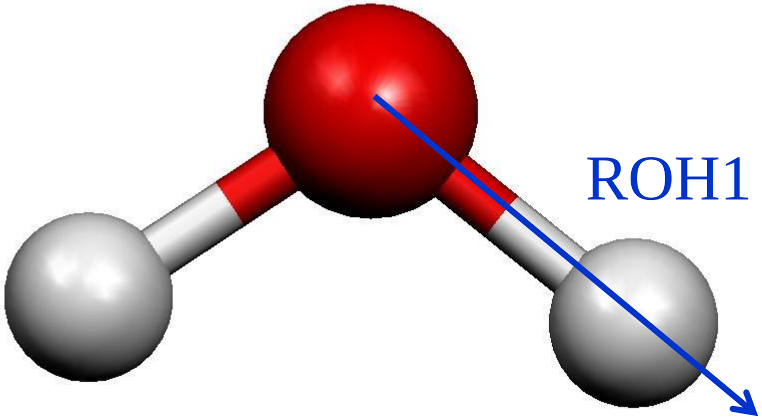
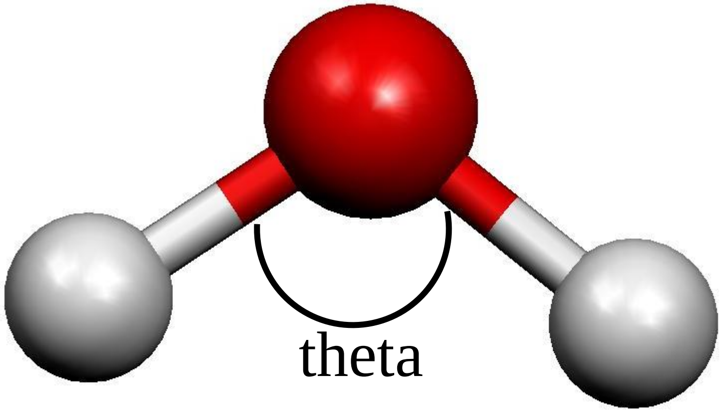
Potential Energy Surface Minimum

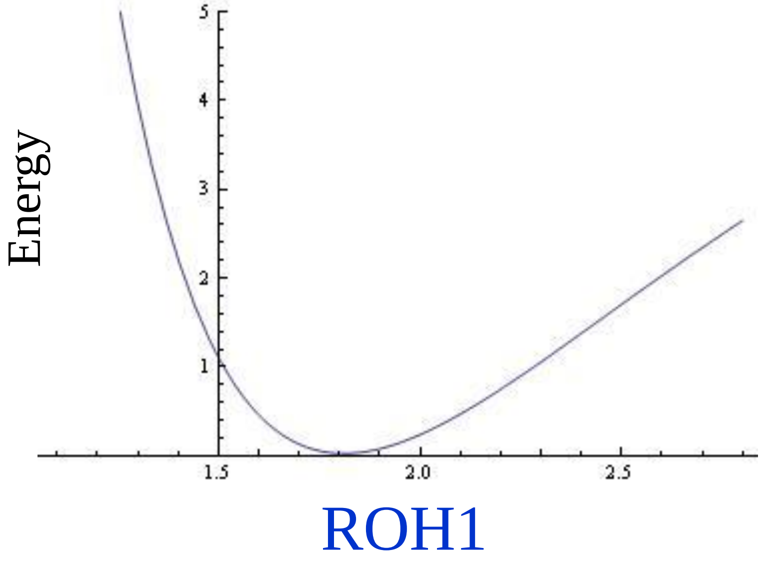
Review

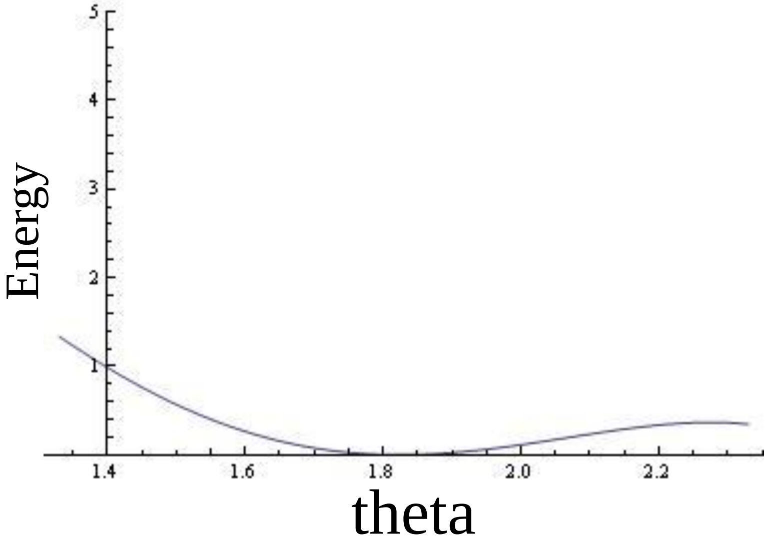
- Last week we did diatomic molecules with only on bond so we only have to think about forming a bond or breaking that bond
- Today we will consider something more complex molecules

Water Molecule
Potential Energy Curve

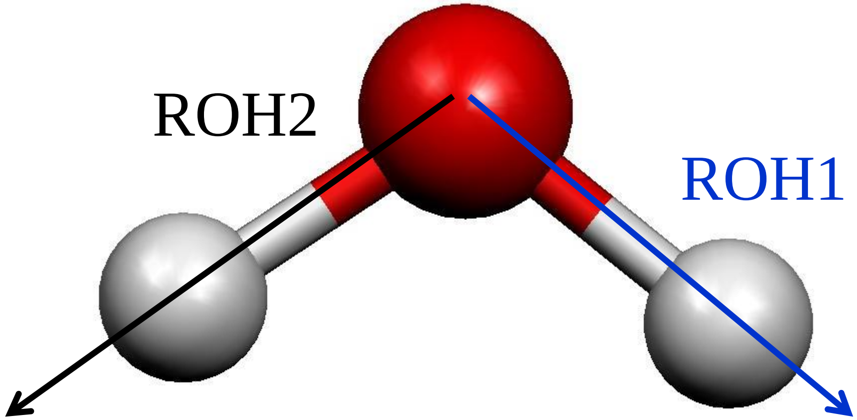




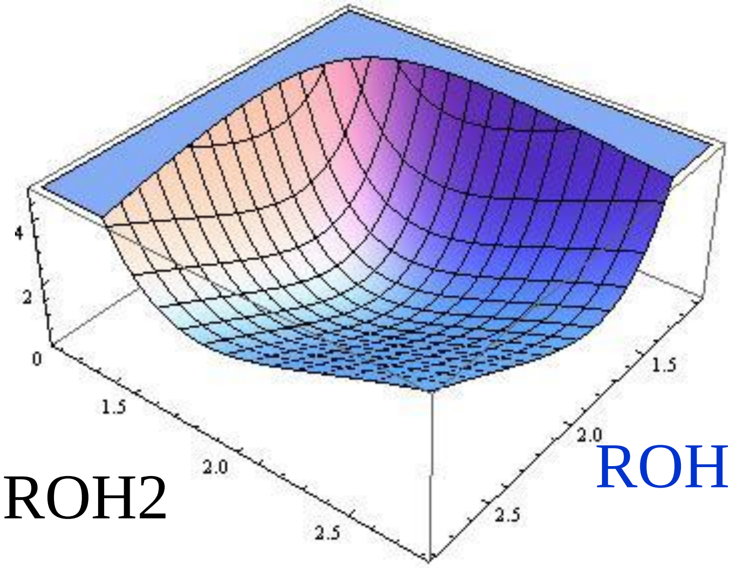




Water Molecule: Stretch Stretch Potential Energy Surface


ROH2

ROH1

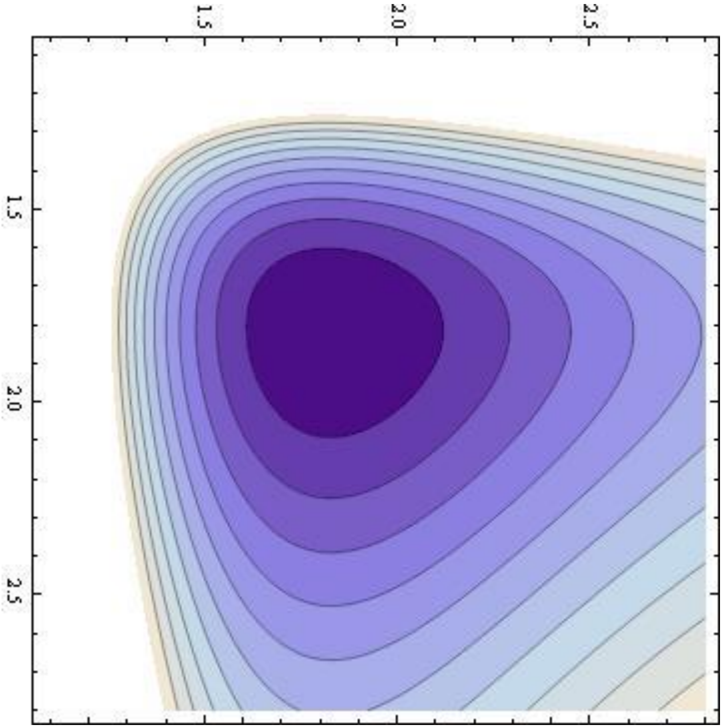


ROH2

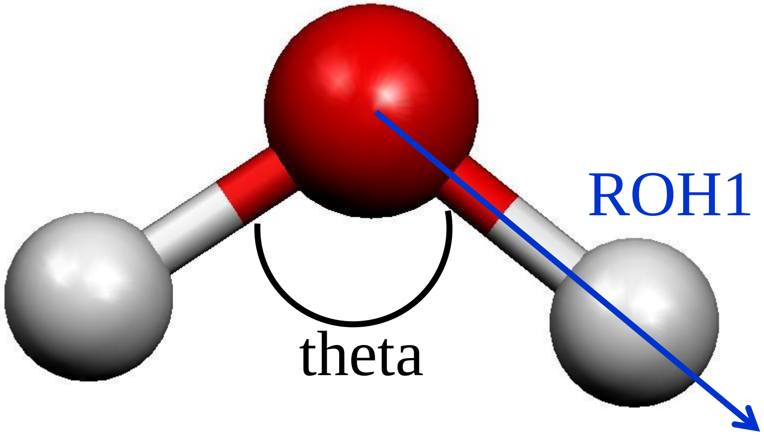
ROH1

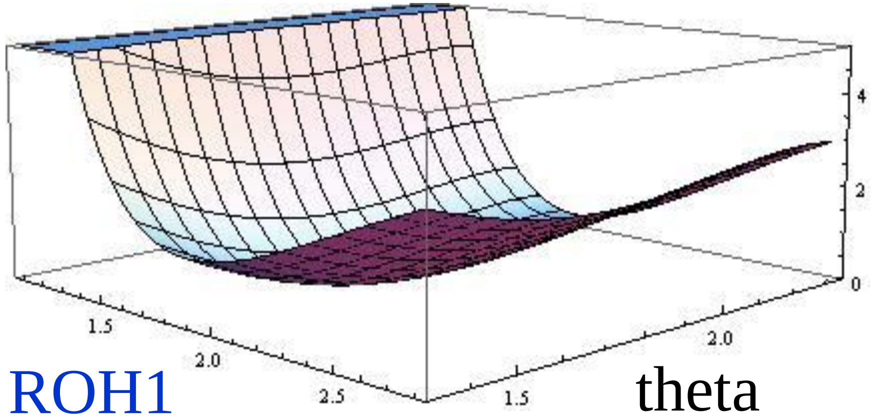
ROH1

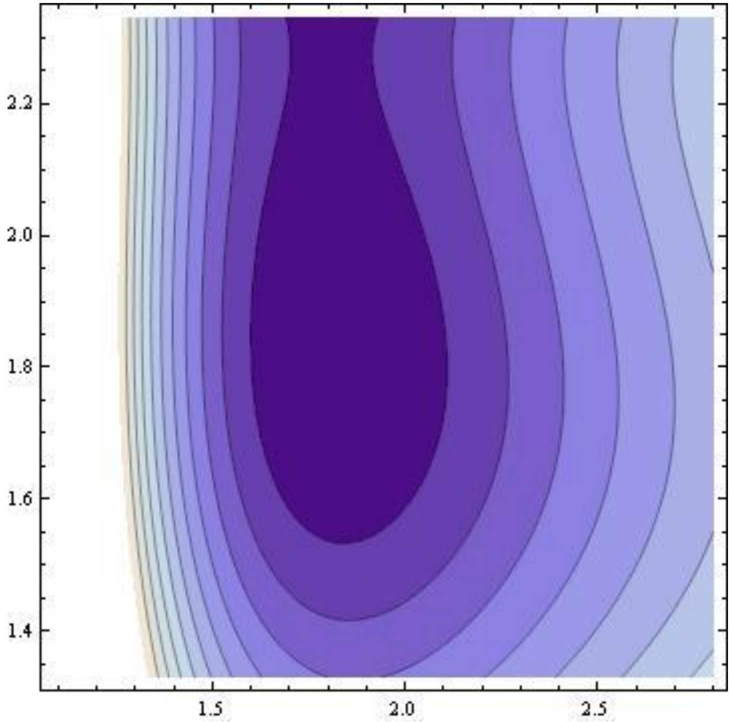
ROH2



Water Molecule: Stretch Bend Potential Energy Surface







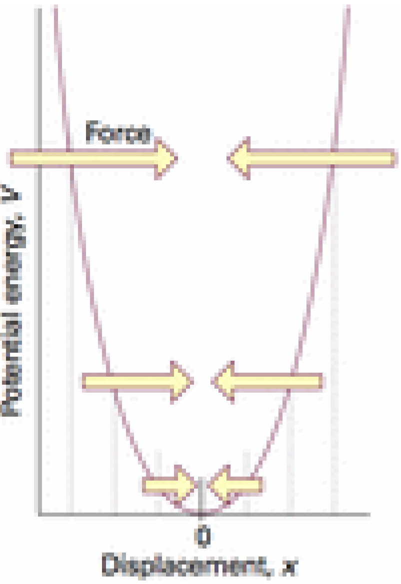
How to quantify Minimum?

- At the minimum the first derivative is zero and the second derivative is always positive

Check the Hessian (second derivative)

In Gaussian you can use the freq keyword

Harmonic Oscillator

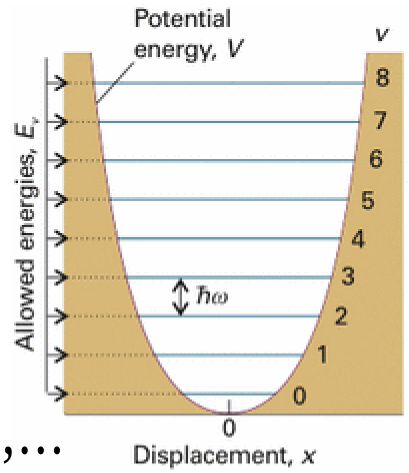


$$F = m\frac{d^2x}{dt^2} = -kx$$

k: force constant

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 \quad -\infty < x < \infty$$

$$\omega = \sqrt{\frac{k}{m}} \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0,1,2,\ldots$$



Normal Mode Vibration 1

First we consider mass –weight Cartesian Coordinates

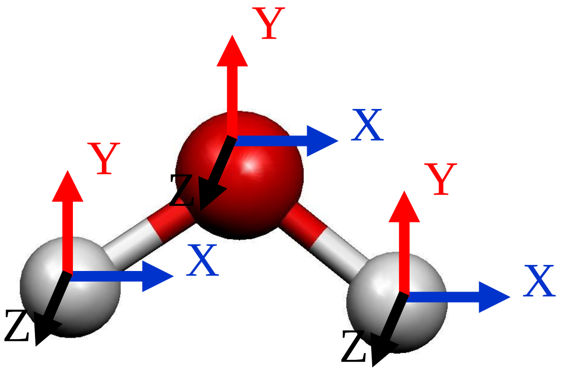
$$q_1 = m_1^{1/2}\Delta X_1; q_2 = m_1^{1/2}\Delta Y_1; q_3 = m_1^{1/2}\Delta Z_1; q_4 = m_2^{1/2}\Delta x_2; \ldots q_{3N} = m_N^{1/2}\Delta Z_N$$

Next expand the potential energy to second term <u>near equilibrium</u>

$$V = V(0) + \sum_I^{3N} K_I q_I + \frac{1}{2}\sum_I^{3N}\sum_J^{3N} K_{IJ} q_I q_J = \frac{1}{2}\sum_I^{3N}\sum_J^{3N} K_{IJ} q_I q_J$$

In these mass-weight Cartesian we say 0 is equilibrium geometry

$$K_I = \left.\frac{\partial V}{\partial q_I}\right|_{q_I=0} = 0; K_{IJ} = \left.\frac{\partial^2 V}{\partial q_I \partial q_J}\right|_{q_I=0;q_J=0}$$



Total energy with mass-weight Cartesian is given as

$$H = \frac{1}{2}\sum_I^{3N}\dot{q}_I^2 + \frac{1}{2}\sum_I^{3N}\sum_J^{3N} K_{IJ} q_I q_J$$

Cross term

We hate this coupling of I and J so want to change to a different coordinate

Normal Mode Vibration 2

We want to redefine a coordinate to Q_I

$$Q_I = \sum_{J=1}^{3N} L_{IJ} q_J \qquad I = 1,3N$$

So in this new coordinate we can write the Hamiltonian as

$$H = \frac{1}{2}\sum_{I}^{3N} \dot{Q}_I^2 + \frac{1}{2}\sum_{I}^{3N} \lambda_I Q_I^2$$

If we diagonalize K_{IJ}

$$H = \frac{1}{2}\sum_{I}^{3N} \dot{q}_I^2 + \frac{1}{2}\sum_{I}^{3N}\sum_{J}^{3N} K_{IJ} q_I q_J$$

$$L^{-1}KL = \Lambda \quad \text{where}$$

$$\Lambda = diag[\lambda_I]$$

We get 5/6 Modes have zero λ_I TRANSLATION/ROTATION

3N-6(5 for linear molecule) remaining are

VIBRATION NORMAL MODES

Normal Mode Vibration 3

So if we are interested in the vibration of the molecule we only have to look at

$$H^{vib} = \frac{1}{2}\sum_{I}^{3N-5/6}\dot{Q}_I^2 + \frac{1}{2}\sum_{I}^{3N-5/6}\lambda_I Q_I^2 = \sum_{I}^{3N-5/6}\frac{1}{2}\left(\dot{Q}_I^2 + \lambda_I Q_I^2\right)$$

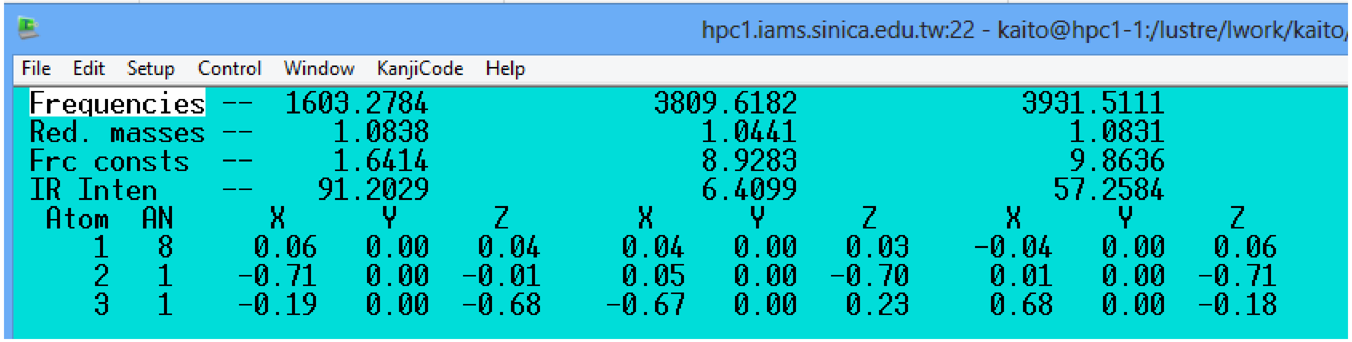
Where $\lambda_I = \frac{\partial^2 V}{\partial Q_I^2}$ $Q_I = \sum_{J=1}^{3N} L_{IJ} q_J$ $I = 1{,}3N-5/6$

Q_I for $I = 3N-4/5{,}3N$ is translation and rotation

Quantum mechanical answer

$$E\left[n_1, n_2 \ldots n_{3N-5/6}\right] = \sum_{I}^{3N-5/6}\hbar\sqrt{\lambda_I}\left(n_I + \frac{1}{2}\right) = \sum_{I}^{3N-5/6}\hbar\omega_I\left(n_I + \frac{1}{2}\right)$$

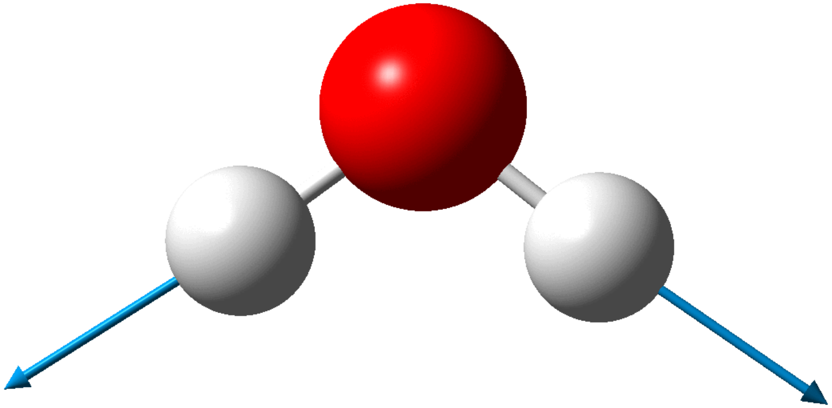
Results for H_2O



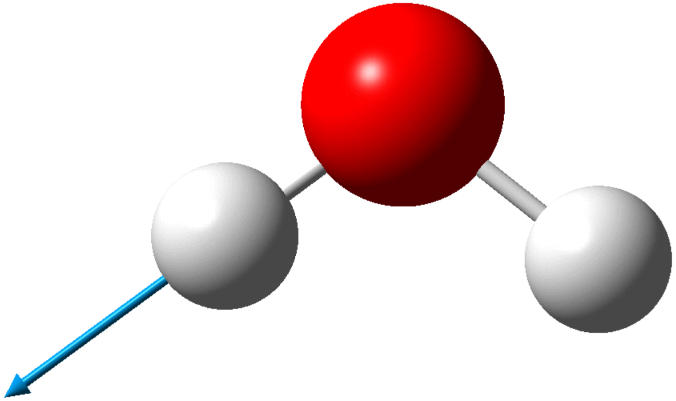
```
Frequencies --   1603.2784                3809.6182                3931.5111
Red. masses --      1.0838                   1.0441                   1.0831
Frc consts  --      1.6414                   8.9283                   9.8636
IR Inten    --     91.2029                   6.4099                  57.2584
 Atom  AN      X      Y      Z        X      Y      Z        X      Y      Z
    1   8     0.06   0.00   0.04     0.04   0.00   0.03    -0.04   0.00   0.06
    2   1    -0.71   0.00  -0.01     0.05   0.00  -0.70     0.01   0.00  -0.71
    3   1    -0.19   0.00  -0.68    -0.67   0.00   0.23     0.68   0.00  -0.18
```

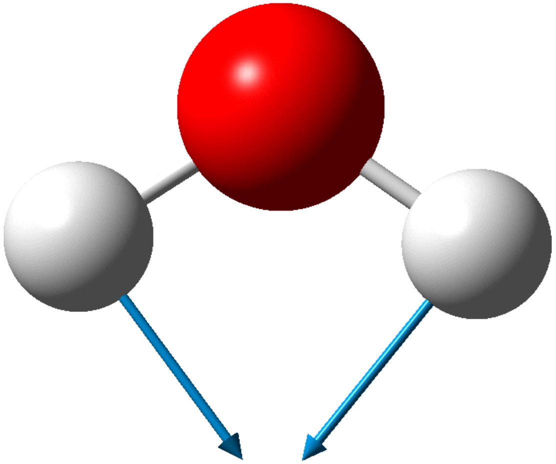
Normal Modes of Water

Symmetric stretch



Antisymmetric stretch





Bend

Beyond Hartree Fock:
Electron Correlation Methods CI

Hartree Fock Review

- Hatree Fock Results=By considering one slater determinant we obtained the best results

Molecular Orbital $$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua}\theta_u \qquad a = 1,2,\ldots Nbasis$$

Spin Orbital $$\psi_i(\mathbf{x}) = \phi_a(\mathbf{r}_1)\sigma_m(\mathrm{s}) \qquad i = 1,2,\ldots Nbasis, Nbasis+1\ldots 2Nbasis$$

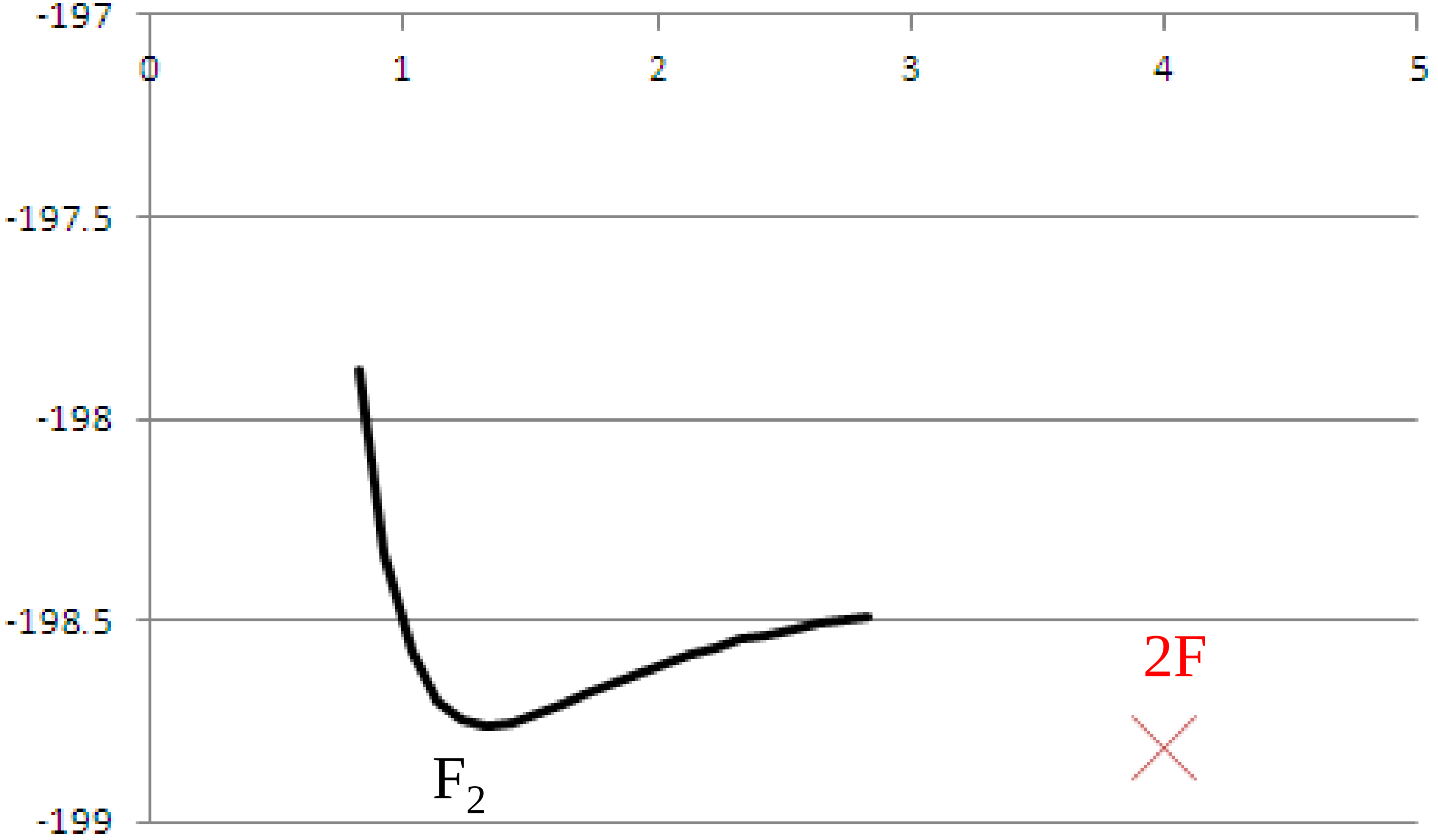
$$\mathrm{a} = 1,2\ldots Nbasis; \quad m = \alpha, \beta$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \cdots\cdots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \cdots\cdots & \psi_n(\mathbf{x}_2) \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \cdots\cdots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

$$= \left\| \psi_i \quad \psi_j \quad \cdots\cdots \quad \psi_n \right\|$$

One Slater Determinant

Failure of Hartree Fock



The cross is the energy for two F atoms.

For Hartree Fock the minimum energy for F2 molecule at 1.2 angstrom ?

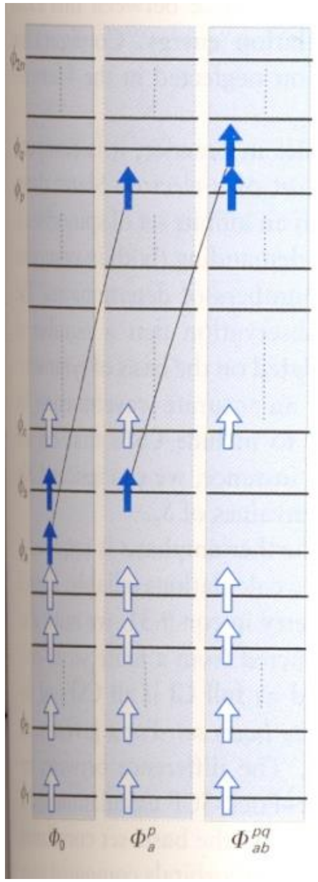
So to go beyond Hartree Fock

- Use more than one slater determinant
    - CISD: ?
    - MCSCF: ?
    - MR-CISD: ?
    - CCSD: ?
- Add in Corrections to Hartree Fock Energy
    - ?
- Explicitly Correlated methods F12
- Totally Change the Hamiltonian (put all that you don’t know and hope someone will do it for you)
    - ?
- Mixed methods G3, CBS

Configuration Interaction SD

n-electron system HF solution $D_0 = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_i \psi_j \cdots\cdots\cdots \quad \psi_n \right\|$

You have 2Nbasis-n unoccupied orbitals so you can use them



Single excitation from HF solution

$$D_i^a = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_a \psi_j \cdots\cdots\cdots \quad \psi_n \right\|$$

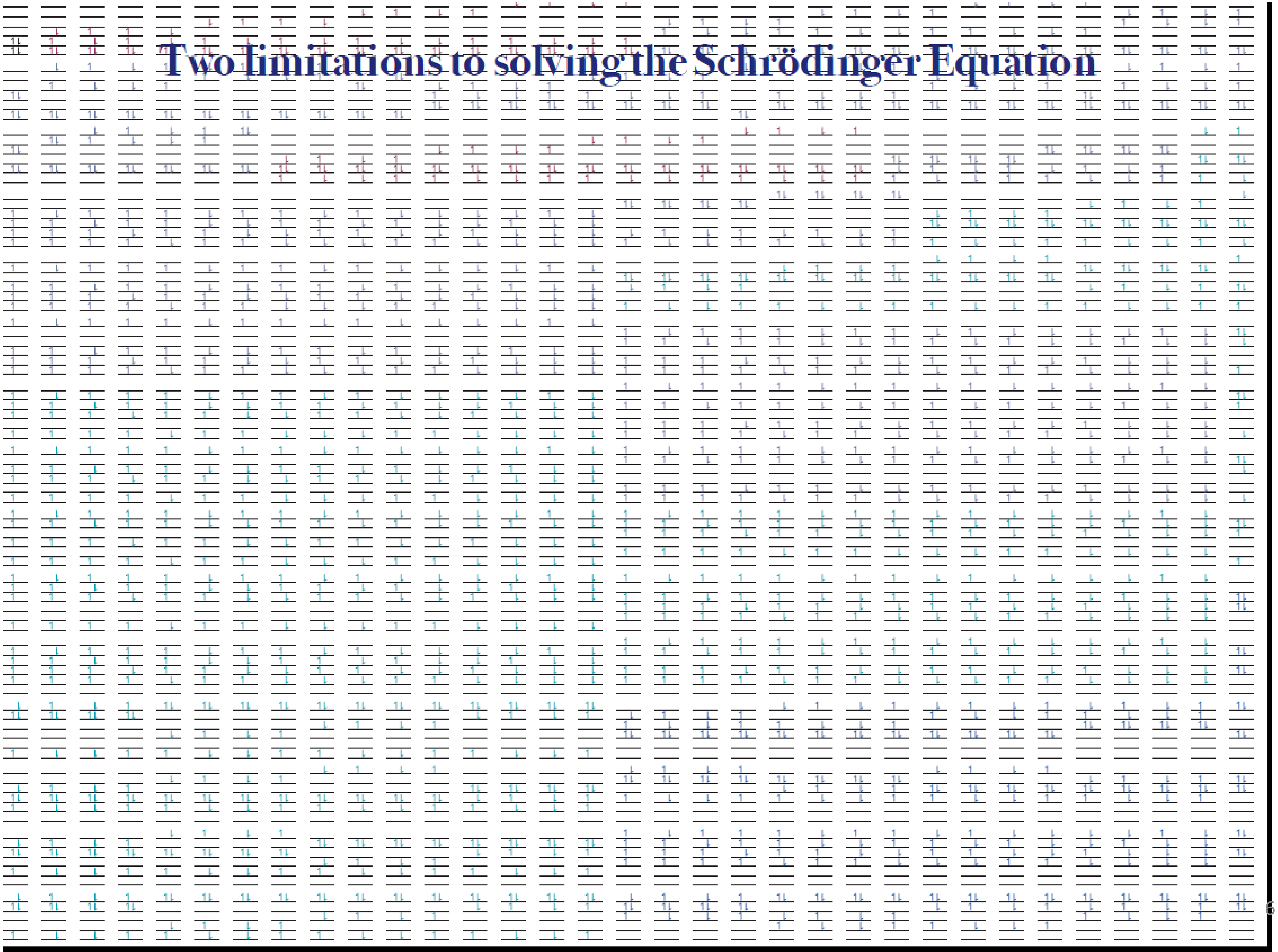
Double excitation from HF solution

$$D_{ij}^{ab} = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_a \psi_b \cdots\cdots\cdots \quad \psi_n \right\|$$

We use the orbitals for the Hartree Fock calculations

$$\Psi_{CI} = C_0 D_0 + \sum_{i,a} C_i^a D_i^a + \sum_{i<j,a<b} C_{ij}^{ab} D_{ij}^{ab} + \sum_{i<j<k,a<b<c} C_{ijk}^{abc} D_{ijk}^{abc} + \ldots$$

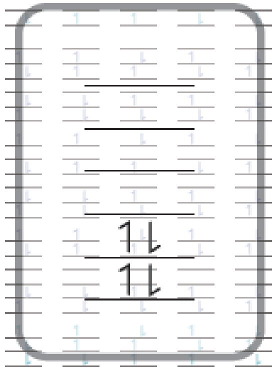
Two limitations to solving the Schrödinger Equation



Two limitations to solving the Schrödinger Equation

Arrange Four Electrons in Six Orbitals

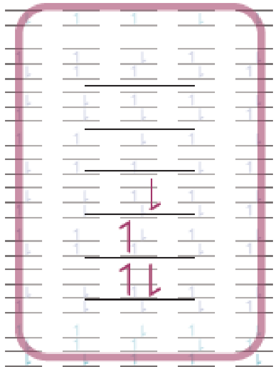
1 Ground Configuration HF



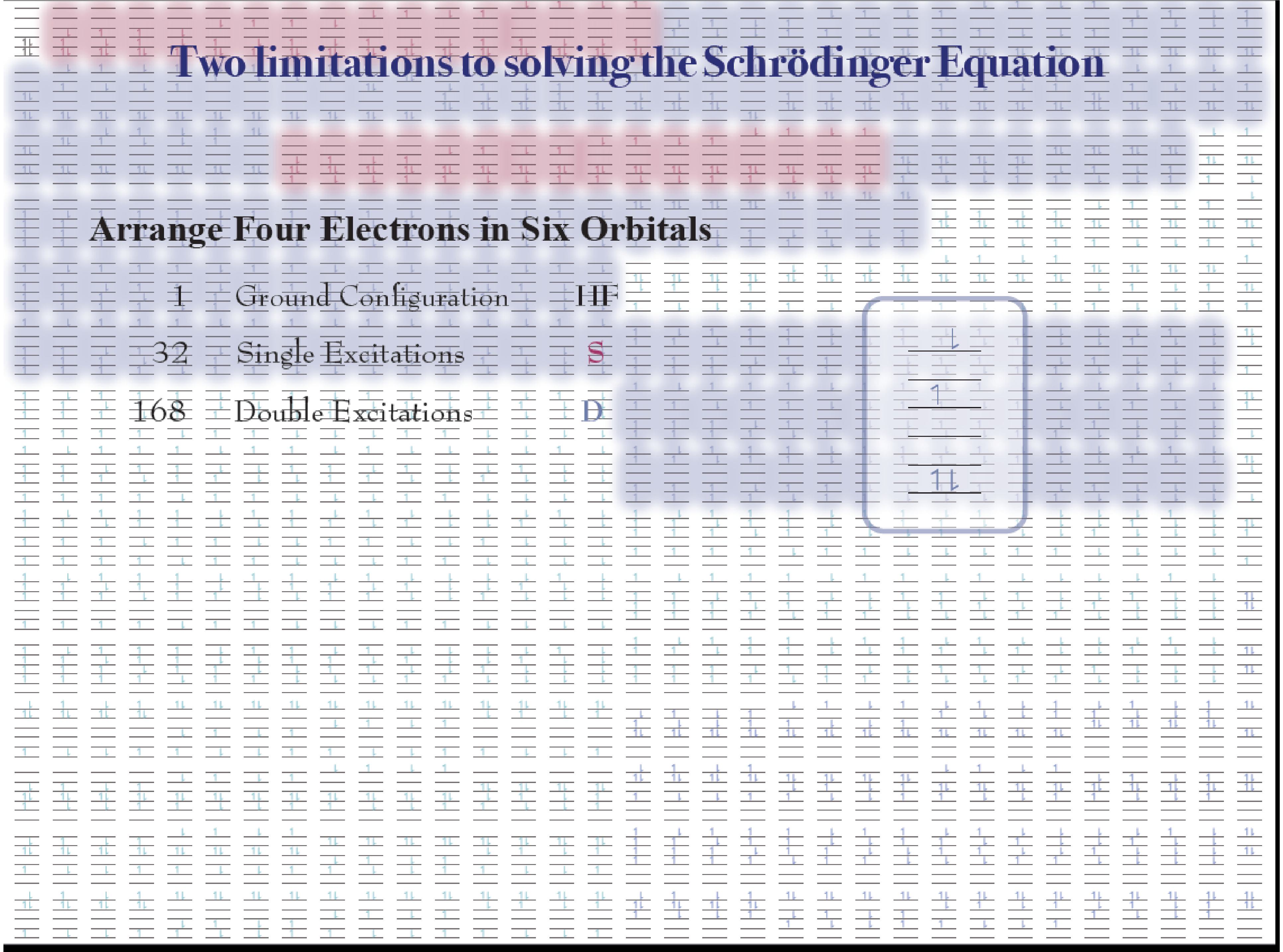
Two limitations to solving the Schrödinger Equation

Arrange Four Electrons in Six Orbitals

1	Ground Configuration	HF
32	Single Excitations	S



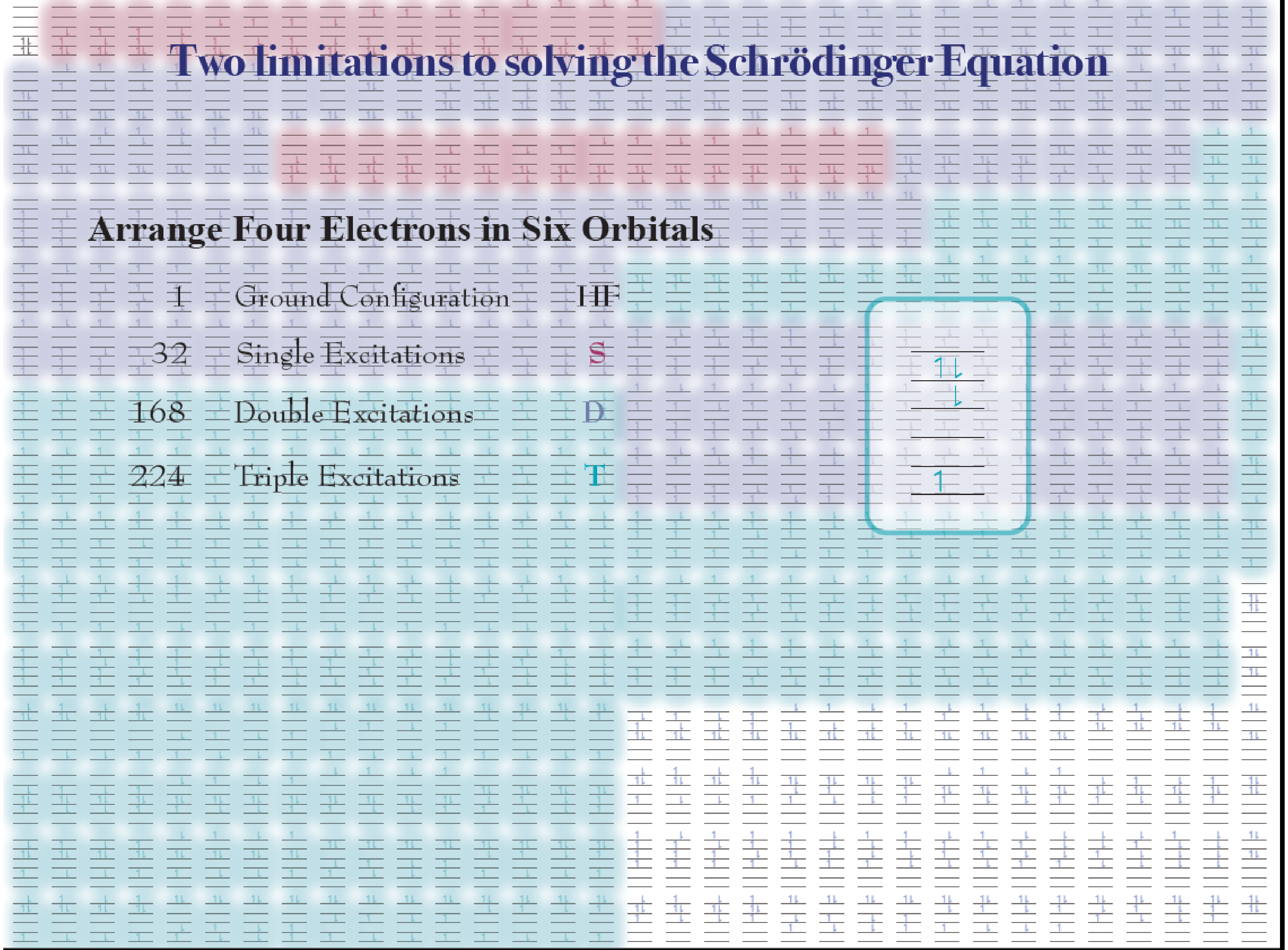
Two limitations to solving the Schrödinger Equation



Arrange Four Electrons in Six Orbitals

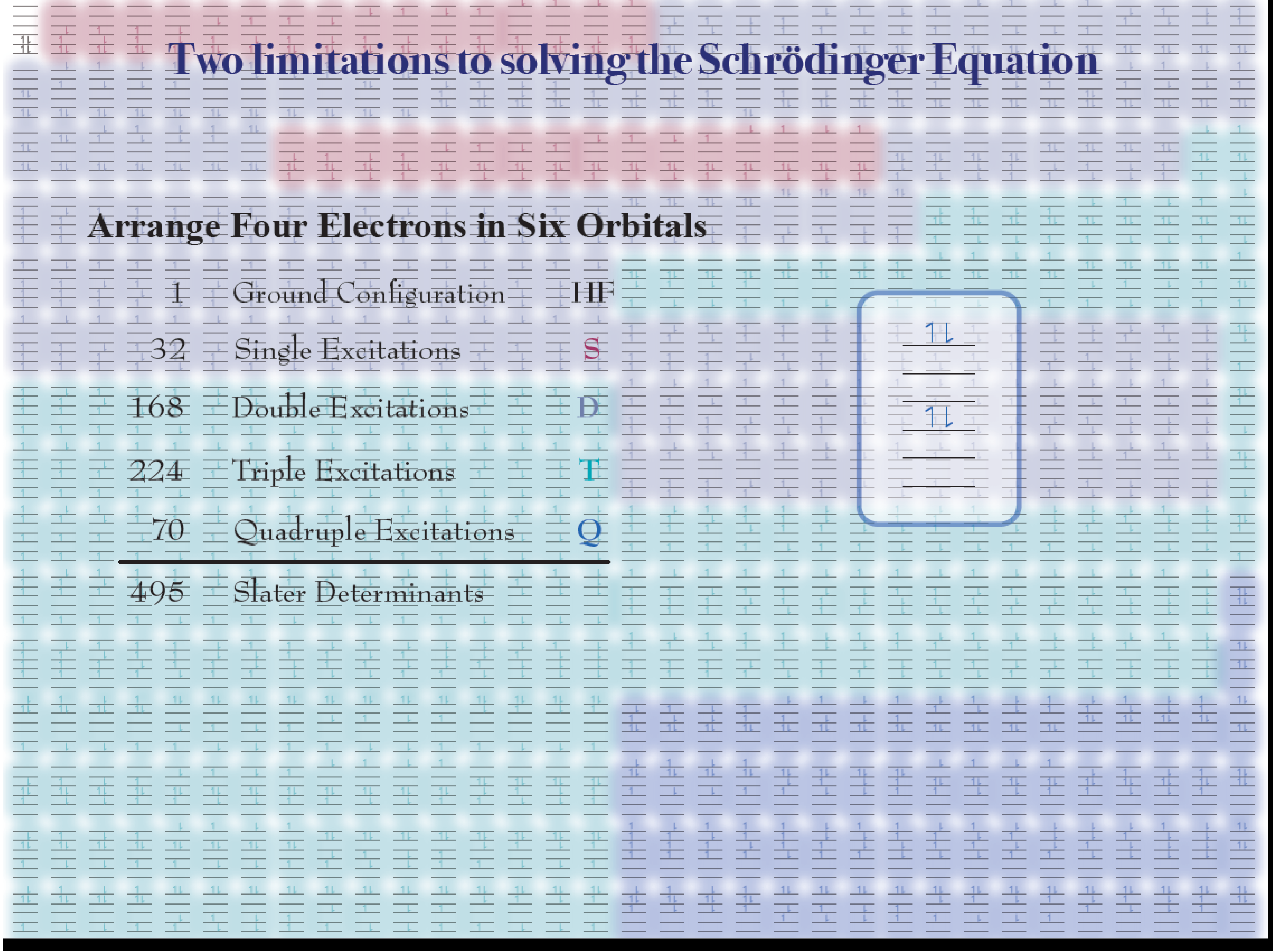
1	Ground Configuration	HF
32	Single Excitations	S
168	Double Excitations	D

Two limitations to solving the Schrödinger Equation



Arrange Four Electrons in Six Orbitals

1	Ground Configuration	HF
32	Single Excitations	S
168	Double Excitations	D
224	Triple Excitations	T



Two limitations to solving the Schrödinger Equation

Arrange Four Electrons in Six Orbitals

1	Ground Configuration	HF
32	Single Excitations	S
168	Double Excitations	D
224	Triple Excitations	T
70	Quadruple Excitations	Q
495	Slater Determinants	

Second quantization
(creation and annihilation operators)

Operators for creating an orbital a is written as $\hat{a}^\dagger$

Operators for annihilating (removing) an orbital j is written as $\hat{j}$

So using these operators we can write one electron excitation as

$$D_i^a =$$

And the two electron excitation as

$$D_{ij}^{ab} =$$

*In my notes i,j,k,l will be used for occupied orbital and a,b,c,d will be used for unoccupied orbitals

H_2 Potential Curve Revisited Review

This is equivalent to using CI double excitation for the wave function

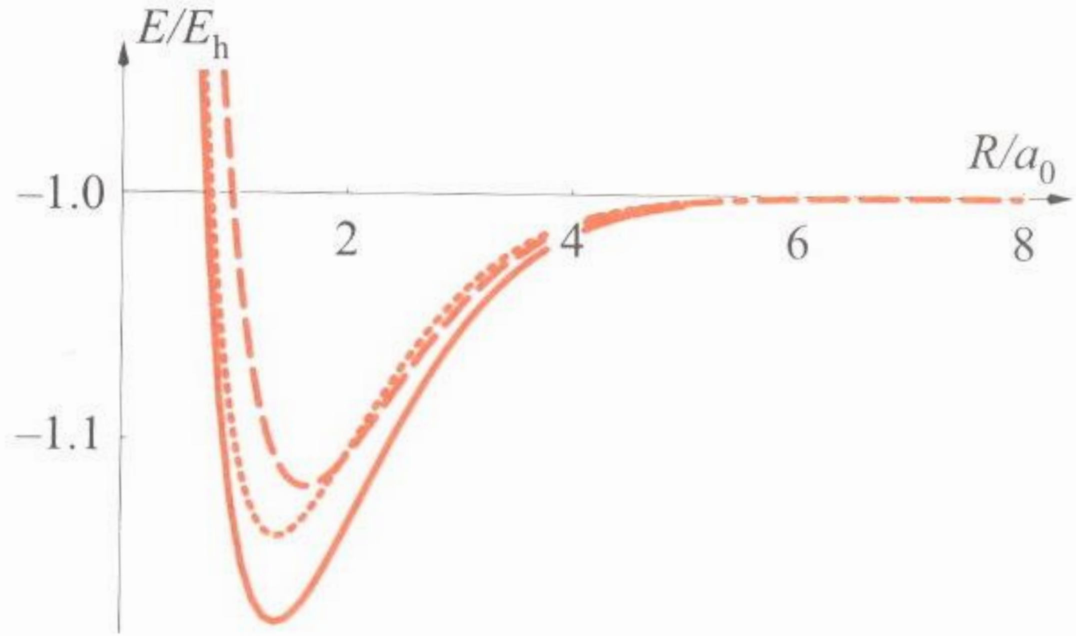


FIGURE 10.25
The configuration-interaction energy E_{CI} of the ground-state energy of H_2 for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R. The "exact" results of Kolos and Wolniewicz (solid curve) are shown for comparison.

H_2 Configuration Interaction Review

Two 1S orbitals can make TWO molecular orbitals
Why not use the two and make combinations

$$|D_0\rangle = \begin{vmatrix} \alpha(1)|+\rangle_1 & \beta(1)|+\rangle_1 \\ \alpha(2)|+\rangle_2 & \beta(2)|+\rangle_2 \end{vmatrix} \qquad |D_{++}^{--}\rangle = \begin{vmatrix} \alpha(1)|-\rangle_1 & \beta(1)|-\rangle_1 \\ \alpha(2)|-\rangle_2 & \beta(2)|-\rangle_2 \end{vmatrix}$$

$$|D_0\rangle \approx |++\rangle(\alpha\beta-\beta\alpha) \qquad |D_{++}^{--}\rangle \approx |--\rangle(\alpha\beta-\beta\alpha)$$

Configuration 1: two electron in bonding orbital
Ground state Hartree Fock solution

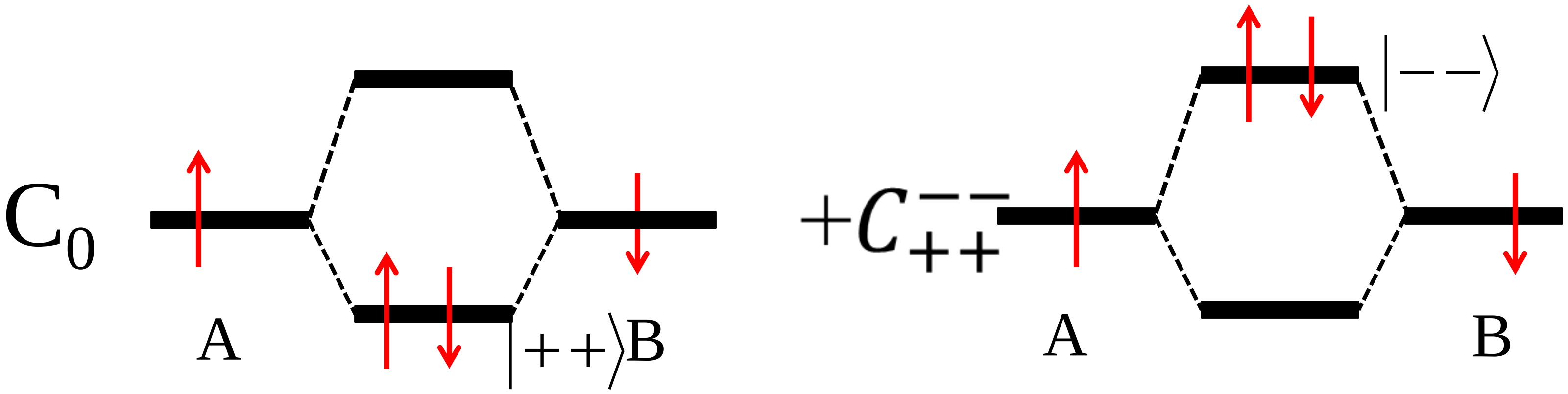
Configuration 2: two electron in antibonding orbital; two electron excitation from HF

$$|D_0\rangle \approx |++\rangle(\alpha\beta-\beta\alpha) \qquad |D_{++}^{--}\rangle \approx |--\rangle(\alpha\beta-\beta\alpha)$$

$$|\Psi_{CI}\rangle = C_0|D_0\rangle + C_{++}^{--}|D_{++}^{--}\rangle = C_0|++\rangle + C_{++}^{--}|--\rangle$$

What we did in H_2 is minimal basis CID

Using two 1S orbitals you can get two molecular orbitals



Use variational theory to calculate the values of C_0 and C_{++}^{--}

?

Brillouin's Theorem

Interaction between the Hartree Fock solution and the one electron excitation determinant is zero

$$\left\langle D_0 \middle| H \middle| D_i^a \right\rangle = \left\langle i \middle| h \middle| a \right\rangle + \sum_{j=1}^{n_{electron}} \left\langle ij \mid aj \right\rangle - \left\langle ij \mid ja \right\rangle = h_{ia} + \sum_{j=1}^{n_{electron}} \left\langle i \middle| J_j \middle| a \right\rangle + \left\langle i \middle| K_j \middle| a \right\rangle$$

$$= \left\langle i \middle| f \middle| a \right\rangle = \delta_{ia}$$

?

Slater Condon Rule

If two slater determinants made by Hartree Fock orbitals differ in more than two spin orbitals then the interaction energy is zero

$$\hat{H}^0(\mathbf{r};\mathbf{R}) = \left[-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{I=1}^{N}\sum_{J\neq I}^{N}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right]$$

one electron operators for n electron system $\sum_{i=1}^{n} h_i$

Electron Hamiltonian is sum of

two electron operator for n electron system $\sum_{i=1}^{n}\sum_{j\neq i}^{n} |\mathbf{r}_{ij}|^{-1}$

$$\langle D_0 | H | D_{ijk}^{abc} \rangle =$$

because ?

CI Straight forward solutions

$$\Psi_{CI} = C_0 D_0 + \sum_{i,a} C_i^a D_i^a + \sum_{i<j,a<b} C_{ij}^{ab} D_{ij}^{ab} + \sum_{i<j<k,a<b<c} C_{ijk}^{abc} D_{ijk}^{abc} + \ldots$$

By Brillouin's theorem one electron excitation should not interact with D_0

By Slater Condon rule three electron excitation should not interact with D_0

So only should need D_{ij}^{ab}

Why do we need D_i^a and D_{ijk}^{abc} and higher ones?

?

$$\left\langle D_{ij}^{ab} \middle| H \middle| D_{ijk}^{abc} \right\rangle \qquad \left\langle D_{ij}^{ab} \middle| H \middle| D_i^a \right\rangle$$

?