4. Variational Principle and Numerical Solutions

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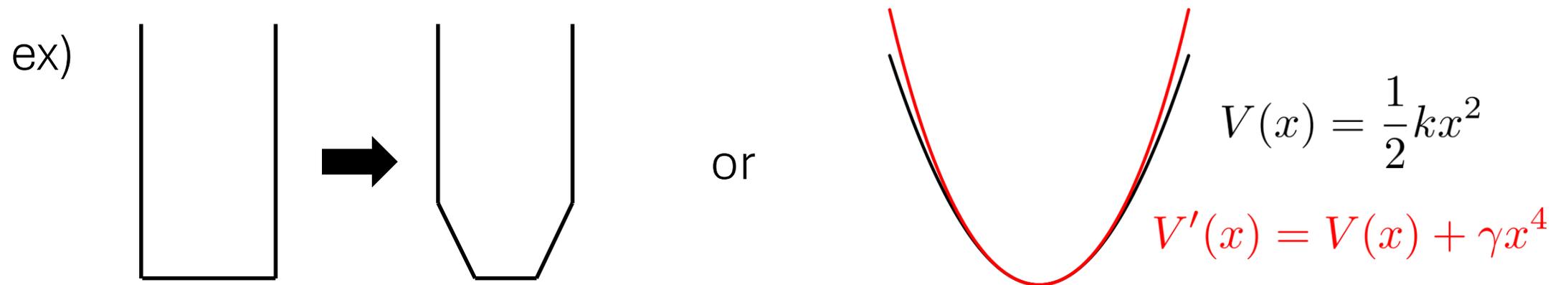Computational Chemistry Group
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Motivation

There are many systems for which we cannot find exact analytical solutions for Schrödinger equation. This problem arises even when the analytically solvable potentials are only slightly modified:

ex)

or

$$V(x) = \frac{1}{2}kx^2$$

$$V'(x) = V(x) + \gamma x^4$$

For chemical systems, any atoms or molecules with more than two electrons cannot be exactly solved.

In such cases, we need to find approximate solutions.

2

Approximate Solutions for Schrödinger Equation

There are two approaches to find approximate solutions: perturbation theory and variational method.

The perturbation theory is useful when the Hamiltonian can be expressed as

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad \text{with} \quad \hat{H}_0 \gg \hat{H}_1,$$

and we know the solution for $\hat{H}_0$. This is useful for obtaining approximate analytical solutions, but quickly loses its utility as $\hat{H}_1$ becomes larger.

In contrast, the variational method can be applied to an arbitrary Hamiltonian to yield numerical solutions.

Moreover, the accuracy of the solution can be systematically increased.

The Variational Principle

Theorem: Suppose we want to solve the Schrödinger eqn, $\hat{H}\psi = E\psi$.
If we denote (unknown) ground state energy as E_1, the inequality

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1$$

is satisfied for an arbitrary wavefunction ϕ, where the equality only holds when ϕ is exactly proportional to the true ground state eigenfunction ψ_1.

Recall that (chapter 1, slide 7)

$$\int \langle \cdots \rangle \, d\tau$$

indicates integrating the function in $\langle \cdots \rangle$ over all space that it is defined.

The Variational Principle

Proof: We start by normalizing ϕ by dividing by the normalization constant:

$$\phi' = \frac{\phi}{\left(\int \phi^* \phi \, d\tau \right)^{1/2}}$$

which satisfies

$$\int \phi'^* \phi' \, d\tau = 1.$$

As ϕ' is a wavefunction, it can be expressed by a linear combination of the normalized solutions $\{\psi_j\}$, even though we do not know them:

$$\phi' = \sum_{j=1}^{\infty} c_j \psi_j \quad \text{with} \quad c_j = \int \psi_j^* \phi' \, d\tau, \quad \sum_{j=1}^{\infty} |c_j|^2 = 1.$$

The Variational Principle

We can now insert this expansion of ϕ' in the original expression

$$(\hat{H}\psi_k = E_k\psi_k)$$

$$\int \phi'^* \hat{H} \phi' \, d\tau = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k \int \psi_j^* \hat{H} \psi_k \, d\tau = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k E_k \int \psi_j^* \psi_k \, d\tau$$

$$= \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k E_k \delta_{jk} = \sum_{j=1}^{\infty} |c_j|^2 E_j \geq \sum_{j=1}^{\infty} |c_j|^2 E_1 = E_1.$$

(orthonormality)　　　　　　　　　　　　　　　$(E_j \geq E_1)$

Finally, converting back from ϕ' to ϕ gives

$$\int \phi'^* \hat{H} \phi' \, d\tau \geq E_1 \quad \blacktriangleright \quad \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1.$$

Optimizing the Trial Function

We can therefore find an approximate numerical solution by minimizing the quantity

$$E = \frac{\displaystyle\int \phi^* \hat{H} \phi \, d\tau}{\displaystyle\int \phi^* \phi \, d\tau}$$

as ϕ will become closer to the true solution ψ as E approaches E_0.

Therefore, we can assume a reasonable trial function with adjustable parameters

$$\phi = \phi(a, b, c \cdots),$$

which makes the energy expectation value also a function of the parameters

$$E = E(a, b, c \cdots).$$

Optimizing the Trial Function

Then, we can make the trial function as close as possible to the true ground state wavefunction by finding the parameters that minimize E.

The necessary condition for such situation is that the partial derivatives should vanish altogether,

$$\frac{\partial E}{\partial a} = 0, \ \frac{\partial E}{\partial b} = 0, \cdots.$$

The most widely used form of the trial function is a linear combination of basis functions $\{\phi_j\} = \{\phi_1, \ \phi_2, \ \cdots, \ \phi_N\}$,

$$\phi = \sum_{j=1}^{N} d_j \phi_j,$$

where we will assume both $\{\phi_j\}$ and the coefficients $\{d_j\}$ to be real.

Optimizing the Trial Function

ex) For a quantum harmonic oscillator, pretend that we do not know the exact solution and assume a trial function of the form

$$\phi(x) = Ae^{-ax^2}.$$

Find the value of a that minimizes E and confirm that the solution indeed makes $\phi(x)$ the exact ground state wavefunction.

Linear Trial Function

For a linear trial function,

$$\int \phi \hat{H} \phi \, d\tau = E \int \phi^2 \, d\tau,$$

$$\sum_{j=1}^{N} \sum_{k=1}^{N} d_j d_k \int \phi_j \hat{H} \phi_k \, d\tau = E \sum_{j=1}^{N} \sum_{k=1}^{N} d_j d_k \int \phi_j \phi_k \, d\tau.$$

Recall that $\{\phi_j\}$ are not the eigenfunctions of $\hat{H}$, and we also did not assume any orthonormality between $\{\phi_j\}$. We now introduce the notation

$$\int \phi_j \phi_k \, d\tau = S_{jk}, \quad \int \phi_j \hat{H} \phi_k \, d\tau = H_{jk},$$

which converts the original expression to

$$\sum_{j=1}^{N} \sum_{k=1}^{N} d_j d_k H_{jk} = E \sum_{j=1}^{N} \sum_{k=1}^{N} d_j d_k S_{jk}.$$

Linear Trial Function

Our goal is to find the coefficients $\{d_j\}$ that minimize E. To do this, we see E as a function of $\{d_j\}$, and find the conditions for the minimum

$$\frac{\partial E}{\partial d_j} = 0.$$

Differentiating the last expression in the previous slide by d_1 leads to

$$2\sum_{j=1}^{N} d_j H_{1j} = \frac{\partial E}{\partial d_1} \sum_{j=1}^{N}\sum_{k=1}^{N} d_j d_k S_{jk} + 2E \sum_{j=1}^{N} d_j S_{1j},$$

where we have used the relation

$$S_{jk} = S_{kj}, \quad H_{jk} = H_{kj}.$$

Note the factor 2 which comes from both $j = 1$ and $k = 1$.

Linear Trial Function

Rearranging the equation gives

$$\sum_{j=1}^{N}(H_{1j} - ES_{1j})d_j = 0.$$

By differentiating also with d_2, d_3, $\cdots$ d_N, we get a set of N linear simultaneous equations

$$\sum_{j=1}^{N}(H_{nj} - ES_{nj})d_j = 0, \quad n = 1, 2, \cdots, N.$$

We can easily find the solution of $d_1 = d_2 = \cdots = d_N = 0$, but it means

$$\phi = \sum_{j=1}^{N}\phi_j = 0,$$

which is trivial and therefore not interesting at all.

Secular Equation

We have learned that the condition for a nontrivial solution is

$$
\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN}
\end{vmatrix} = 0,
$$

which is called secular equation, while the determinant is called secular determinant.

The secular equation is an N-th order polynomial equation of E, and therefore solving it leads to N values of E with possible degeneracy.

Finally, we plug $E_1, \ E_2, \ \cdots, \ E_N$ in the original simultaneous equation and solve for $\{d_j\}$ to construct the solutions $\phi_1, \ \phi_2, \ \cdots, \ \phi_N$.

Example: H_2^+

H_2^+ is the simplest molecular ion which consists of two protons and one electron.
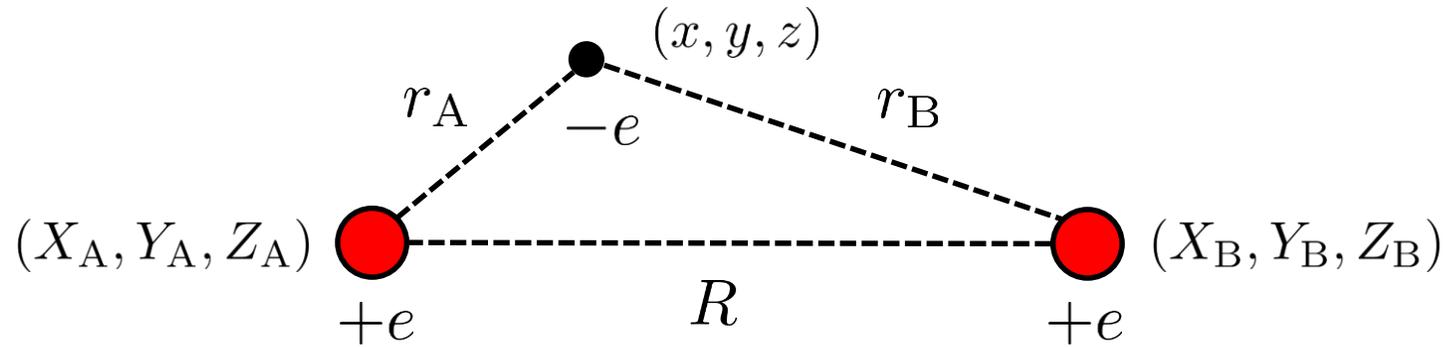
We start by applying Born-Oppenheimer approximation, which assumes that the nuclei are fixed point charges.

This reflects the fact that the nuclei are much heavier than the electron, and therefore can be treated as static classical particles.

As a result, the three-particle problem reduces to an one-particle problem only for the electron.

14

Example: H$_2^+$

The Hamiltonian operator for the electron is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\epsilon_0 r_{\mathrm{A}}} - \frac{e^2}{4\pi\epsilon_0 r_{\mathrm{B}}} + \frac{e^2}{4\pi\epsilon_0 R},$$

$$\underbrace{\hat{\nabla}^2 \text{ (Laplacian)}}$$

where

$$r_{\mathrm{A}}(x, y, z) = \sqrt{(x - X_{\mathrm{A}})^2 + (y - Y_{\mathrm{A}})^2 + (z - Z_{\mathrm{A}})^2},$$

$$r_{\mathrm{B}}(x, y, z) = \sqrt{(x - X_{\mathrm{B}})^2 + (y - Y_{\mathrm{B}})^2 + (z - Z_{\mathrm{B}})^2}.$$

It is not possible to find analytical solutions of the Schrödinger equation for such a complicated Hamiltonian, so we need to solve it numerically by using the variational principle.

The question is: what are the good basis functions?

Example: H$_2^+$

A good starting point will be the hydrogen orbitals centered at the position of individual nuclei.

The minimal basis set is the smallest basis set that suits the given system, which are the two 1s orbitals

$$1s_A(x, y, z) = \left(\frac{1}{\pi a^3}\right)^{1/2} e^{-r_A/a}, \quad 1s_B(x, y, z) = \left(\frac{1}{\pi a^3}\right)^{1/2} e^{-r_B/a}.$$

Note that r_A and r_B are functions of x, y, and z. As we have two basis functions, the secular determinant is a 2-by-2 matrix and

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0.$$

Example: H_2^+

The integrals are

$$S_{\mathrm{AA}} = S_{\mathrm{BB}} = 1, \quad S_{\mathrm{AB}} = S_{\mathrm{BA}} = S,$$

$$H_{\mathrm{AA}} = H_{\mathrm{BB}} = E_{1\mathrm{s}} + J, \quad H_{\mathrm{AB}} = H_{\mathrm{BA}} = E_{1\mathrm{s}}S + K,$$

where $E_{1\mathrm{s}}$ is the 1s orbital energy of a single hydrogen atom and S, J, and K are defined as

$$S = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} 1\mathrm{s}_{\mathrm{A}} 1\mathrm{s}_{\mathrm{B}} \, dx \, dy \, dz, \qquad \text{(overlap integral)}$$

$$J = -\frac{e^2}{4\pi\epsilon_0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} 1\mathrm{s}_{\mathrm{A}} \left(\frac{1}{r_{\mathrm{B}}} - \frac{1}{R} \right) 1\mathrm{s}_{\mathrm{A}} \, dx \, dy \, dz, \qquad \text{(Coulomb integral)}$$

$$K = -\frac{e^2}{4\pi\epsilon_0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} 1\mathrm{s}_{\mathrm{A}} \left(\frac{1}{r_{\mathrm{A}}} - \frac{1}{R} \right) 1\mathrm{s}_{\mathrm{B}} \, dx \, dy \, dz. \qquad \text{(Exchange integral)}$$

17

Example: H$_2^+$

As a result, the secular equation becomes

$$\begin{vmatrix} E_{1s} + J - E & E_{1s}S + K - ES \\ E_{1s}S + K - ES & E_{1s} + J - E \end{vmatrix} = 0.$$

Expanding the determinant gives a 2$^\text{nd}$-order equation on E,

$$(E_{1s} + J - E)^2 - (E_{1s}S + K - ES)^2 = 0.$$

which yields two solutions

$$E_+ = E_{1s} + \frac{J + K}{1 + S}, \quad E_- = E_{1s} + \frac{J - K}{1 - S}.$$

Note that the values of S, J, and K depend on the internuclear distance

$$R = \sqrt{(X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2}.$$

Example: H_2^+

We still need to find the wavefunctions. This can be done by solving the simultaneous equation constructed from the variational principle

$$\sum_{j=1}^{N}(H_{nj} - ES_{nj})d_j = 0,$$

which becomes

$$(H_{AA} - ES_{AA})d_A + (H_{AB} - ES_{AB})d_B = 0,$$
$$(H_{BA} - ES_{BA})d_A + (H_{BB} - ES_{BB})d_B = 0,$$

$$S_{AA} = S_{BB} = 1,$$
$$S_{AB} = S_{BA} = S,$$
$$H_{AA} = H_{BB} = E_{1s} + J,$$
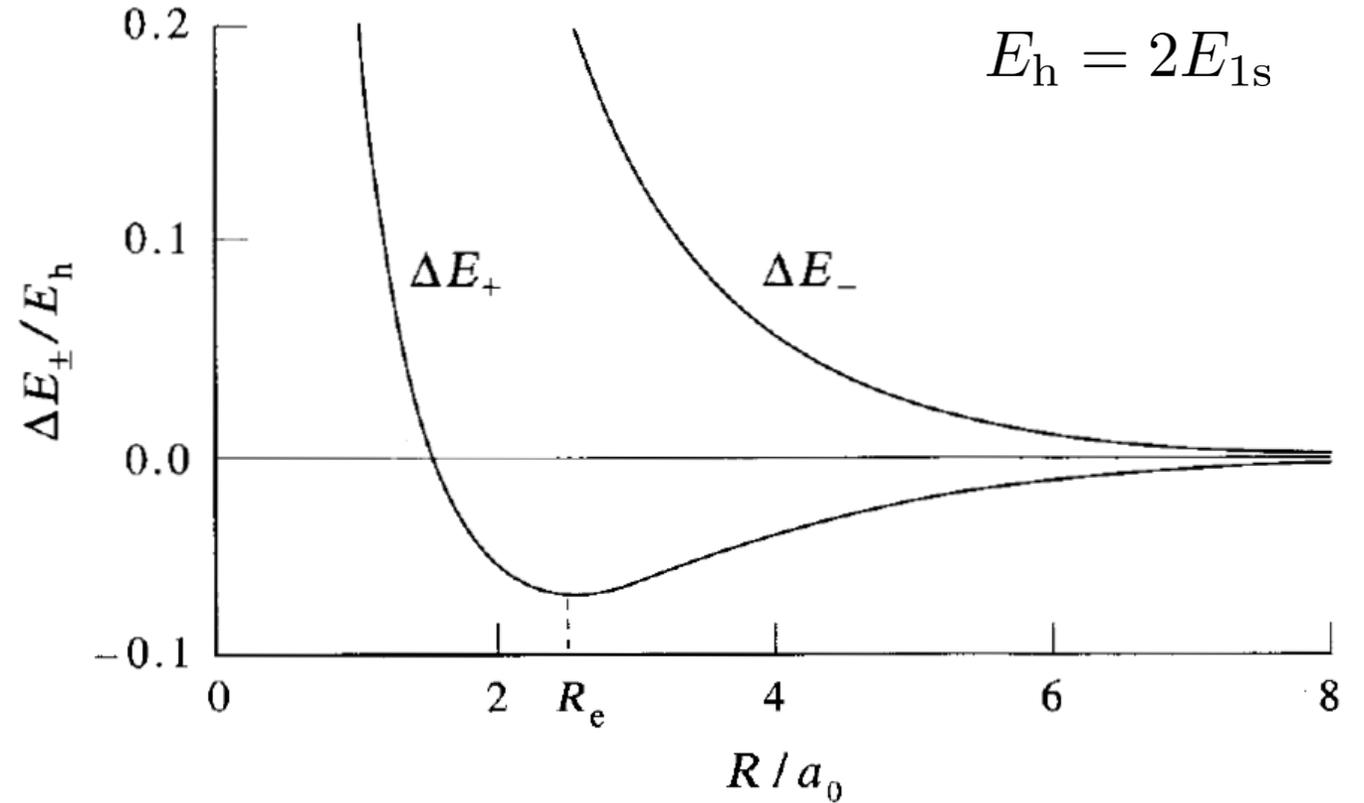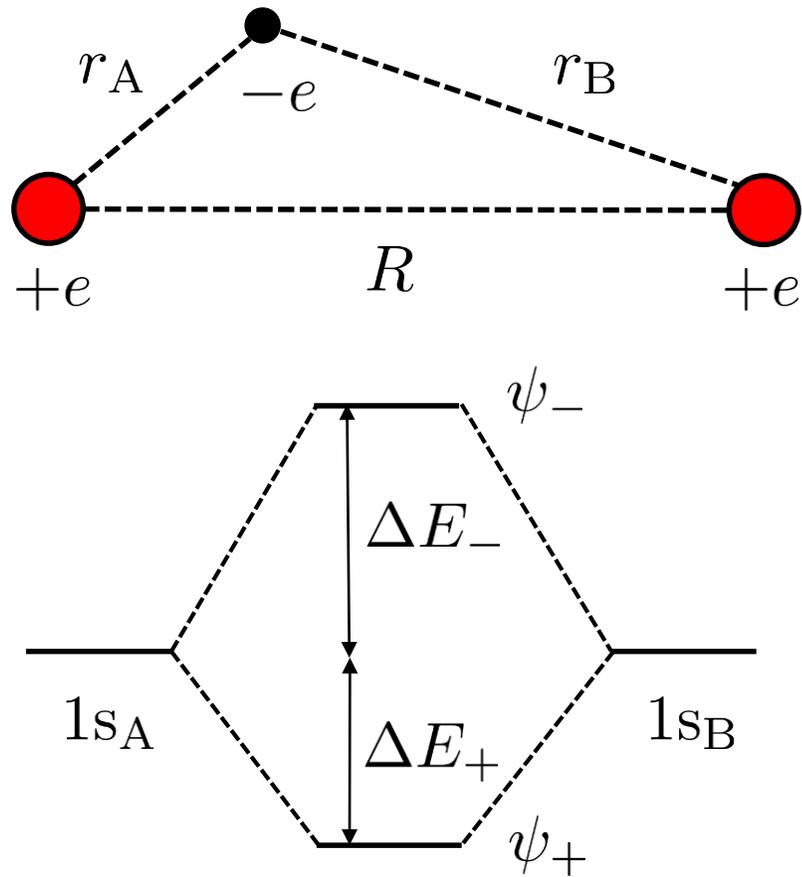$$H_{AB} = H_{BA} = E_{1s}S + K$$

in our system. Inserting $E = E_+$ and solving for d_A and d_B gives

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B),$$
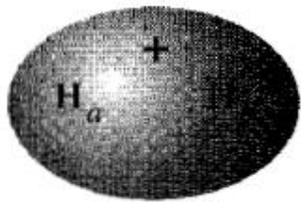
while for $E = E_-$ we have

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B).$$
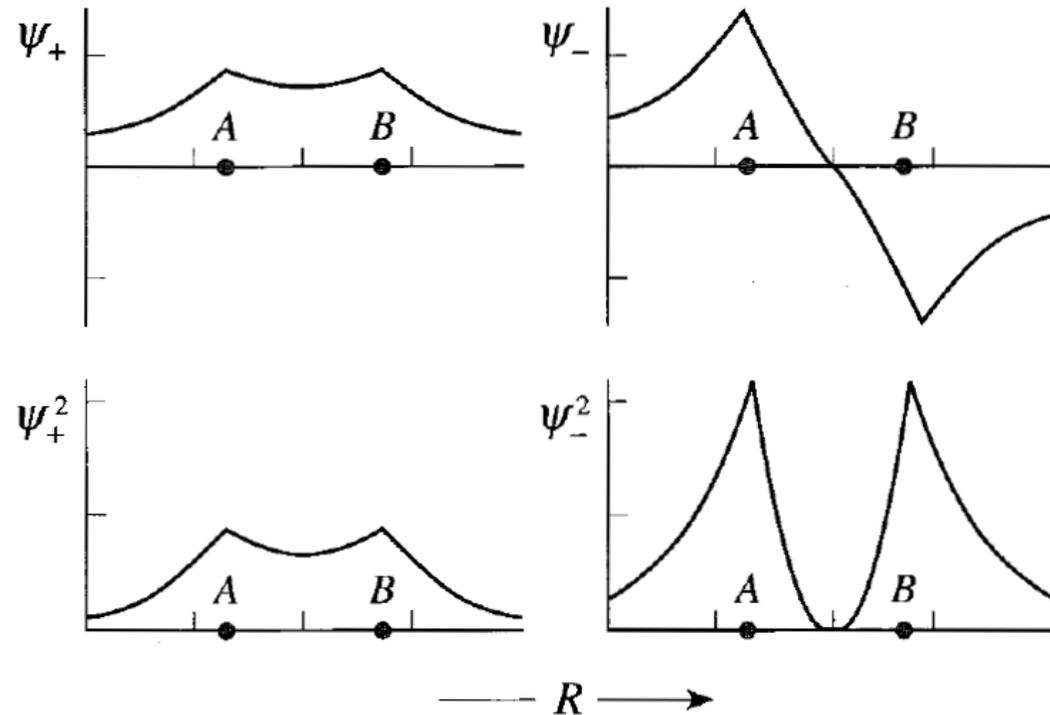
19
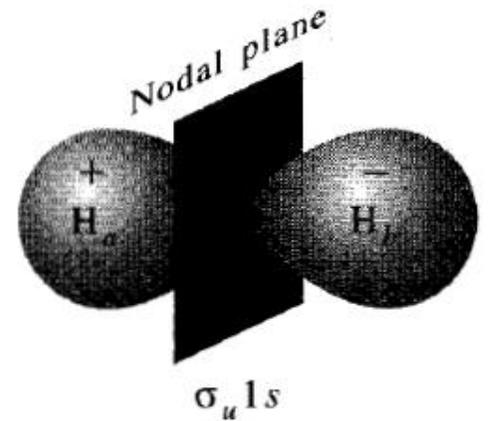
Molecular Orbital Diagram and Energy Curve

$$E_{\mathrm{h}} = 2E_{1\mathrm{s}}$$

McQuarrie, D. A.; Simon, J. D. Physical Chemistry: a Molecular Approach, Ch. 9

Shape of Molecular Orbital

$$\psi_+ \propto 1s_A + 1s_B$$

$$\psi_- \propto 1s_A - 1s_B$$

McQuarrie, D. A.; Simon, J. D. Physical Chemistry: a Molecular Approach, Ch. 9

Summary: H_2^+

Application of the variational principle to the two 1s atomic orbitals led to bonding and antibonding molecular orbitals.

The bonding orbital has relatively large electron density between the nuclei, which stabilizes H_2^+ when $R \sim R_e$.

The antibonding orbital has a nodal plain between the nuclei, which destabilizes H_2^+. Generally, a node indicates that the wavefunction undergo a sharp change near there, which increases the kinetic energy.

Although we have used the minimal basis of two 1s orbitals, inclusion of the other orbitals (2s, 2p…) will lead to more accurate molecular orbitals, which will be reflected in lower energy expectation values.