

10/02/2024

- Review Midterm 1
- Many-electron atoms
 - Helium, by variation and perturbation
- The Pauli principle
- Slater determinants
- The Born-Oppenheimer Approximation
 - Hydrogen molecule ion on a single axis
 - Potential energy surfaces
- This lecture is designed to help you achieve the following learning objectives
 - Use perturbation theory to extend the models to more realistic situations
 - Describe variation theory and the use of basis sets

Helium

- The full Schrodinger equation is

$$\left(-\frac{\hbar^2}{2M} \nabla^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \right) \Psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) + \left(-\frac{2e^2}{4\pi\epsilon_o |\mathbf{R} - \mathbf{r}_1|} - \frac{2e^2}{4\pi\epsilon_o |\mathbf{R} - \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_o |\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2)$$

- \mathbf{R} - Position of nucleus
- \mathbf{r}_1 and \mathbf{r}_2 - Positions of electrons
- M - Mass of nucleus
- m_e - Mass of electron
- ∇^2 - Laplacian w.r.t. position of nucleus
- ∇_1^2 and ∇_2^2 - Laplacian w.r.t. position of electrons

- If the nucleus is fixed relative to the electrons,

$$-\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) \Psi(\mathbf{r}_1, \mathbf{r}_2) - \frac{2e^2}{4\pi\epsilon_o} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) + \frac{e^2}{4\pi\epsilon_o |\mathbf{r}_1 - \mathbf{r}_2|} \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2)$$

- The interelectronic repulsion is

$$\frac{e^2}{4\pi\epsilon_o |\mathbf{r}_1 - \mathbf{r}_2|} \Psi(\mathbf{r}_1, \mathbf{r}_2)$$

- the reason that we cannot obtain an exact solution and need to approximate

Atomic Units

- $a_o = \frac{4\pi\epsilon_o\hbar^2}{m_e e^2}$ is the Bohr radius
- $E_h = \frac{m_e e^4}{16\pi^2\epsilon_o^2\hbar^2}$ is a Hartree
- In atomic units, the Hamiltonian for the Helium atom is much simpler,
$$\hat{\mathbf{H}} = -\frac{1}{2}\hat{\nabla}_1^2 - \frac{1}{2}\hat{\nabla}_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Perturbation Theory

$$\hat{\mathbf{H}} = -\frac{1}{2}\hat{\nabla}_1^2 - \frac{1}{2}\hat{\nabla}_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

- What is $\hat{\mathbf{H}}^{(0)}$ and what is $\hat{\mathbf{H}}^{(1)}$?

- $E^{(1)} = \langle 0 | \frac{1}{r_{12}} | 0 \rangle = \frac{5Z}{8}$

- $E = E^{(0)} + E^{(1)}$

$$= -\frac{1}{2}Z^2 - \frac{1}{2}Z^2 + \frac{5}{8}Z$$

$$= -Z^2 + \frac{5}{8}Z = -2.750 \text{ Hartrees}$$

Variation Theory

- As a reminder, the ground state wavefunction of hydrogen is $\Psi_{1s}(r_j) = 2 \left(\frac{Z^3}{\pi} \right)^{\frac{1}{2}} e^{-Zr_j}$
- Choose the trial function $\phi_0(r_1, r_2) = \Psi_{1s}(r_1)\Psi_{1s}(r_2)$ where
$$\Psi_{1s}(r_j) = \left(\frac{\zeta^3}{\pi} \right)^{1/2} e^{-\zeta r_j}$$
- By varying ζ , we obtain the Rayleigh ratio is $E(\zeta) = \zeta^2 - \frac{27}{8}\zeta$ in atomic units
- The minimum energy is achieved with $\zeta_{min} = 27/16 \approx 1.68$, compared to $Z = 2$ for the reference system.
- With this variational parameter, $E_{min} = - \left(\frac{27}{16} \right)^2 = -2.8477$ Hartrees.

Assessment of approximations

- Variational and perturbation results are within a few percent of experiment
 - Good as an absolute number
 - Not *that* good for ionization energies and other properties
- How to improve?
 - For variation theory, use more basis functions
 - For perturbation theory, use higher-order terms

Method	Energy (Hartrees)
Perturbation (1st order)	-2.750
Variation (Exponential decay)	-2.8477
Experimental	-2.9033

The Pauli Principle

- A sixth postulate: the total wavefunction (including spin) must be antisymmetric, $\Psi(1,2) = -\Psi(2,1)$, with respect to the interchange of any pair of fermions (particles with odd half-integer spin), e.g. electrons.
- We have focused on spatial orbitals. To satisfy the Pauli principle we need to consider spinorbitals that incorporate both space and spin, e.g.
 $\Psi_{1s}^{\alpha}(m) = \Psi_{1s}(r_m)\alpha(m)$ and $\Psi_{1s}^{\beta}(n) = \Psi_{1s}(r_n)\beta(n)$.
- Exercise: construct a linear combination $\Psi(1,2)$ of spinorbitals, $\Psi_{1s}^{\alpha}(m)$ and $\Psi_{1s}^{\beta}(n)$ that satisfies the Pauli Principle for two electrons. ($m \in \{1,2\}$ and $n \in \{1,2\}$).
- The Pauli exclusion principle: No two electrons can occupy the same state.
 - It is a consequence of the Pauli principle.

Slater Determinants

$$\bullet \quad \Psi(1,2,\dots,N) = \sqrt{\frac{1}{N!}} \begin{vmatrix} u_1(1) & u_2(1) & \dots & u_N(1) \\ u_1(2) & u_2(2) & \dots & u_N(2) \\ \dots & \dots & \dots & \dots \\ u_1(N) & u_2(N) & \dots & u_N(N) \end{vmatrix},$$

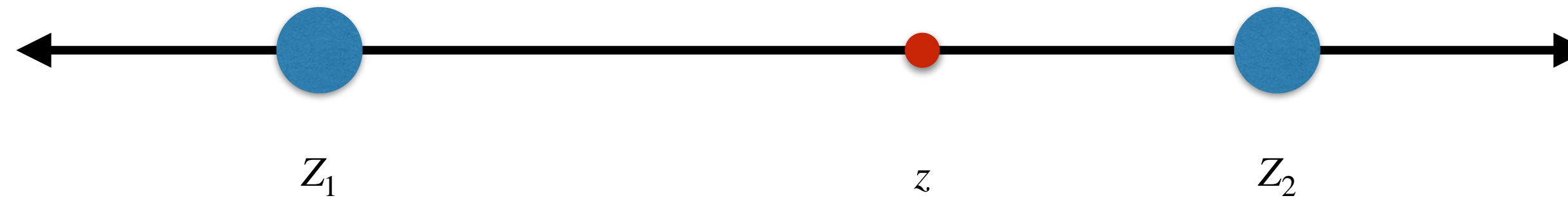
where $u_n(m)$ is a spinorbital for electron m

- $\Psi(1,2,\dots,N) = \sqrt{\frac{1}{N!}} |u_1(1)u_2(2)\dots u_N(N)|$ is a shorthand notation
- Changes sign upon interchange any two rows or columns; determinants are antisymmetric, satisfying the Pauli principle
- If columns are identical, occupying the same orbital, the Slater determinant is zero

The Born-Oppenheimer Approximation

- Nuclei are much heavier than electrons and move much more slowly.
- In the Born-Oppenheimer approximation, one solves an *approximate* Schrodinger equation for a given *nuclear* arrangement.
- Basis of most computational chemistry calculations

Hydrogen molecule ion on a single axis



- Let's look at an example of the BO approximation

- $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \sum_{I=1}^2 \frac{\hbar^2}{2m_I} \frac{\partial^2}{\partial Z_I^2} + V(z, Z_1, Z_2)$ is the full Hamiltonian

- $\hat{\mathbf{H}} = T_e + T_N + V$ is a simplification in terms of kinetic and potential energies
- What is included in V that is not part of the hydrogen atom?

Separation of variables

- $\hat{H}\Psi(z, Z_1, Z_2) = E\Psi(z, Z_1, Z_2)$ is the Schrodinger equation
- We will try to separate the wavefunction into,
 $\Psi(z, Z_1, Z_2) \approx \Psi(z; Z_1, Z_2)\Psi(Z_1, Z_2) = \Psi\Psi_N$
- $\hat{H}\Psi\Psi_N = \hat{T}_e\Psi\Psi_N + \hat{T}_N\Psi\Psi_N + \hat{V}\Psi\Psi_N$ uses the separated wavefunction
 $= \Psi_N\hat{T}_e\Psi + \Psi\hat{T}_N\Psi_N + \hat{W} + \hat{V}\Psi\Psi_N = E\Psi\Psi_N$
- \hat{W} comes from the nuclear kinetic energy operator

$$\hat{\mathbf{W}}$$

- $\hat{\mathbf{W}}$ comes from the nuclear kinetic energy operator

$$\begin{aligned} \bullet \quad \frac{\partial^2}{\partial Z_I^2} (\Psi \Psi_N) &= \frac{\partial}{\partial Z_I} \left[\Psi_N \frac{\partial \Psi}{\partial Z_I} + \Psi \frac{\partial \Psi_N}{\partial Z_I} \right] \\ &= \frac{\partial \Psi_N}{\partial Z_I} \frac{\partial \Psi}{\partial Z_I} + \Psi_N \frac{\partial^2 \Psi}{\partial Z_I^2} + \frac{\partial \Psi}{\partial Z_I} \frac{\partial \Psi_N}{\partial Z_I} + \Psi \frac{\partial^2 \Psi_N}{\partial Z_I^2} \end{aligned}$$

$$\bullet \quad W = \sum_{I=1}^2 \frac{\hbar^2}{2m_I} \left(2 \frac{\partial \Psi}{\partial Z_I} \frac{\partial \Psi_N}{\partial Z_I} + \Psi_N \frac{\partial^2 \Psi}{\partial Z_I^2} \right)$$

- Is non-zero, but small compared to other terms. $m_I \ll m_e$ is in the denominator

Completing the separation

- In the BO approximation we drop $\hat{\mathbf{W}}$ such that,

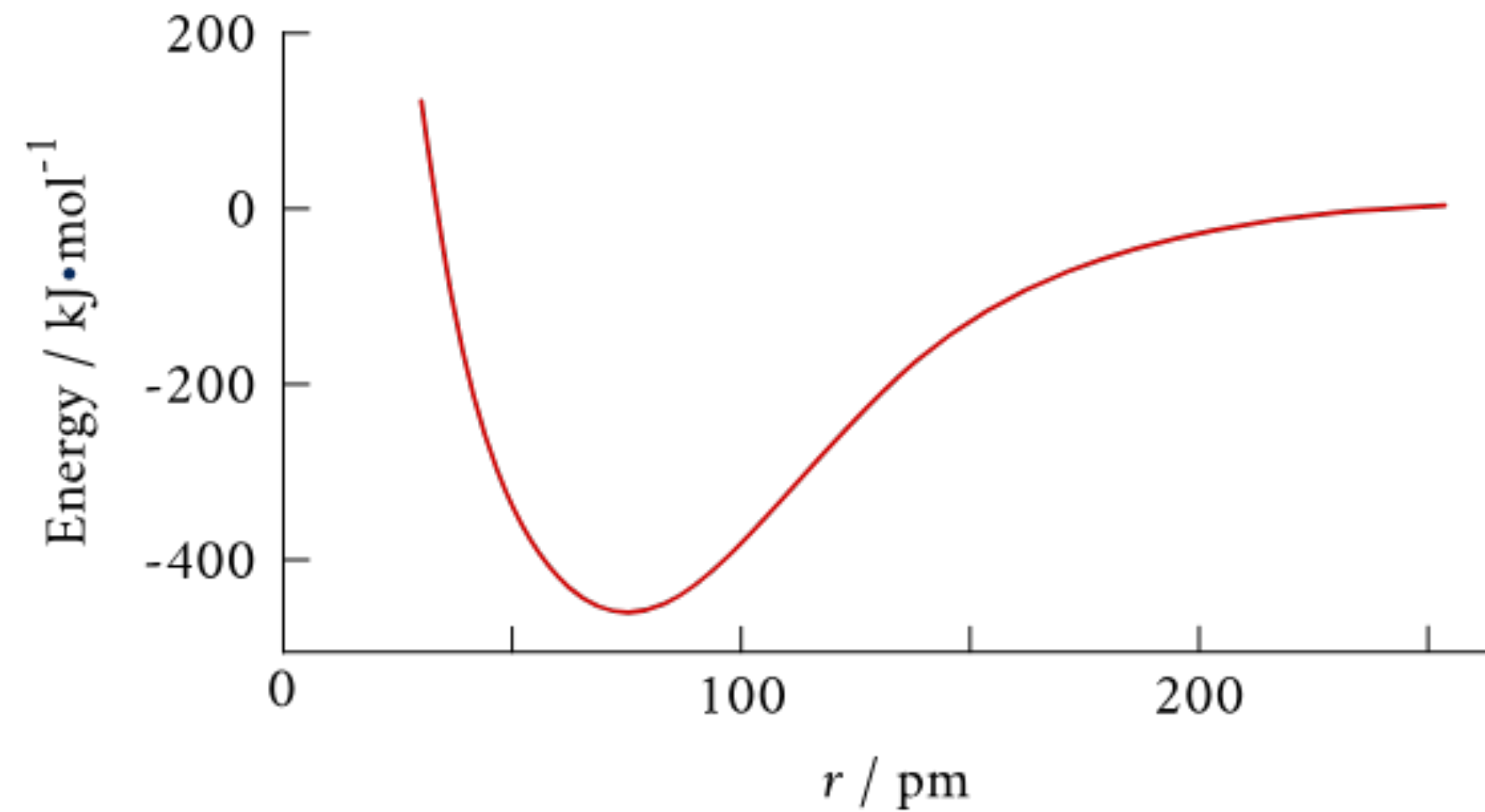
$$\hat{\mathbf{H}}\Psi\Psi_N \approx \Psi_N\hat{\mathbf{T}}_e\Psi + \Psi\hat{\mathbf{T}}_N\Psi_N + \hat{\mathbf{V}}\Psi\Psi_N = E\Psi\Psi_N$$
- $$\Psi\hat{\mathbf{T}}_N\Psi_N + \left(\hat{\mathbf{T}}_e\Psi + \hat{\mathbf{V}}\Psi\right)\Psi_N = E\Psi\Psi_N$$
- If nuclear positions are fixed, then the *electronic* Schrodinger equation is,

$$\hat{\mathbf{T}}_e\Psi + \hat{\mathbf{V}}\Psi = E_e(T_1, T_2)\Psi$$
- It is exactly solvable, even in 3D, but very complicated.
- If we solve this equation, then we can substitute the solution

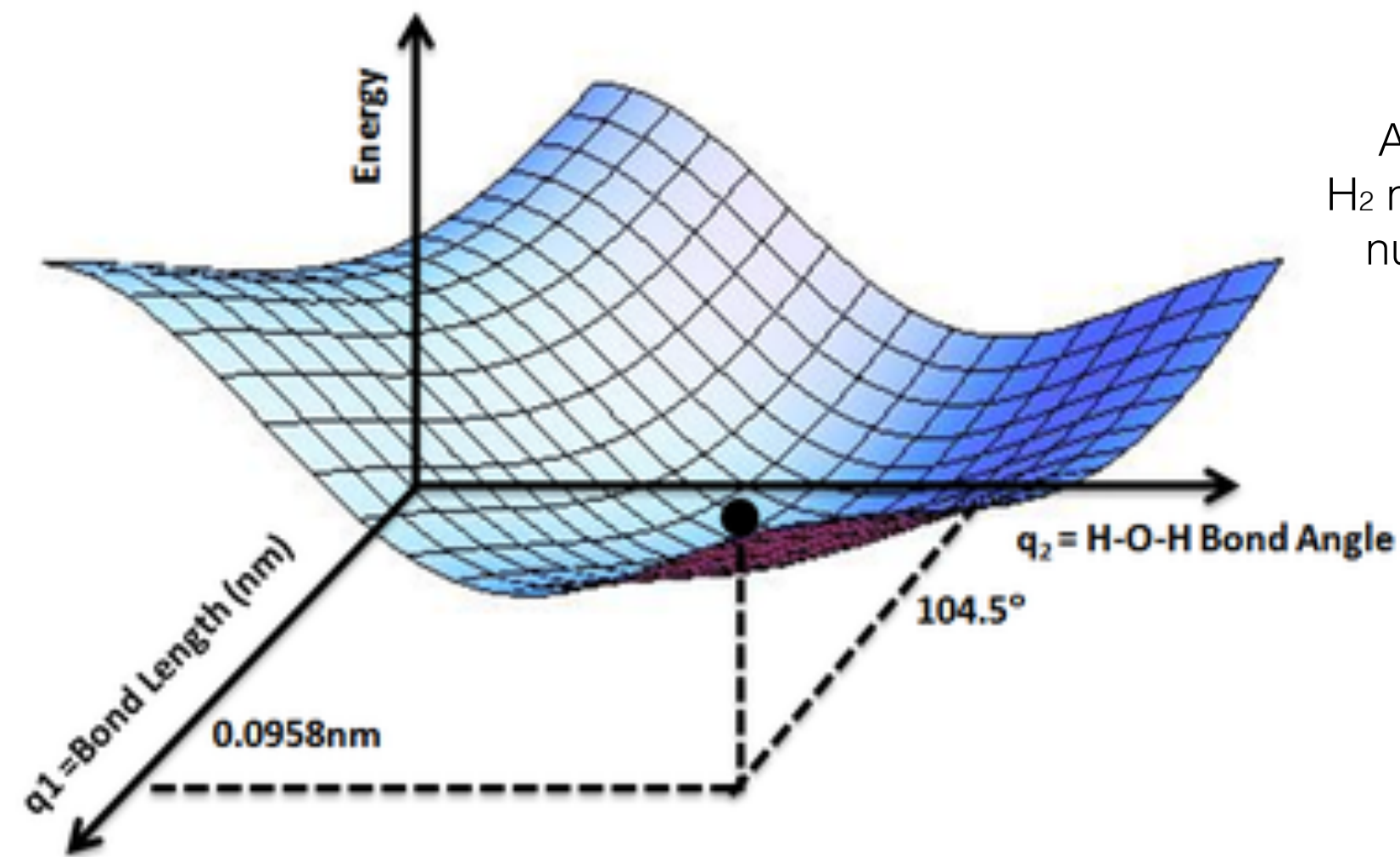
$$\Psi\hat{\mathbf{T}}_N\Psi_N + E_e\Psi\Psi_N = E\Psi\Psi_N$$
and can divide by Ψ to get the a *nuclear* Schrodinger equation, $\hat{\mathbf{T}}_N\Psi_N + E_e\Psi_N = E\Psi_N$, that depends on the electronic wavefunction.

Potential energy surfaces

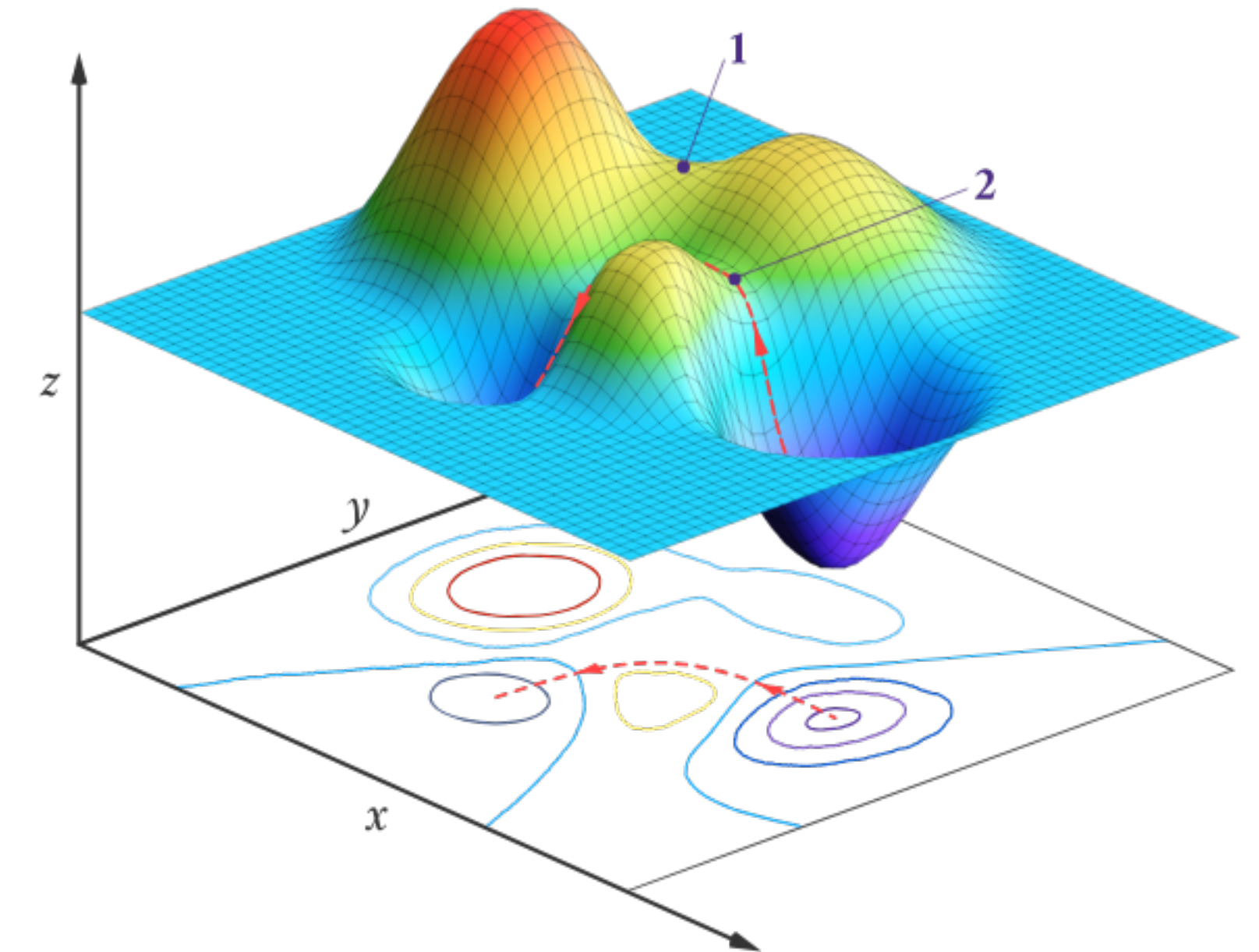
The ground-state energy as a function of one or two order parameters



A potential energy curve for the covalent bond in a H_2 molecule. The distance r is the distance between the nuclei of the two H atoms. (CC BY-NC Ümit Kaya via LibreTexts)



PES for water molecule showing the energy minimum corresponding to optimized molecular structure for water- O-H bond lengths of 0.0958 nm and H-O-H bond angle of 104.5° of Wikipedia (Credit: Aimnature)



A 2-D contour map and corresponding Potential Energy Surface for a hypothetical endothermic reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

Review Questions

- What term makes the Schrodinger equation for helium difficult to solve?
- How does the Pauli exclusion principle follow from the Pauli principle?
- Why are Slater determinants helpful for constructing wavefunctions that satisfy the Pauli principle?
- How does the Born-Oppenheimer approximation simplify the Schrodinger equation?
- What is a potential energy surface and how can they be interpreted?