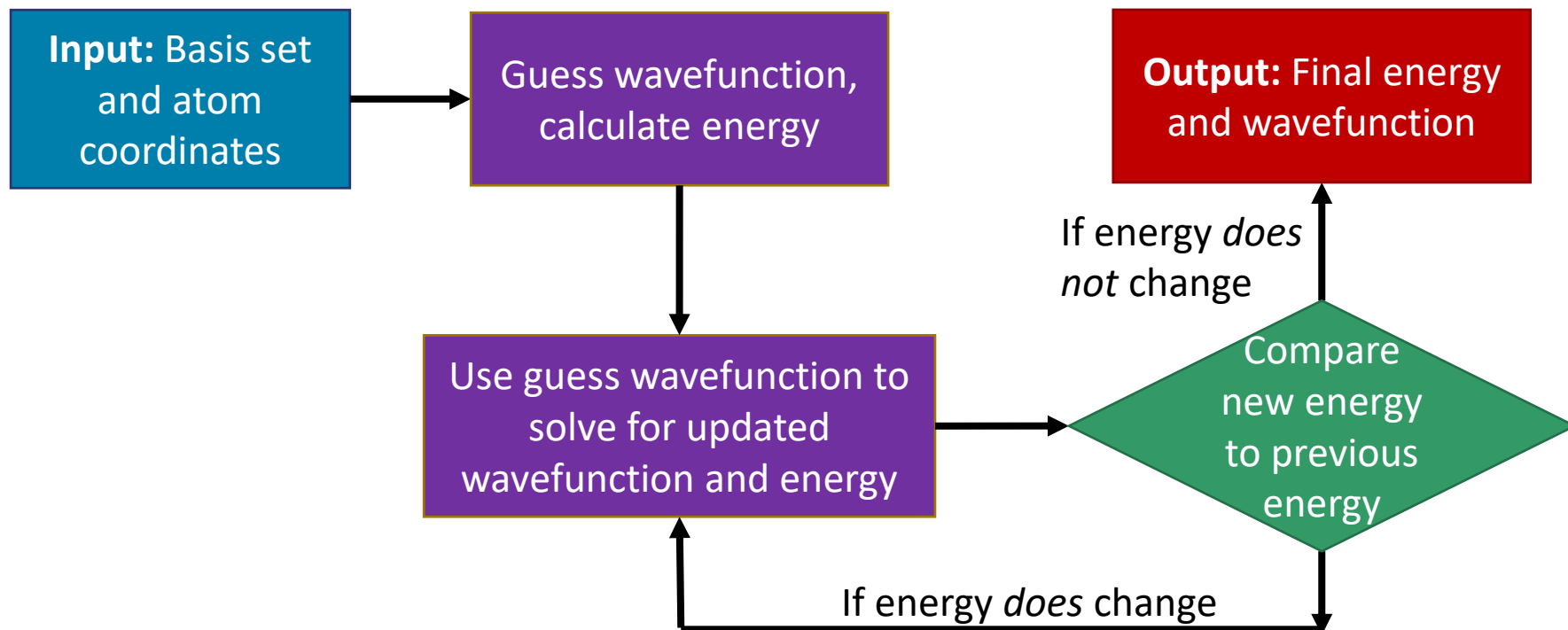


- Diffuse functions:

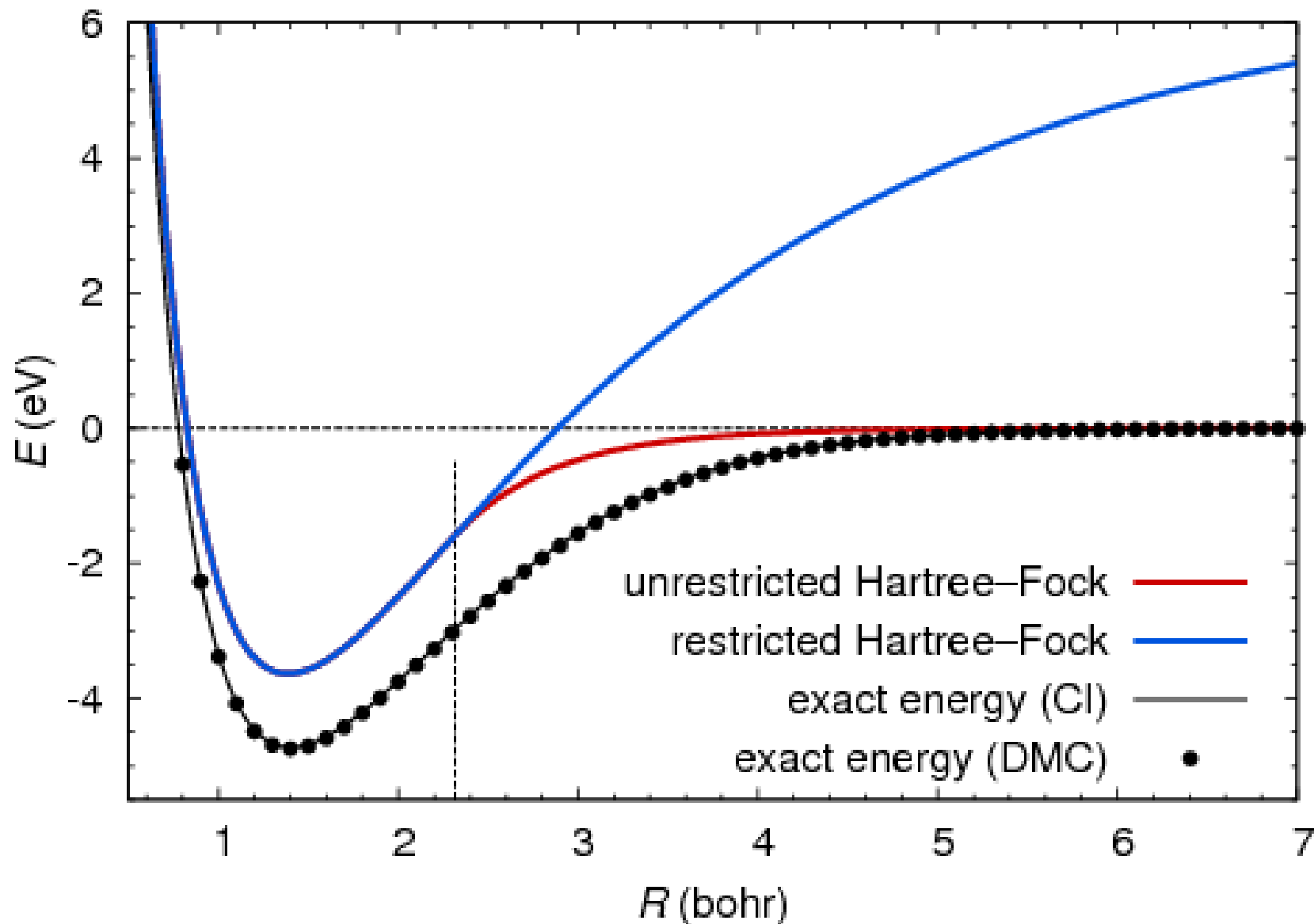
⇒ Add extra “high principle quantum number” states to better describe anions and excited states

# Self-Consistent Field (Hartree-Fock) Method

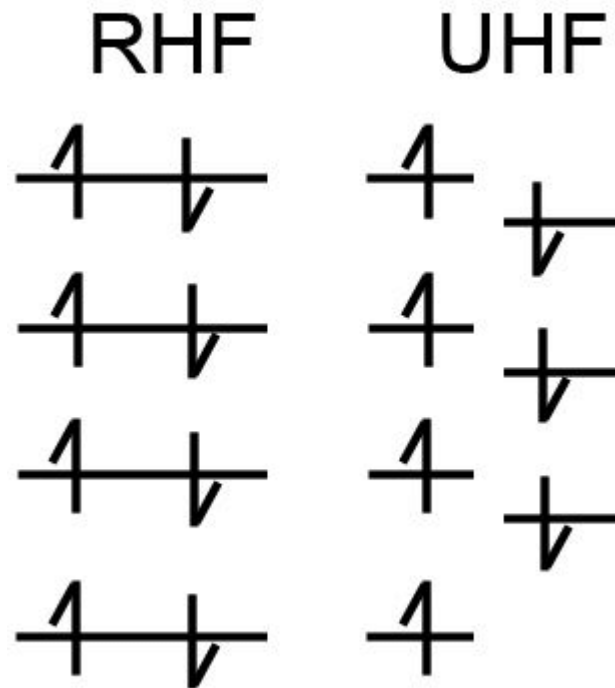
- Method used to find “best” unknown wavefunction in terms of known gaussian functions
- Computers can solve these types of problems very efficiently



# Restricted and Unrestricted HF

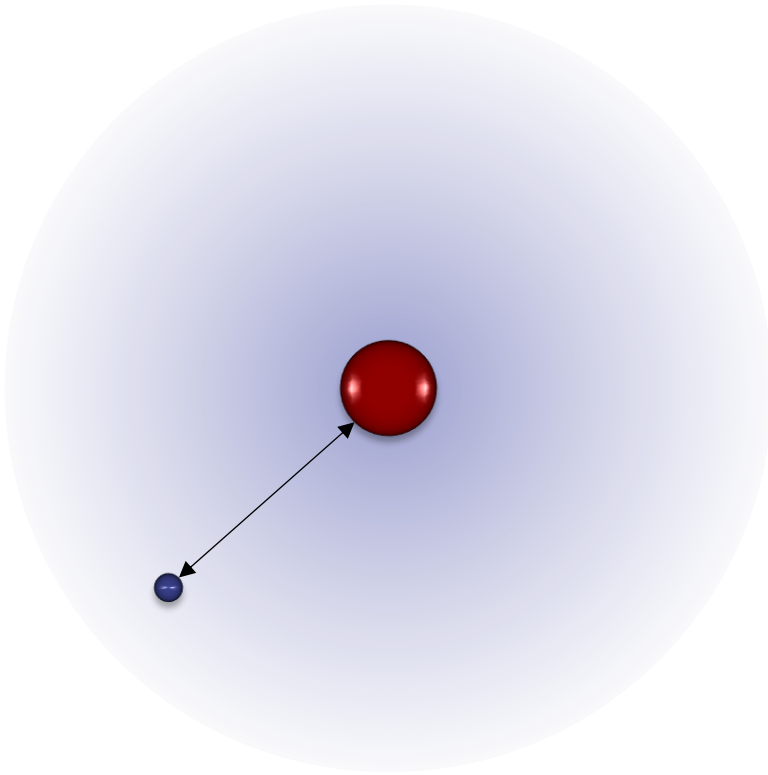


# Restricted and Unrestricted HF

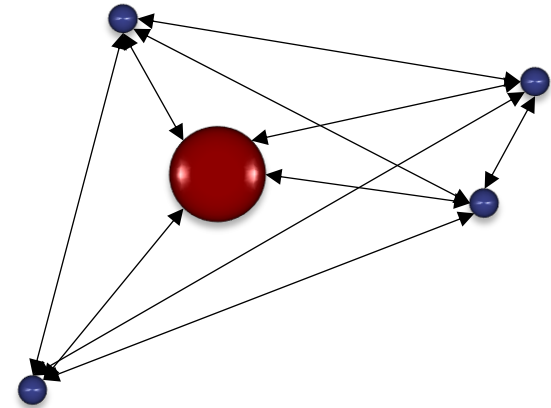


# Electron Correlation

HF theory treats electrons in average field of other electrons,  
electron correlation is missing  $E_{corr} = E_{exact} - E_{HF}$



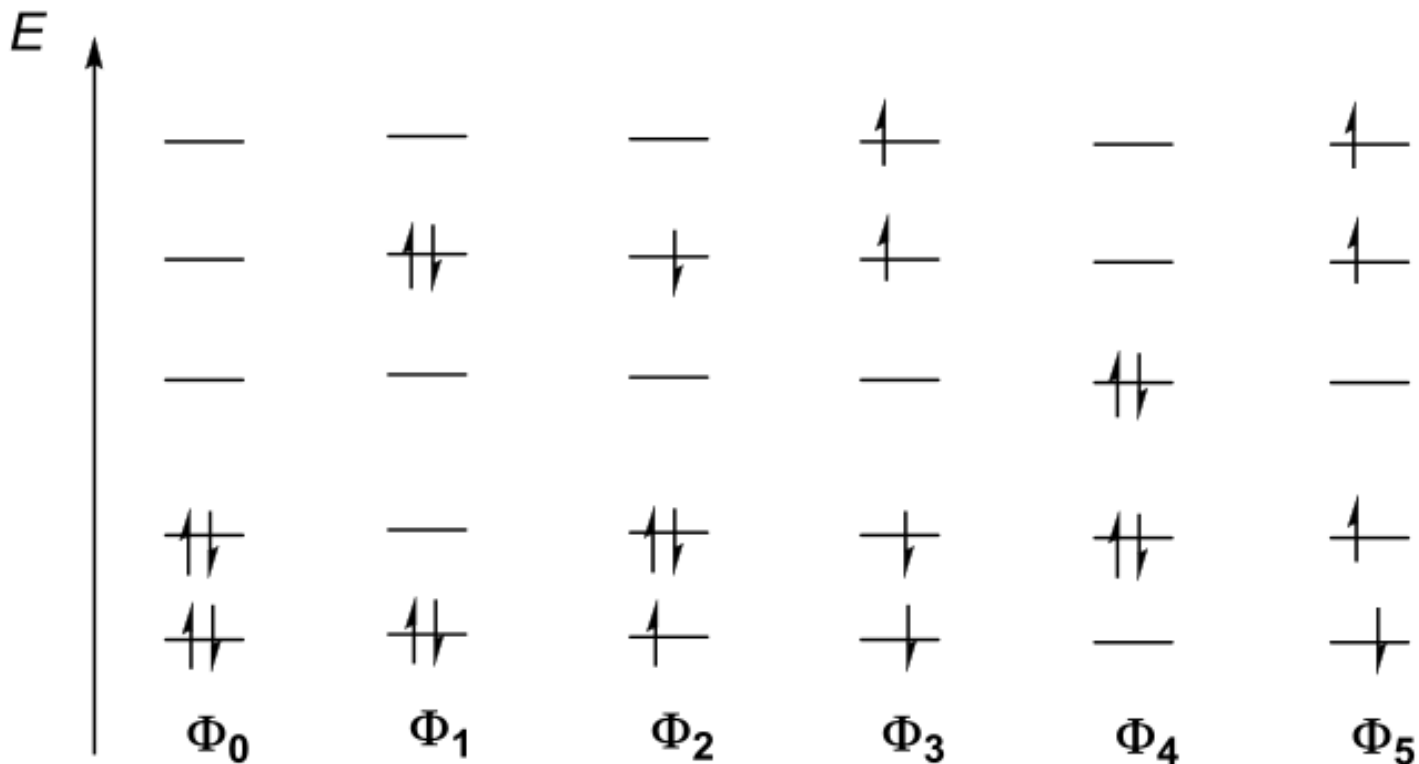
Average Field



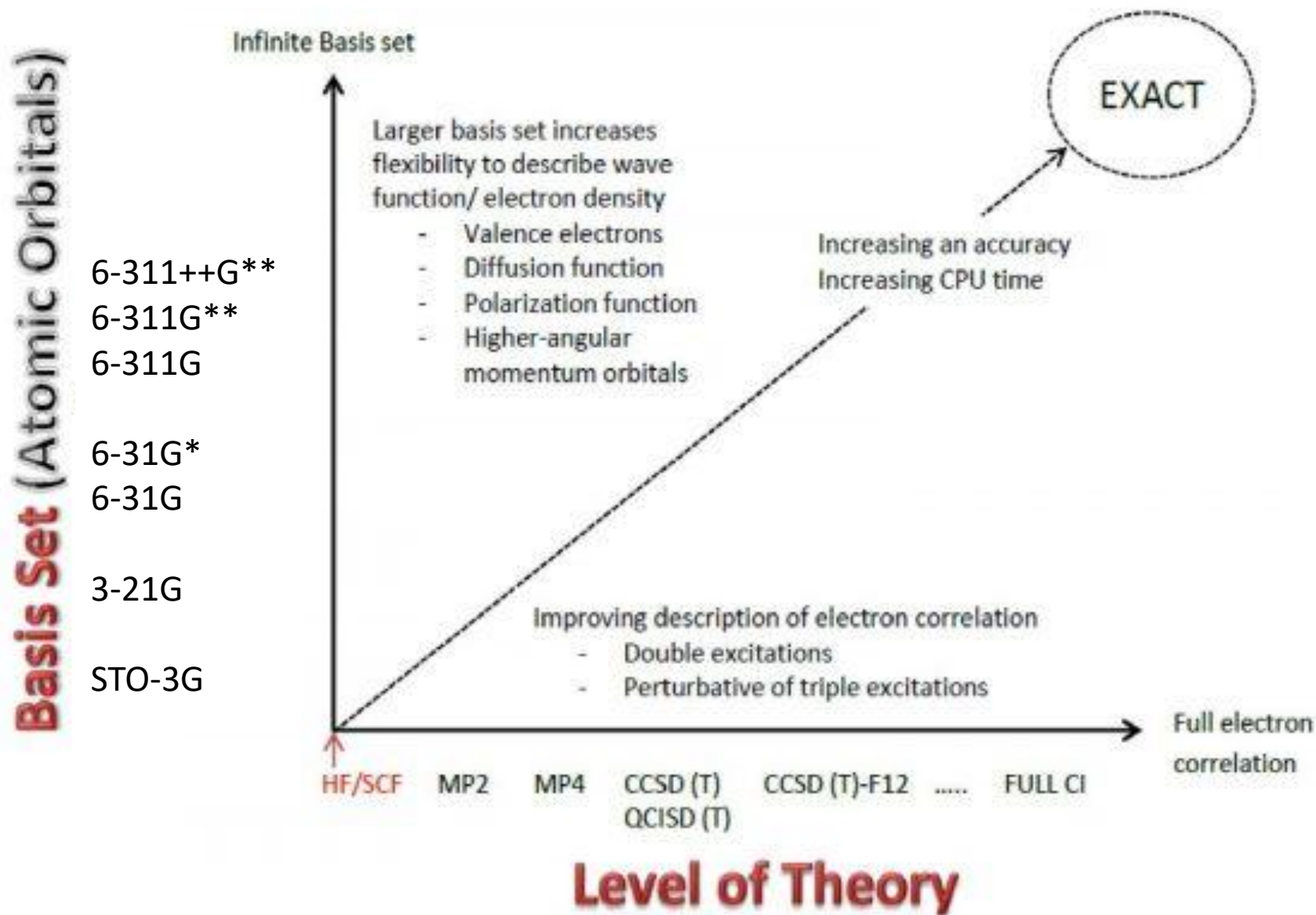
Electron Correlation

# Electron Correlation

- Increasing electron correlation
  - ⇒ Perturbation theory (dynamic correlation)
  - ⇒ Variational method with more than one determinant (static correlation)



# Beyond Hartree-Fock



# Density Functional Theory

## Time-Independent Schrödinger Equation

Hamiltonian  $\rightarrow \hat{H}\Psi = E\Psi \leftarrow$  Wavefunction

$$\Psi_e = \Psi(r_1, r_2, \dots, r_n; R)$$

### Benzene

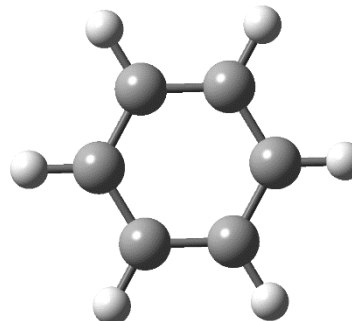
$$N = 42 \text{ e}^-$$

Degrees of Freedom

$$3N = 126$$

Single-determinant Wavefunction

$$N! = 1.4 \times 10^{51} \text{ terms}$$





# Density Functional Theory

## Time-Independent Schrödinger Equation

Hamiltonian  $\rightarrow \hat{H}\Psi = E\Psi \leftarrow$  Wavefunction

$$\Psi_e = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; R)$$

$$\rho(\mathbf{r}) = |\Psi|^2 = \int d\mathbf{r}_2 \dots \int d\mathbf{r}_n \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n; R) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n; R)$$

3 degrees  
of freedom

# Density Functional Theory

- Many dimensional wavefunction  $\Rightarrow$  3D density
- In principle DFT is exact (Hohenberg-Kohn Theorems)

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$$

$$E[\rho(\mathbf{r})] = (T_e + E_{Ne} + E_{ee}) [\rho(\mathbf{r})]$$

- In practice use Kohn-Sham Method

$$E_{KS}[\rho(\mathbf{r})] = (T_s + E_{Ne} + E_J + E_{XC}) [\rho(\mathbf{r})]$$

Further Reading on DFT:

K. Burke, L.O. Wagner, “DFT in a Nutshell”, *Int. J. Quantum Chem.* **2012**, DOI: 10.1002/qua.24259

W. Koch, M.C. Holthausen *A Chemist's Guide to Density Functional Theory*, Second Edition **2001** Wiley-VCH Verlag

# Assessment of Correlated Methods

| Method  | Av. Error (kcal/mol)<br>vs FCI | Approx. Time Factor |
|---------|--------------------------------|---------------------|
| HF      | 5-30                           | $ON^{2-3}$          |
| DFT     | 2-10                           | $ON^3$              |
| MP2     | 17.4                           | $ON^4$              |
| MP3     | 14.4                           |                     |
| MP4     | 3.7                            | $ON^5$              |
| MP5     | 3.2                            |                     |
| CISD    | 13.8                           | $ON^6$              |
| CCSD    | 4.4                            |                     |
| CCSD(T) | 0.7                            | $O^2N^7$            |
| CCSDT   | 0.5                            | $O^2N^{>7}$         |
| CCSDTQ  | 0.0                            | $O^2N^{>>7}$        |

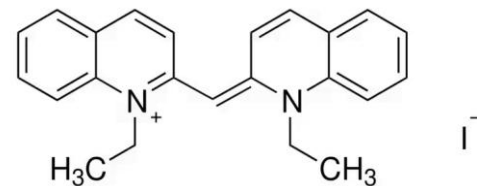
# Minimum requirements for Quantum Chemistry calculations

1. Starting structure
2. Type of calculation
  - ⇒ Energy
  - ⇒ Geometry optimization (molecular structure)
  - ⇒ Frequencies (confirm minimum, IR)
  - ⇒ Transition states
  - ⇒ etc.
3. Method
  - ⇒ HF, DFT, MP2, CCSD, etc.
4. Basis set
  - ⇒ 6-31G, cc-pVTZ, etc.

# Cyanine dye exercise before tomorrow morning

## 1. Optimize geometry

- ⇒ Quick option HF/PM3
- ⇒ More accurate B3LYP/6-31G\*



1,1'-diethyl-2,2'-cyanine iodide

## 2. Calculate excited states (single-point)

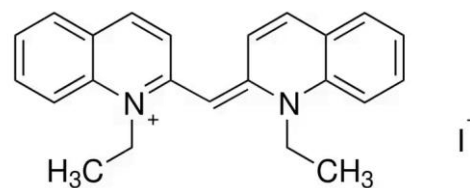
- ⇒ Quick option HF/3-21G
- ⇒ More accurate B3LYP/6-311+G\*\*

## • Notes

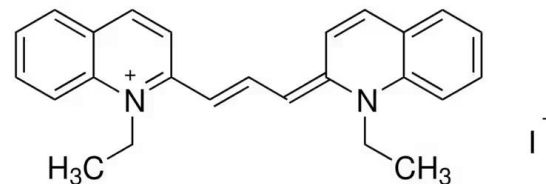
- ⇒ Remove I-, run with +1 charge
- ⇒ Can use other levels of theory...expect ~1 hr for "more accurate" options
- ⇒ Run with 8 processor cores
- ⇒ Ok to run multiple jobs simultaneously if logged in
- ⇒ Follow jobs under "Dashboard"

# Cyanine dye exercise before tomorrow morning

1,1'-diethyl-2,2'-cyanine iodide



1,1'-diethyl-2,2'-carbocyanine iodide



1,1'-diethyl-2,2'-dicarbocyanine iodide

