<p style="text-align:center">Hydrogen molecule ion: H₂⁺</p>

Hydrogen molecule ion: H$_2{}^+$

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(Date: April 20, 2016)

What is a hydrogen molecule ion?

The hydrogen molecular ion, or H$_2{}^+$, is the simplest molecular ion. It is composed of two positively charged protons and one negatively charged electron, and can be formed from ionization of a neutral hydrogen molecule. It is of great historical and theoretical interest because, having only one electron, the Schrödinger equation for the system can be solved in a relatively straightforward way due to the lack of electron–electron repulsion (electron correlation).

Linear combination of atomic orbitals (LCAO)

In order to construct approximate energy eigenstates, we use the method of linear combination of atomic orbitals (LCAO), which assumes that we can use the atomic energy eigenstates as basis functions.

1.   Prediction for the ground state energy from the Bohr theory

We first discuss the classical theory for the circular motion of one electron (with a charge -e) around the positive ion with the charge Ze.

$$m_e \frac{v^2}{r} = \frac{Ze^2}{r^2}$$

$$m_e v^2 r = Ze^2$$

Angular momentum:

$$L_z = m_e v r = n\hbar$$

Then we get

$$r = \frac{n^2 \hbar^2}{m_e e^2 Z}, \qquad v = \frac{Ze^2}{n\hbar}.$$

The total energy:

$$E = \frac{1}{2} m_e v^2 - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} = -\frac{m_e e^2 Z^2}{2\hbar^2 n^2} = -\frac{1}{2} m_e c^2 \frac{(Z\alpha)^2}{n^2} = -\frac{RZ^2}{n^2}$$

where R is the Rydberg constant and α is the fine structure constant.

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We now consider the hydrogen molecule formed of one electron and two protons, where these two protons are widely separated. What is the lowest energy of this system? There are two possible states.
(i) The electron is close to one of the proton, forming a hydrogen atom in the ground state. (ii) The electron is close to the other proton, forming a hydrogen atom in the ground state.
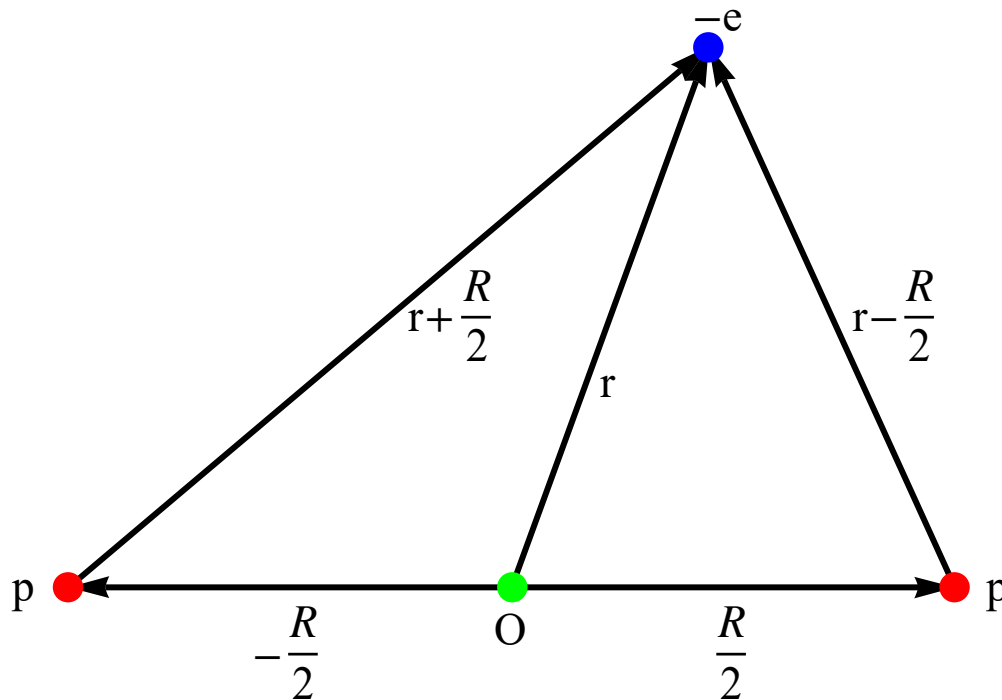

Fig.   The co-ordinates of the two protons and one electron used in the discussion of hydrogen molecule ion. R is the distance between two protons.

(i)   When R becomes very large and the electron is close to one of the proton, the total energy of the electron is close to the energy of the hydrogen atom.

$E_0 = -13.6$ eV.

(ii)   When R becomes very small, the total energy of the electron is close to the energy of the He atom (system of the two protons and one electron),
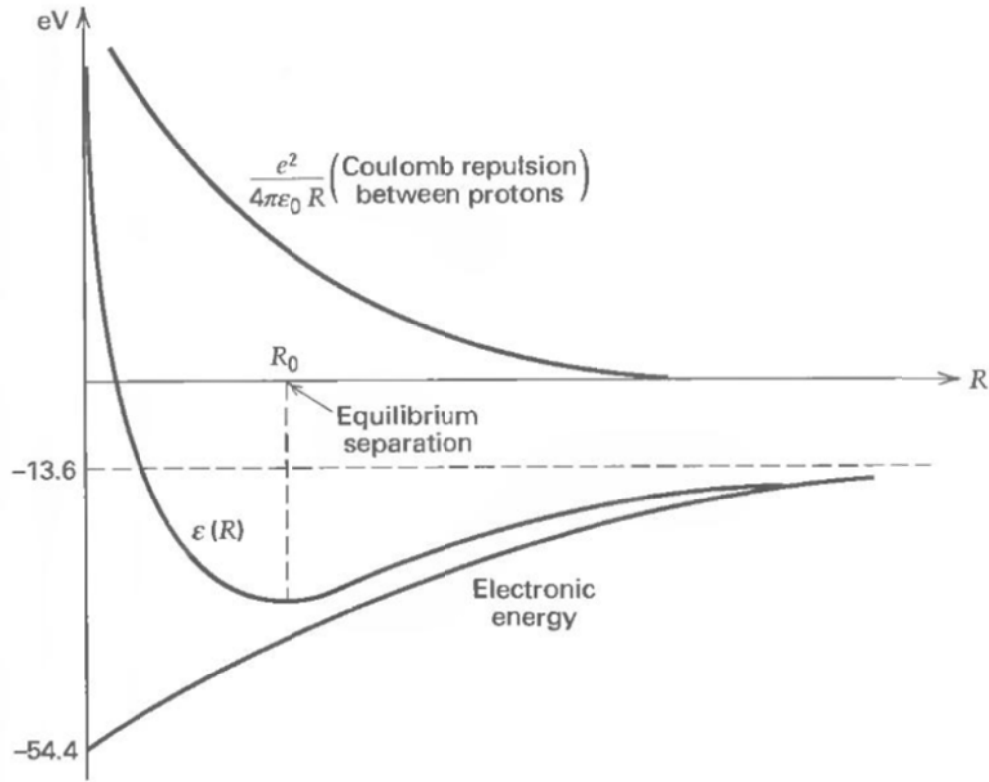
$E_0 = -54.4$ eV.

Fig. Rough prediction of E_0 vs R. R increases with increasing R from -54.4 eV at $R = 0$ [He atom (system of the two protons and one electron)) to -13.6 eV at $R = \infty$ (hydrogen atom)

2. Wave function and Hamiltonian

We consider the wave function of the system of one electron and two protons.
The wave function of electron is given by

$$\psi_{1s}(\boldsymbol{r}_1) = \langle \boldsymbol{r}_1 | 1s \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{|r_1|}{a_0}} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|r - \frac{1}{2}R\right|} = \langle \boldsymbol{r}_1 | \psi_1 \rangle$$

$$\psi_{1s}(\boldsymbol{r}_2) = \langle \boldsymbol{r}_2 | 1s \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{|r_2|}{a_0}} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|r + \frac{1}{2}R\right|} = \langle \boldsymbol{r}_1 | \psi_1 \rangle$$

where a_0 (=0.53 Å) is a Bohr radius,

$$E_{1s} = -\frac{e^2}{2a_0} = -R = \text{-13.6 eV}$$

and

$$r_1 = r - \frac{1}{2}R, \qquad r_2 = r + \frac{1}{2}R.$$

The Hamiltonian of the system is given by

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{\left|\hat{r} - \dfrac{R}{2}\right|} - \frac{e^2}{\left|\hat{r} + \dfrac{R}{2}\right|} + \frac{e^2}{|R|}.$$

We have the commutation relation for the parity operator as

$$\hat{\pi}\hat{H}\hat{\pi} = \hat{H}, \qquad \text{or} \qquad [\hat{\pi}, \hat{H}] = 0$$

since

$$\hat{\pi}\hat{p}\hat{\pi}^+ = -\hat{p}, \qquad \hat{\pi}\hat{r}\hat{\pi}^+ = -\hat{r}, \qquad \hat{\pi} = \hat{\pi}^+ = \hat{\pi}^{-1}.$$

3.   Properties of the kets $|\psi_1\rangle$ and $|\psi_2\rangle$

A positively ionized hydrogen molecule consists of two protons with one electron worming its way around them. If two protons are very far apart, the electron will stay close to one proton and form a hydrogen atom in its lowest state, and the other proton will remain alone as a positive ion. If the two protons are far apart, we can visualize one physical state in which the electron is attached to one of protons. There is another state symmetric to the one, in which the electron is near the other proton, and the first proton is the one that is an ion. We will take these two states as our basis states, and we call these $|\psi_1\rangle$ and $|\psi_2\rangle$.
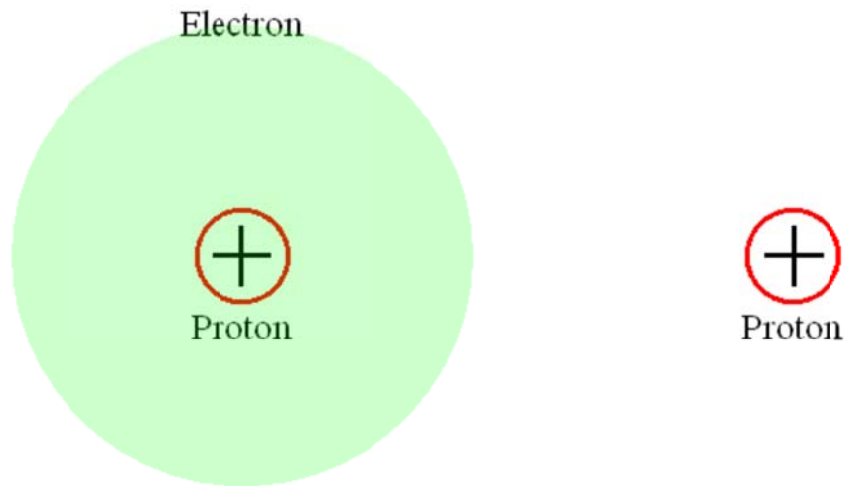
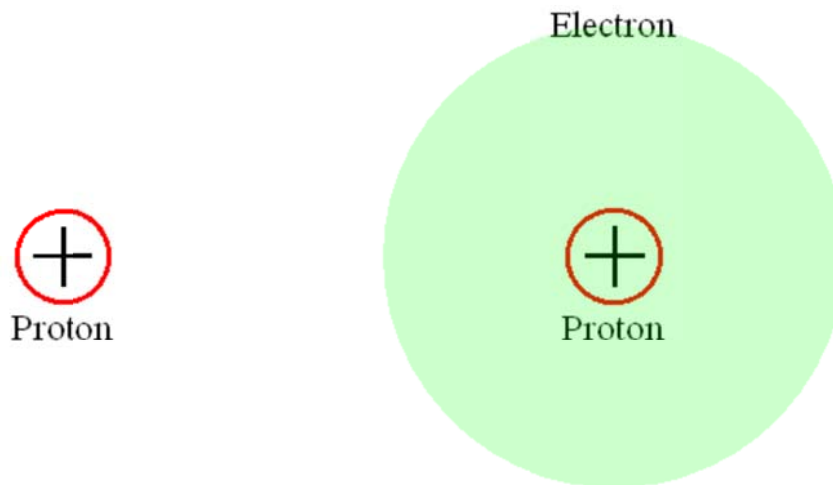**Fig.** The state $|\psi_1\rangle$ for the two protons and one electron.

Fig. The state $|\psi_2\rangle$ for the two protons and one electron

$|\psi_1\rangle$ and $|\psi_2\rangle$ are the eigenkets such that

$$(\frac{\hat{p}^2}{2m_e} - \frac{e^2}{\left|\hat{r} - \dfrac{R}{2}\right|})|\psi_1\rangle = E_{1s}|\psi_1\rangle$$

$$(\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} + \dfrac{\boldsymbol{R}}{2}\right|})|\psi_2\rangle = E_{1s}|\psi_2\rangle$$

Note that $\langle \boldsymbol{r}|\psi_1\rangle = \psi_1(\boldsymbol{r})$ is the wave function of the hydrogen atom when only proton 1 exists. $\langle \boldsymbol{r}|\psi_2\rangle = \psi_2(\boldsymbol{r})$ is the wave function of the hydrogen atom when only proton 2 exists. In practice, proton 1 or proton 2 does not exist alone, but the two protons exist with a finite separation. Even them if their separation is very large, we can consider either $\psi_1(\boldsymbol{r})$ or $\psi_2(\boldsymbol{r})$ as the eigenfunction of the whole system in a zeroth order approximation. Thus the state of this system is doubly degenerate in this approximation.

((Note))
We use the properties of the parity operator

$$\hat{\pi}\hat{\boldsymbol{p}}\hat{\pi} = -\hat{\boldsymbol{p}}, \qquad \hat{\pi}\hat{\boldsymbol{r}}\hat{\pi} = -\hat{\boldsymbol{r}}, \qquad \hat{\pi} = \hat{\pi}^{+} = \hat{\pi}^{-1}.$$

We have the relation such that

$$\hat{\pi}\hat{H}_1\hat{\pi} = \hat{H}_2, \qquad \hat{\pi}\hat{H}_2\hat{\pi} = \hat{H}_1$$

or

$$\hat{\pi}\hat{H}_1 = \hat{H}_2\hat{\pi}, \qquad \hat{\pi}\hat{H}_2 = \hat{H}_1\hat{\pi}$$

where

$$\hat{H}_1 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} - \dfrac{\boldsymbol{R}}{2}\right|}, \quad \hat{H}_2 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} + \dfrac{\boldsymbol{R}}{2}\right|}$$

Suppose that $|\psi_1\rangle$ is the eigenket of $\hat{H}_1$ with the eigenvalue E_{1s};

$$\hat{H}_1|\psi_1\rangle = E_{1s}|\psi_1\rangle$$

$|\psi_2\rangle$ is the eigenket of $\hat{H}_2$ with the same eigenvalue E_{1s};

$$\hat{H}_2|\psi_2\rangle = E_{1s}|\psi_2\rangle$$

In the $|r\rangle$ representation, we have

$$\langle r|\hat{H}_1|\psi_1\rangle = E_{1s}\langle r|\psi_1\rangle, \qquad \langle r|\hat{H}_2|\psi_2\rangle = E_{1s}\langle r|\psi_2\rangle$$

or

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|r - \frac{R}{2}\right|})\psi_1(r) = E_{1s}\psi_1(r) \tag{1}$$

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|r + \frac{R}{2}\right|})\psi_2(r) = E_{1s}\psi_2(r) \tag{2}$$

When the replacement ($r \rightarrow -r$) is made in Eq.(1), Eq,(1) is changed into

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|r + \frac{R}{2}\right|})\psi_1(-r) = E_{1s}\psi_1(-r) \tag{3}$$

The comparison between Eqs.(2) and (3) leads to the relation

$$\psi_1(-r) = \psi_2(r)$$

or

$$\langle -r|\psi_1\rangle = \langle r|\psi_2\rangle$$

or

$$\langle r|\hat{\pi}|\psi_1\rangle = \langle r|\psi_2\rangle$$

where we use the parity operator; $\hat{\pi}|r\rangle = |-r\rangle$ and $\langle r|\hat{\pi} = \langle -r|$. So that we get the final result

$$\hat{\pi}|\psi_1\rangle = |\psi_2\rangle, \qquad \text{or} \qquad \hat{\pi}|\psi_2\rangle = \hat{\pi}^2|\psi_1\rangle = |\psi_1\rangle$$

Note that

$$\langle r|\hat{\pi}|\psi_1\rangle = \langle -r|\psi_1\rangle = \langle r|\psi_2\rangle, \qquad \text{or} \qquad \psi_1(-r) = \psi_2(r)$$

$$\langle r|\hat{\pi}|\psi_2\rangle = \langle -r|\psi_2\rangle = \langle r|\psi_1\rangle, \text{ or} \qquad \text{or} \qquad \psi_2(-r) = \psi_1(r)$$

4. Even function and odd function

Since $[\hat{\pi}, \hat{H}] = 0$, there is a simultaneous eigenket of $\hat{H}$ and $\hat{\pi}$.

$$\hat{H}|\psi\rangle = E|\psi\rangle, \qquad \hat{\pi}|\psi\rangle = \lambda|\psi\rangle$$

We use the relation

$$\hat{\pi}|\psi_1\rangle = |\psi_2\rangle, \qquad \hat{\pi}|\psi_2\rangle = |\psi_1\rangle$$

The matrix of $\hat{\pi}$ under the basis of $\{|\psi_1\rangle, |\psi_2\rangle\}$ is given by

$$\hat{\pi} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}_x$$

The eigenkets of $\hat{\pi}$ is as follows.

(i) Even parity (the gerade (even) state); eigenvalue (+1)

$$|\psi_e\rangle = C_e(|\psi_1\rangle + |\psi_2\rangle),$$

or

$$\psi_e(r) = \langle r|\psi_e\rangle = C_e[\psi_1(r) + \psi_2(r)]$$

(ii) Odd parity (the ungerade (odd) state); eigenvalue (-1)

$$|\psi_o\rangle = C_o(|\psi_1\rangle - |\psi_2\rangle)$$

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or

$$\psi_o(r) = \langle r | \psi_o \rangle = C_o[\psi_1(r) - \psi_2(r)]$$

Note that constants C_e and C_o can be determined from the normalization condition later.

5. Correlation function $S(R) = \langle \psi_1 | \psi_2 \rangle$

We consider the correlation function

$$
\begin{aligned}
S(R) &= \langle \psi_1 | \psi_2 \rangle \\
&= \int d^3 r \, \psi_1^*(r) \psi_2(r) \\
&= \int d^3 r \, \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{1}{a_0} \left| r - \frac{R}{2} \right|} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{1}{a_0} \left| r + \frac{R}{2} \right|} \\
&= \frac{1}{\pi a_0^3} \int d^3 r \, e^{-\frac{1}{a_0} \left| r - \frac{R}{2} \right|} e^{-\frac{1}{a_0} \left| r + \frac{R}{2} \right|} \\
&= \frac{1}{\pi a_0^3} \int d^3 r' \, e^{-\frac{1}{a_0} |r' - R|} e^{-\frac{1}{a_0} r'}
\end{aligned}
$$

where $r' = r + \dfrac{R}{2}$,

or

$$
\begin{aligned}
S(R) &= \frac{1}{\pi a_0^3} \int d^3 r \, e^{-\frac{1}{a_0} |r - R|} e^{-\frac{1}{a_0} r} \\
&= \frac{2}{a_0^3} \int_0^\infty r^2 e^{-\frac{1}{a_0} r} dr \int_0^\pi \sin \theta \, d\theta \, e^{-\frac{1}{a_0} \sqrt{r^2 + R^2 - 2rR\cos\theta}} \\
&= e^{-\frac{R}{a_0}} \left(1 + \frac{R}{a_0} + 3 \frac{R^2}{a_0^2} \right)
\end{aligned}
$$

where

$$d^3 r = 2\pi r^2 dr \sin \theta \, d\theta$$

and

$$|\boldsymbol{r} - \boldsymbol{R}| = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$
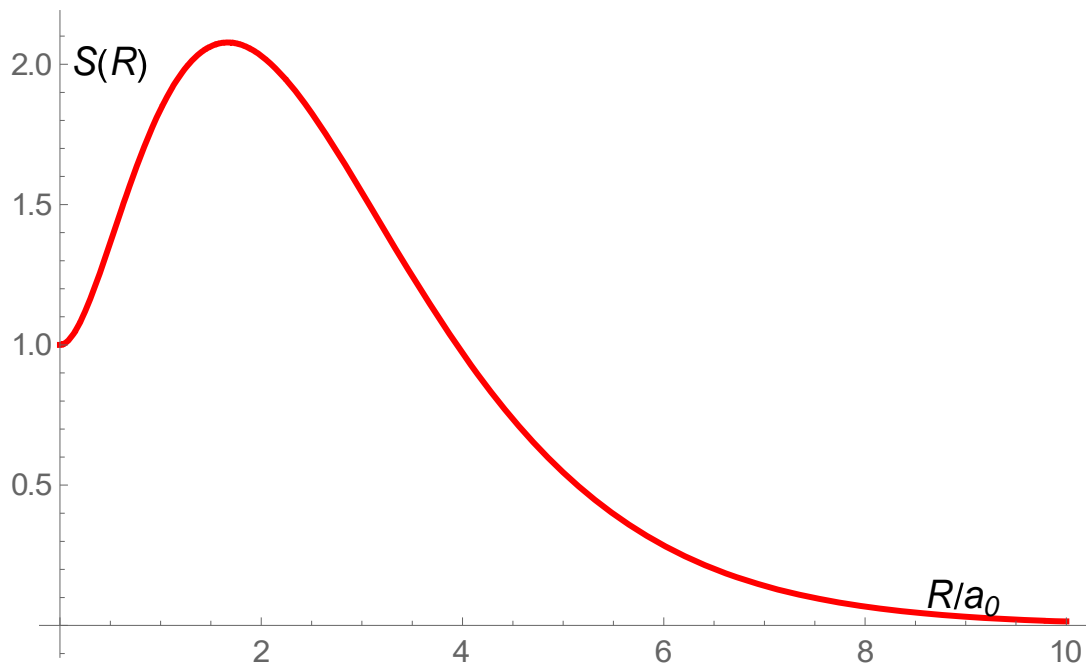
We make a plot of $S(R)$ as a function of R.

Fig. $S(R)$ vs R/a_0. $a_0 = 0.53$ Å. $dS(R)/dR = 0$ at $R/a_0 = 1.61803$ (i.e. $R = 0.8575$ Å).

((**Mathematica**))   Calculation of $S(R)$

```
Clear["Global`*"]; p1 = Sqrt[r^2 - 2 r R Cos[θ] + R^2];
```

$$f1 = 2\pi\,Sin[\theta]\;\frac{1}{a0^3\,\pi}\;Exp\!\left[-\frac{p1}{a0}\right];$$

```
f2 = Integrate[f1, {θ, 0, π}] //
   FullSimplify[#, {R > 0, a0 > 0, r > 0,
      (r - R)^2 > 0}] &;
```

$$f21 = Exp\!\left[\frac{-r}{a0}\right]\,f2\;//\;Simplify[\#,\,r < R]\;\&;$$

$$f22 = Exp\!\left[\frac{-r}{a0}\right]\,f2\;//\;Simplify[\#,\,r > R]\;\&;$$

$$a1 = Integrate\!\left[r^2\,f21,\,\{r,\,0,\,R\}\right]\;//\;Simplify;$$

$$a2 = Integrate\!\left[r^2\,f22,\,\{r,\,R,\,\infty\}\right]\;//$$
$$\quad Simplify[\#,\,a0 > 0]\;\&;$$

```
S = a1 + a2 // FullSimplify
```

$$\frac{e^{-\frac{R}{a0}}\left(3\,a0^2 + 3\,a0\,R + R^2\right)}{3\,a0^2}$$

6, **Normalization:** $\langle\psi_1|\psi_1\rangle = 1$ and $\langle\psi_2|\psi_2\rangle = 1$

$$\langle\psi_1|\psi_1\rangle = \int d^3r\,\psi_1^{\,*}(r)\psi_1(r)$$

$$= \int d^3r\,\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|r-\frac{R}{2}\right|}\,\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|r-\frac{R}{2}\right|}$$

$$= \frac{1}{\pi a_0^{\,3}}\int d^3r\,e^{-\frac{2}{a_0}\left|r-\frac{R}{2}\right|}$$

$$= \frac{1}{\pi a_0^{\,3}}\int d^3r'\,e^{-\frac{2}{a_0}|r'|}$$

where $r' = r - \dfrac{R}{2}$.

or

$$\langle \psi_1 | \psi_1 \rangle = \frac{1}{\pi a_0^3} \int d^3 r \, e^{-\frac{2}{a_0}|r|} = \frac{4\pi}{\pi a_0^3} \int r^2 dr \, e^{-\frac{2}{a_0}|r|} = 1$$

or

$$\langle \psi_1 | \psi_1 \rangle = 1$$

Similarly we have

$$\langle \psi_2 | \psi_2 \rangle = 1$$

((**Mathematica**)) **Calculation of** $\langle \psi_1 | \psi_1 \rangle$

```
Clear["Global`*"];

f1 = 4 π  r²
         ────  Exp[- 2 r ];
         a0³ π       a0

a1 = Integrate[f1, {r, 0, ∞}] //
    Simplify[#, a0 > 0] &

1
```

7.   Calculation of the expectation

$$\langle \psi_e | \psi_e \rangle = C_e^2 \left(\langle \psi_1 | + \langle \psi_2 | \right)\left(| \psi_1 \rangle + | \psi_2 \rangle \right)$$
$$= C_e^2 [2 + \langle \psi_1 | \psi_2 \rangle + \langle \psi_2 | \psi_1 \rangle]$$
$$= C_e^2 [2 + 2S(R)]$$

$$\langle \psi_o | \psi_o \rangle = C_o^2 \left(\langle \psi_1 | - \langle \psi_2 | \right)\left(| \psi_1 \rangle - | \psi_2 \rangle \right)$$
$$= C_o^2 [2 - \langle \psi_1 | \psi_2 \rangle - \langle \psi_2 | \psi_1 \rangle]$$
$$= C_o^2 [2 - 2S(R)]$$

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$$\langle \psi_e | \psi_o \rangle = C_e C_o (\langle \psi_1 | + \langle \psi_2 |)(|\psi_1\rangle - |\psi_2\rangle)$$
$$= C_e C_o [-\langle \psi_1 | \psi_2 \rangle + \langle \psi_2 | \psi_1 \rangle]$$
$$= 0$$

$$\langle \psi_e | \psi_o \rangle = \langle \psi_o | \psi_e \rangle^* = 0.$$

From the normalization condition $\langle \psi_e | \psi_e \rangle = \langle \psi_o | \psi_o \rangle = 1$, we get the constants C_e and C_o as

$$C_e = \frac{1}{\sqrt{2 + 2S(R)}}$$

$$C_o = \frac{1}{\sqrt{2 - 2S(R)}}$$

We have

$$\psi_e(\mathbf{r}) = \frac{\psi_1(\mathbf{r}) + \psi_2(\mathbf{r})}{\sqrt{2 + 2S(R)}}$$

$$\psi_o(\mathbf{r}) = \frac{\psi_1(\mathbf{r}) - \psi_2(\mathbf{r})}{\sqrt{2 - 2S(R)}}$$

with

$$\psi_1(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\mathbf{r} - \frac{1}{2}\mathbf{R}\right|}$$

$$\psi_2(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\mathbf{r} + \frac{1}{2}\mathbf{R}\right|}$$

$$S(R) = e^{-\frac{R}{a_0}} (1 + \frac{R}{a_0} + 3\frac{R^2}{a_0^2})$$
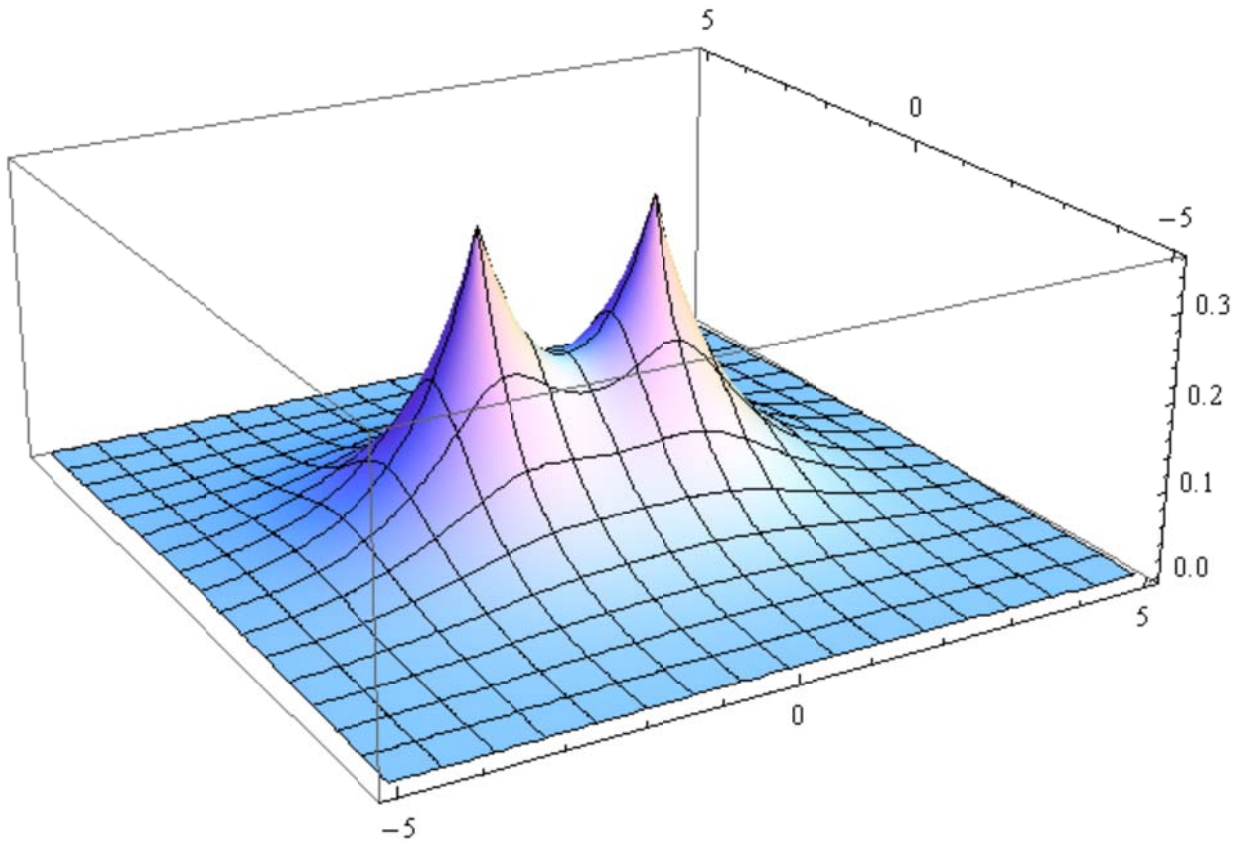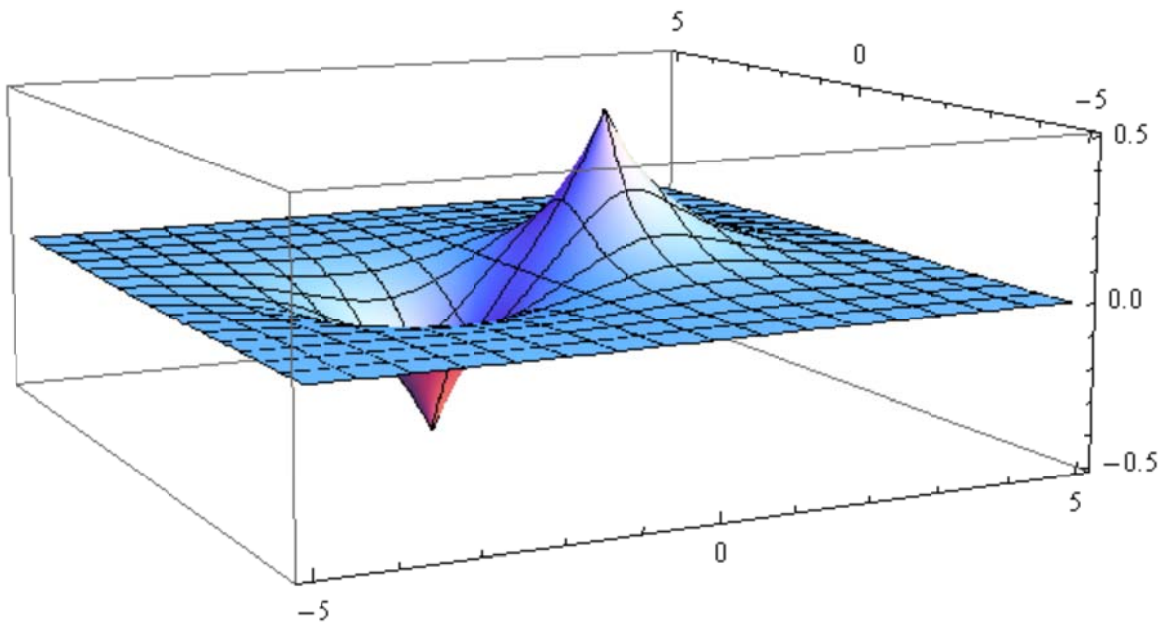
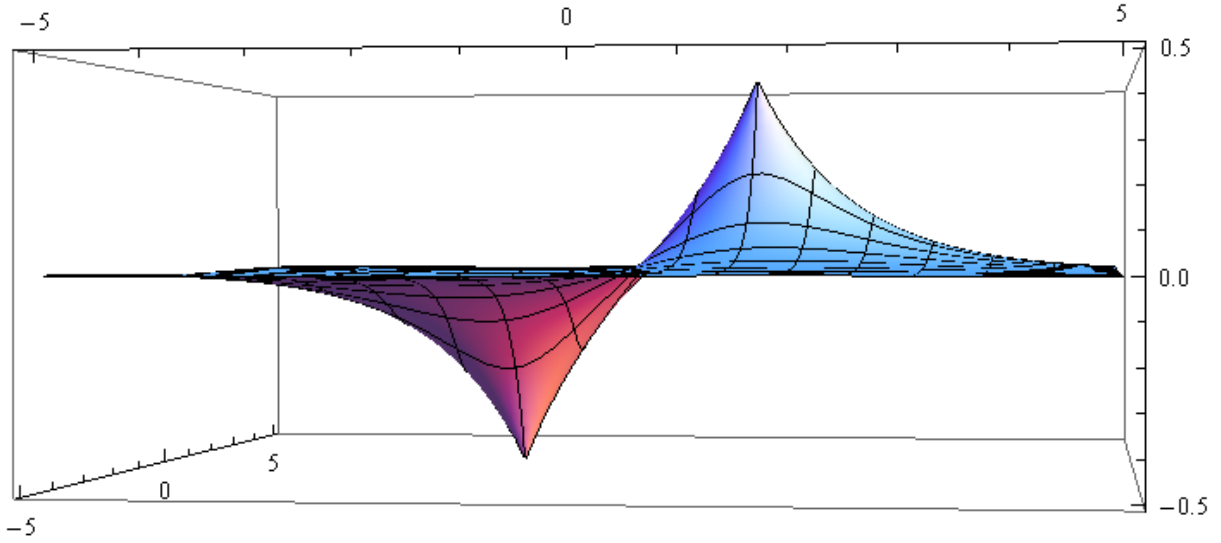**Fig.** Plot3D of the wave function $\psi_e(\boldsymbol{r})$. $R/a_0 = 2.49283$.

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Fig. Plot3D of the wave function $\psi_o(\mathbf{r})$. $R/a_0 = 2.49283$.

8. Matrix element of the Hamiltonian

The matrix element of the Hamiltonian is given by

$$\langle \psi_e | \hat{H} | \psi_e \rangle = C_e^2 (\langle \psi_1 | + \langle \psi_2 |) \hat{H} (|\psi_1\rangle + |\psi_2\rangle)$$
$$= C_e^2 [\langle \psi_1 | \hat{H} | \psi_1 \rangle + \langle \psi_1 | \hat{H} | \psi_2 \rangle + \langle \psi_2 | \hat{H} | \psi_1 \rangle + \langle \psi_2 | \hat{H} | \psi_2 \rangle]$$

where

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{\left|\hat{r} - \dfrac{R}{2}\right|} - \frac{e^2}{\left|\hat{r} + \dfrac{R}{2}\right|} + \frac{e^2}{|R|}$$

Here we note that

$$\langle \psi_2 | \hat{H} | \psi_1 \rangle = \langle \psi_1 | \hat{\pi} \hat{H} \hat{\pi} | \psi_2 \rangle = \langle \psi_1 | \hat{H} | \psi_2 \rangle$$

$$\langle \psi_2 | \hat{H} | \psi_2 \rangle = \langle \psi_1 | \hat{\pi} \hat{H} \hat{\pi} | \psi_1 \rangle = \langle \psi_1 | \hat{H} | \psi_1 \rangle$$

Then we have

$$\langle \psi_e | \hat{H} | \psi_e \rangle = 2C_e^2 [\langle \psi_1 | \hat{H} | \psi_1 \rangle + \langle \psi_1 | \hat{H} | \psi_2 \rangle]$$

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Similarly, we get

$$\langle \psi_o | \hat{H} | \psi_o \rangle = C_o^2 (\langle \psi_1 | - \langle \psi_2 |) \hat{H} (| \psi_1 \rangle - | \psi_2 \rangle)$$
$$= 2C_o^2 [\langle \psi_1 | \hat{H} | \psi_1 \rangle - \langle \psi_1 | \hat{H} | \psi_2 \rangle]$$

Then

$$\frac{\langle \psi_e | \hat{H} | \psi_e \rangle}{\langle \psi_e | \psi_e \rangle} = \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle + \langle \psi_1 | \hat{H} | \psi_2 \rangle}{1 + S(R)}$$

and

$$\frac{\langle \psi_o | \hat{H} | \psi_o \rangle}{\langle \psi_o | \psi_o \rangle} = \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle - \langle \psi_1 | \hat{H} | \psi_2 \rangle}{1 - S(R)}$$

9. Calculation of $\langle \psi_1 | \hat{H} | \psi_1 \rangle$ and $\langle \psi_1 | \hat{H} | \psi_2 \rangle$

Since

$$\hat{H} | \psi_1 \rangle = [\frac{\hat{p}^2}{2m_e} - \frac{e^2}{\left| \hat{r} - \frac{R}{2} \right|} - \frac{e^2}{\left| \hat{r} + \frac{R}{2} \right|} + \frac{e^2}{|R|}] | \psi_1 \rangle$$

$$= [\frac{\hat{p}^2}{2m_e} - \frac{e^2}{\left| \hat{r} - \frac{R}{2} \right|}] | \psi_1 \rangle - \frac{e^2}{\left| \hat{r} + \frac{R}{2} \right|} | \psi_1 \rangle + \frac{e^2}{|R|} | \psi_1 \rangle$$

we have

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = \langle \psi_1 | [\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}|}] | \psi_1 \rangle - \langle \psi_1 | \frac{e^2}{|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}|} | \psi_1 \rangle + \langle \psi_1 | \frac{e^2}{|\boldsymbol{R}|} | \psi_1 \rangle$$

$$= (E_{1s} + \frac{e^2}{R}) \langle \psi_1 | \psi_1 \rangle - \langle \psi_1 | \frac{e^2}{|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}|} | \psi_1 \rangle$$

$$= E_{1s} + \frac{e^2}{R} - \frac{e^2}{R}[1 - e^{-\frac{2R}{a_0}}(1 + \frac{R}{a_0})]$$

$$= E_{1s} + \frac{e^2}{R} e^{-\frac{2R}{a_0}}(1 + \frac{R}{a_0})]$$

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle = \langle \psi_1 | [\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}|}] | \psi_2 \rangle - \langle \psi_1 | \frac{e^2}{|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}|} | \psi_2 \rangle + \langle \psi_1 | \frac{e^2}{|\boldsymbol{R}|} | \psi_2 \rangle$$

$$= (E_{1s} + \frac{e^2}{R}) \langle \psi_1 | \psi_2 \rangle - \langle \psi_1 | \frac{e^2}{|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}|} | \psi_2 \rangle$$

$$= (E_{1s} + \frac{e^2}{R}) S(\boldsymbol{R}) - \frac{e^2}{a_0}(1 + \frac{R}{a_0}) e^{-\frac{R}{a_0}}$$

10. **Calculation of** $\langle \psi_1 | \frac{e^2}{|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}|} | \psi_1 \rangle$

$$\left\langle \psi_1 \left| \frac{e^2}{\left| \hat{r} + \frac{R}{2} \right|} \right| \psi_1 \right\rangle = \frac{e^2}{\pi a_0^{\;3}} \int d^3 r e^{-2 \frac{\left| r - \frac{R}{2} \right|}{a_0}} \frac{1}{\left| r + \frac{R}{2} \right|}$$

$$= \frac{e^2}{\pi a_0^{\;3}} \int d^3 r e^{-2 \frac{|r-R|}{a_0}} \frac{1}{r}$$

$$= \frac{2e^2}{a_0^{\;3}} \int_0^\infty r^2 \frac{1}{r} dr \int_0^\pi \sin\theta d\theta e^{-2\frac{|r-R|}{a_0}}$$

$$= \frac{2e^2}{a_0^{\;3}} \int_0^\infty r dr \int_0^\pi \sin\theta d\theta e^{-2\frac{|r-R|}{a_0}}$$

$$= \frac{e^2}{R}[1 - e^{-\frac{2R}{a_0}}(1 + \frac{R}{a_0})]$$

where

$$|r - R| = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

((**Mathematica**)) Calculation of $\left\langle \psi_1 \left| \frac{e^2}{\left| \hat{r} + \frac{R}{2} \right|} \right| \psi_1 \right\rangle$

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```
Clear["Global`*"]; p1 = √(r² - 2 r R Cos[θ] + R²) ;

f1 = 2 π Sin[θ] 1/(a0³ π) Exp[- (2 p1)/a0];

f2 = Integrate[f1, {θ, 0, π}] //
   FullSimplify[#, {R > 0, a0 > 0, r > 0,
      (r - R)² > 0}] &;

f21 = r f2 // Simplify[#, r < R] &;

f22 = r f2 // Simplify[#, r > R] &;

a1 = Integrate[ f21, {r, 0, R}] // Simplify;

a2 = Integrate[ f22, {r, R, ∞}] //
   Simplify[#, a0 > 0] &;

S = a1 + a2 // FullSimplify
```

$$\frac{1 - \dfrac{e^{-\frac{2R}{a0}} (a0+R)}{a0}}{R}$$

---

11.   Calculation of $\left\langle \psi_1 \left| \dfrac{e^2}{\left| \hat{r} - \dfrac{R}{2} \right|} \right| \psi_2 \right\rangle$

$$\left\langle \psi_1 \left| \frac{e^2}{\left| \hat{r} - \frac{R}{2} \right|} \right| \psi_2 \right\rangle = \frac{e^2}{\pi a_0^3} \int d^3 r e^{-\frac{\left| r - \frac{R}{2} \right|}{a_0}} \frac{1}{\left| r - \frac{R}{2} \right|} e^{-\frac{\left| r + \frac{R}{2} \right|}{a_0}}$$

$$= \frac{e^2}{\pi a_0^3} \int d^3 r' e^{-\frac{r'}{a_0}} \frac{1}{r'} e^{-\frac{|r'+R|}{a_0}}$$

$$= \frac{2e^2}{a_0^3} \int r dr e^{-\frac{r}{a_0}} \int_0^\pi \sin\theta d\theta e^{-\frac{|r+R|}{a_0}}$$

$$= \frac{e^2}{a_0} e^{-\frac{R}{a_0}} (1 + \frac{R}{a_0})$$

((**Mathematica**)) Calculation of

$$\langle\psi_1|\frac{e^2}{\left|\hat{r}-\dfrac{R}{2}\right|}|\psi_2\rangle.$$

```
Clear["Global`*"]; p1 = Sqrt[r^2 + 2 r R Cos[θ] + R^2] ;

f1 = 2 π Sin[θ] el^2/(a0^3 π) Exp[-p1/a0];

f2 = Integrate[f1, {θ, 0, π}] //
   FullSimplify[#, {R > 0, a0 > 0, r > 0,
      (r - R)^2 > 0}] &;

f21 = r Exp[-r/a0] f2 // Simplify[#, r < R] &;

f22 = r Exp[-r/a0] f2 // Simplify[#, r > R] &;

a1 = Integrate[ f21, {r, 0, R}] // Simplify;

a2 = Integrate[ f22, {r, R, ∞}] //
   Simplify[#, a0 > 0] &;

S = a1 + a2 // FullSimplify
```

$$\frac{e^{-\frac{R}{a0}} \, el^2 \, (a0 + R)}{a0^2}$$

---

12. Bonding orbital and anti-bonding orbital

$$E_e(R) = \frac{\langle\psi_e|\hat{H}|\psi_e\rangle}{\langle\psi_e|\psi_e\rangle} = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_1|\hat{H}|\psi_2\rangle}{1 + S(R)},$$

$$E_o(R) = \frac{\langle\psi_o|\hat{H}|\psi_o\rangle}{\langle\psi_o|\psi_o\rangle} = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle - \langle\psi_1|\hat{H}|\psi_2\rangle}{1 - S(R)},$$

where

$$\langle\psi_1|\hat{H}|\psi_1\rangle = E_{1s} + \frac{e^2}{R}e^{-\frac{2R}{a_0}}(1 + \frac{R}{a_0}),$$

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle = (E_{1s} + \frac{e^2}{R}) S(R) - \frac{e^2}{a_0}(1 + \frac{R}{a_0}) e^{-\frac{R}{a_0}},$$

$$S(R) = e^{-\frac{R}{a_0}}(1 + \frac{R}{a_0} + 3\frac{R^2}{a_0^2}).$$

We make a plot of $E_e(R)$ and $E_o(R)$ below. $E_e(R)$ has a local minimum at $R/a_0 = 2.49283$. $R = 1.3212$ Å. The local minimum value is -15.3634 eV.

(i)   For both $|\psi_e\rangle$ and $|\psi_O\rangle$ states, the energy at large R is simply the hydrogen atom as is expected. At very small R ($<<a_0$), the energy of both states becomes positive and very large due to the strong proton-proton Coulomb repulsion.

(ii)   For intermediate inter-nuclear separation, the even-parity and odd-parity states have different energies. The minimum in the even-parity state energy is indicative of an attraction that leads to a stable molecule with a separation distance t $R = 2.49283$ a_0 (or $R = 1.3212$ Å). The energy of the odd-parity state has no minimum and is repulsive at all distances R, implying that a system in this state will dissociate into a bound hydrogen atom and an isolated proton.

We call the $|\psi_e\rangle$ state as a **bonding orbital** and the odd-parity $|\psi_O\rangle$ state as an **antibonding orbital**
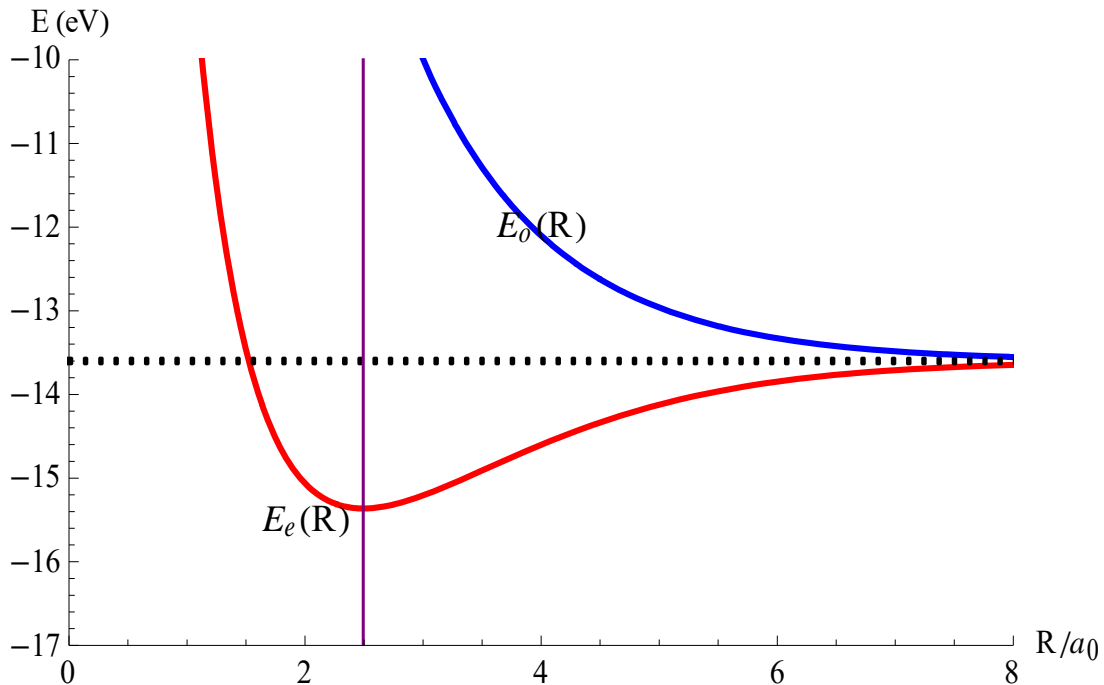
Fig. Plot of $E_e(R)$ and $E_o(R)$ as a function of R/a_0. $E_e(R)$ has a local minimum at $R/a_0 =$ 2.49283. $R = 1.3212$ Å. The local minimum value is -15.3634 eV. The dashed line denotes the ground-state energy of the hydrogen atom.

13. ((Mathematica))

```mathematica
Clear["Global`*"]; E1s = -el^2/(2 a0); S1 = (e^(-R/a0) (3 a0^2 + 3 a0 R + R^2))/(3 a0^2);

H11 = E1s + el^2/R (e^(-2R/a0) (a0 + R))/a0;

H12 = (E1s + el^2/R) S1 - (e^(-R/a0) el^2 (a0 + R))/a0^2;

rule1 = {R → a0 y, el → 1, a0 → 1};

ge = (H11 + H12)/(1 + S1) //. rule1 // Simplify;

go = (H11 - H12)/(1 - S1) //. rule1 // Simplify;

h1 = Plot[{27.2 ge, 27.2 go, -13.6}, {y, 0, 10},
   PlotStyle → {{Red, Thick}, {Blue, Thick},
     {Black, Dotted, Thick}},
   AxesLabel → {"R/a0", "E (eV)"},
   PlotRange → {{0, 8}, {-17, -10}}];
h2 = Graphics[{Text[Style["Ee(R)", Black, 12], {2, -15.5}],
    Text[Style["Eo(R)", Black, 12], {4, -12}], Purple,
    Line[{{2.49283, -17}, {2.49283, -10}}]}];
Show[h1, h2]
```
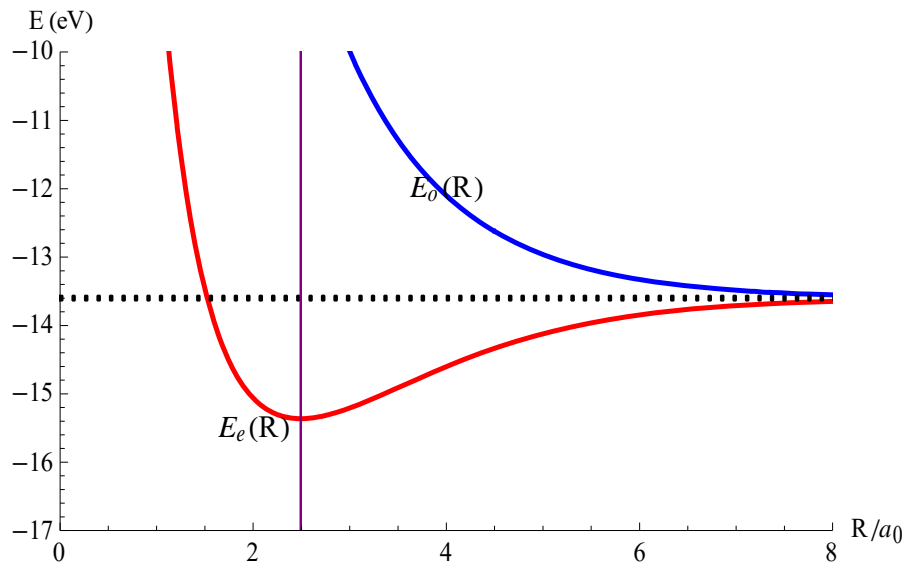
```
eq1 = D[ge, y] // FullSimplify;
```

```
eq2 = FindRoot[eq1 == 0, {y, 1, 4}]
```

$\{y \to 2.49283\}$

```
E1 = 0.53 y /. eq2[[1]]
```

1.3212

```
27.2 ge /. eq2[[1]]
```

-15.3634

15.   ContourPlot

We make a ContourPlot of $\psi_e(\mathbf{r})$ and $\psi_o(\mathbf{r})$ in the x-y plane, where $R = 2.49283\ a_0$.
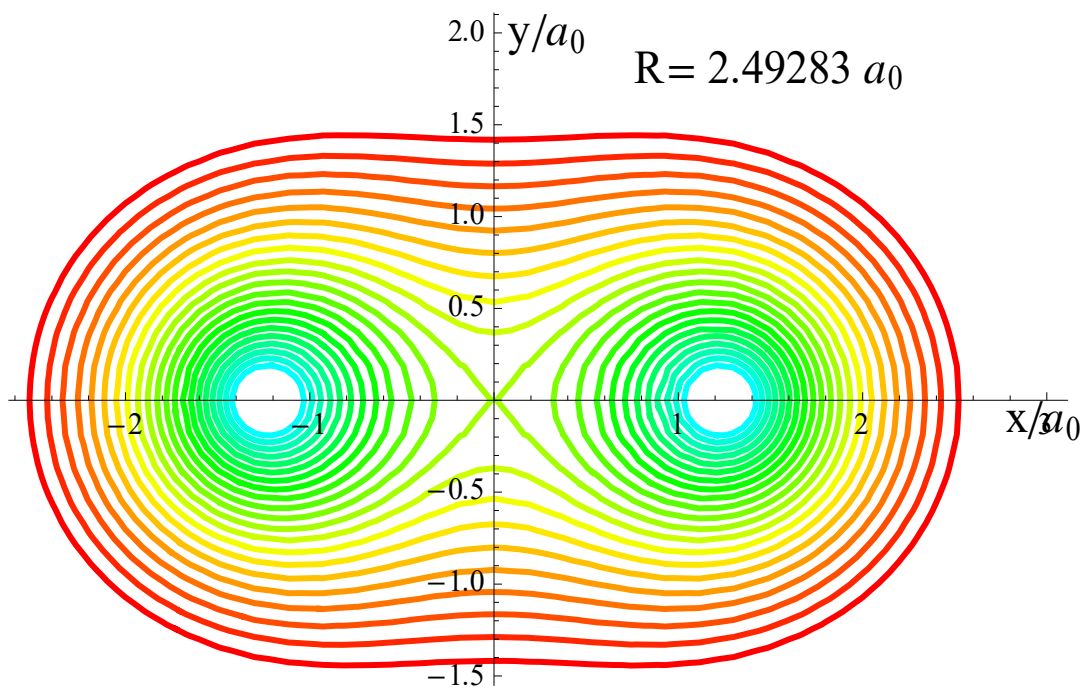
Fig.   ContourPlot of $\psi_e(\boldsymbol{r})$ in the x-y plane, where $R = 2.49283\ a_0$.
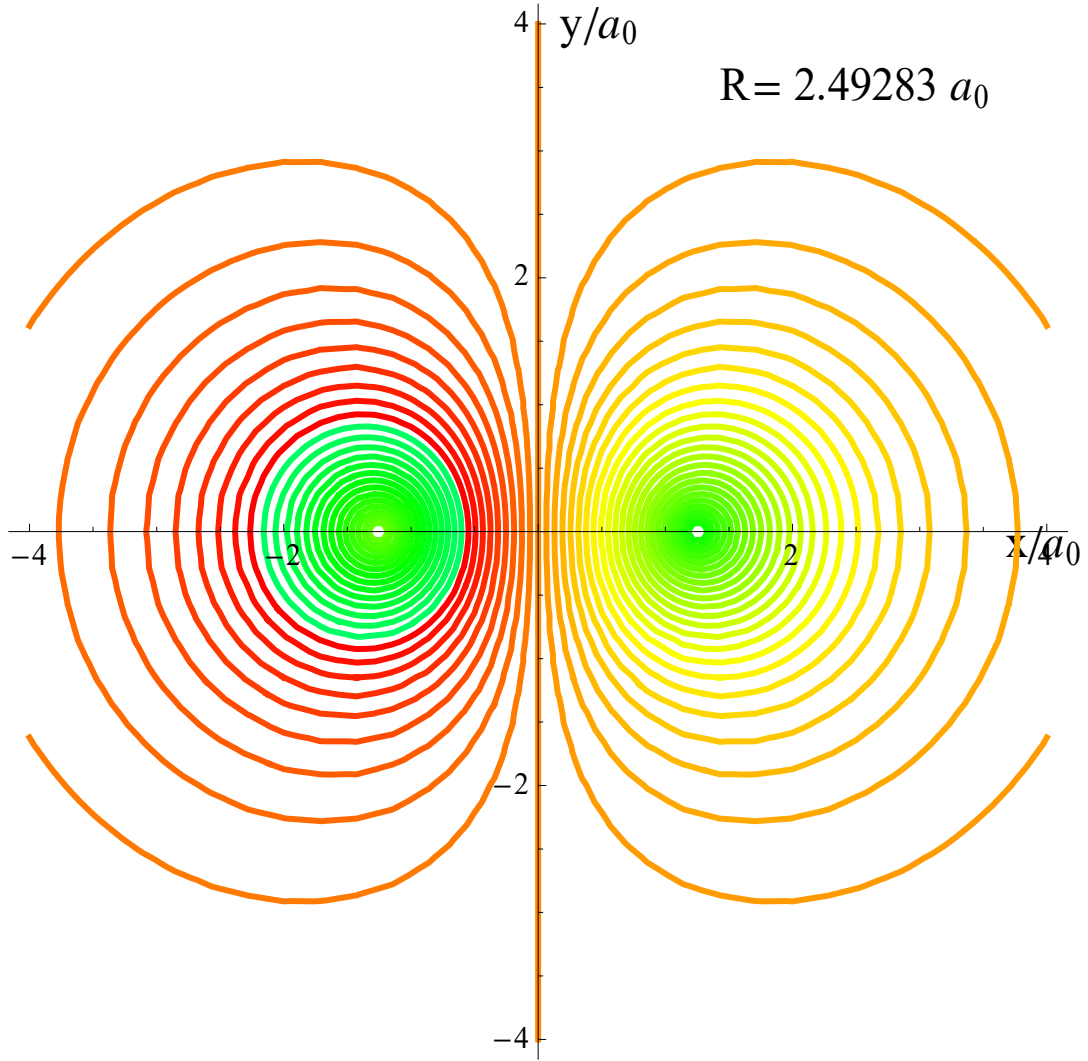
Fig.   ContourPlot of $\psi_o(\mathbf{r})$ in the *x-y* plane, where $R = 2.49283\ a_0$.

15.   Origin of the exchange force [Tomonaga's discussion]

$E_e(R)$ and $E_o(R)$ are the energy eigenvalues of the wave functions $\psi_e(\mathbf{r})$ and $\psi_o(\mathbf{r})$, respectively. We note that

$$E_e(R) < E_a(R).$$

We assume that

$$E_e(R) = 2E_{1s} + J_s(R), \qquad E_a(R) = 2E_{1s} + J_a(R).$$

For large values of *R*, we can say that

$$J_s(R) = -J(R), \qquad J_e(R) = J(R).$$

where $J(R) > 0$, monotonically decreasing toward $J(\infty) = 0$ as R increases. Thus we see that there is an attraction between proton 1 and proton 2 in the symmetric state and a repulsion between them. The system will be stable in the symmetric state but not in the antisymmetric state. The electron is visiting both protons equally, and if the way of visiting is symmetric, there will be an attraction between two protons, and if it is antisymmetric, there will be repulsion.

We now consider a wave packet

$$\psi_\pm(\mathbf{r},t) = \frac{1}{\sqrt{2}}[\exp[-\frac{i}{\hbar}J_s(R)t]\psi_s(\mathbf{r}) \pm \exp[-\frac{i}{\hbar}J_a(R)t]\psi_a(\mathbf{r})]]$$

This is certainly a solution of the time-dependent Schrödinger equation. At $t = 0$, we have

$$\psi_\pm(\mathbf{r},t = 0) = \frac{1}{\sqrt{2}}[\psi_s(\mathbf{r}) \pm \psi_a(\mathbf{r})]$$

where

$$\psi_s(\mathbf{r}) = \psi_e(r) = \frac{1}{\sqrt{2}}[\psi_1(\mathbf{r}) + \psi_2(\mathbf{r})],$$

$$\psi_a(\mathbf{r}) = \psi_o(r) = \frac{1}{\sqrt{2}}[\psi_1(\mathbf{r}) - \psi_2(\mathbf{r})]$$

and

$$\psi_+(\mathbf{r},t = 0) = \psi_1(\mathbf{r}), \quad \psi_-(\mathbf{r},t = 0) = \psi_2(\mathbf{r}).$$

We obtain

$$|\psi_\pm(\mathbf{r},t)|^2 = \frac{1}{2}|\psi_1(\mathbf{r})|^2[1 \pm \cos(\omega t)] + \frac{1}{2}|\psi_2(\mathbf{r})|^2[1 \mp \cos(\omega t)].$$

where

$$\hbar\omega = J_a(R) - J_s(R).$$

This means that the electron jumps back and forth from proton 1 to proton 2 and from 2 to 1 with the angular frequency ω. The exchange force originates in the shuttling of the electron.
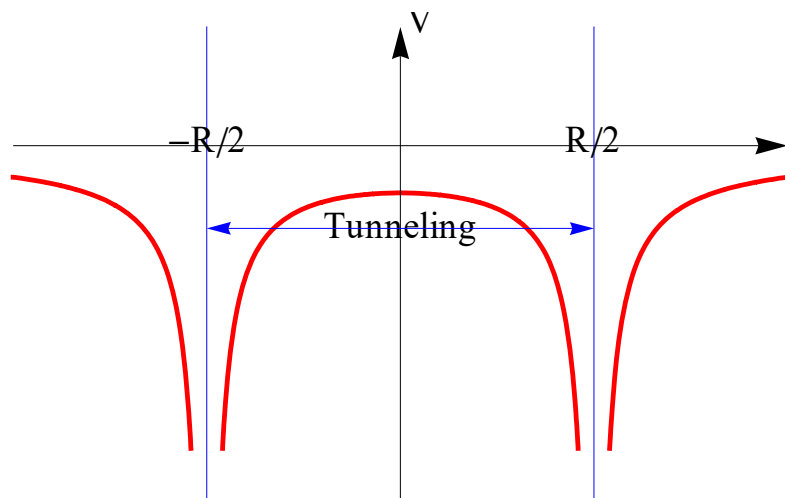
16.   Feynman's discussion

Fig.   Attractive potential energy for the electron in hydrogen molecule H_2^+

From our solution, we see that if a proton and a hydrogen ion are put anywhere near together, the electron will not stay on one of the protons but will flip back and forth between the two protons (tunneling). If it starts on one of the proton, it will oscillate back and forth between the two states $|\psi_1\rangle$ and $|\psi_2\rangle$, giving a time-varying solution. In order to have the lowest energy solution (which does not vary with time), it is necessary to start the system with equal amplitudes for the electron to be around each proton. Remember, there are not two electrons - we are not saying that there is an electron around each proton. There is only one electron, and it has the same amplitude $1/\sqrt{2}$ in magnitude – to be in either position. Now the amplitude A for an electron which is near one proton to get to the other one depends on the separation between the protons. The closer the protons are together, the larger the amplitude.

17.   Toy model of a covalent bond
In order to show how covalent bonding works, we discuss a one-dimensional toy model which is not at all realistic but it is analytically tractable. We consider a particle of mass $\underline{m}$ that moves along the x axis in an attractive double-delta potential. Here we discuss the eigenvalue (the bound state) problem for the Schrödinger equation for the attractive double-delta potential,
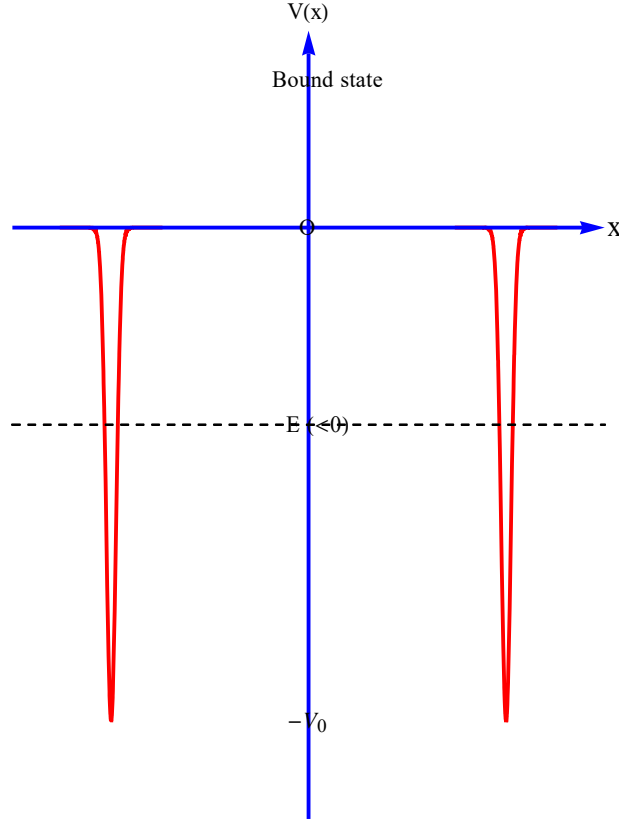
Fig. $V(x) = -V_0[\delta(x-a) + \delta(x+a)]$; attractive Dirac delta-type potential.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) - V_0[\delta(x-a) + \delta(x+a)]\psi(x) = E\psi(x) = -\frac{\hbar^2 k^2}{2m}\psi(x)$$

where the potential energy is an even function of x,

$$V(x) = -V_0[\delta(x-a) + \delta(x+a)],$$

and the energy is given by

$$E = -\frac{\hbar^2 k^2}{2m} \quad (<0)$$

for the bound state. Then we get

$$(\frac{d^2}{dx^2} - k^2)\psi(x) = -2\alpha[\delta(x-a) + \delta(x+a)]\psi(x)$$

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where

$$\alpha = \frac{mV_0}{\hbar^2}.$$

We note that the wave function $\psi(x)$ is either an even function or an odd function of x.

$$\frac{\psi_e(x)}{\psi_e(a)} = \begin{cases} e^{k(x+a)} & x < -a \\ \dfrac{\cosh(kx)}{\cosh[(ka)}, & -a < x < a \\ e^{-k(x-a)} & x > a \end{cases}$$

$$\frac{\psi_o(x)}{\psi_o(a)} = \begin{cases} -e^{k(x+a)} & x < -a \\ \dfrac{\sinh(kx)}{\sinh(ka)} & -a < x < a \\ e^{-k(x-a)} & x > a \end{cases}$$

Here we use the boundary condition:

$$\frac{d}{dx}\psi(x)\big|_{a-0}^{a+0} = -2\alpha\psi(a),$$

for the even and odd function, respectively. Then we have

$$2\alpha a = ka[1 + \tanh(ka)] \qquad \text{for the even parity}$$

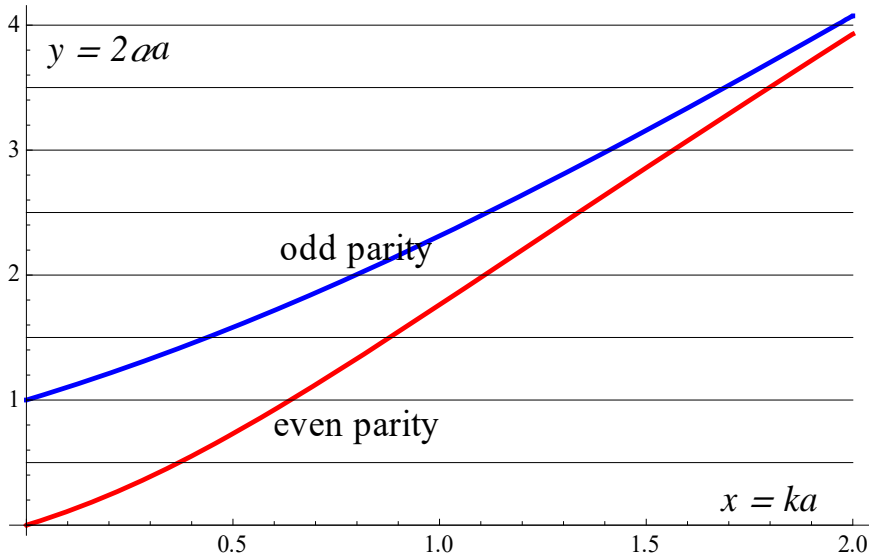$$2\alpha a = ka[1 + \coth(ka)] \qquad \text{for the odd parity}$$

Fig. Plot of $y = 2a\alpha$ vs ka for the even parity and the odd parity. $y = \dfrac{2amV_0}{\hbar^2}$
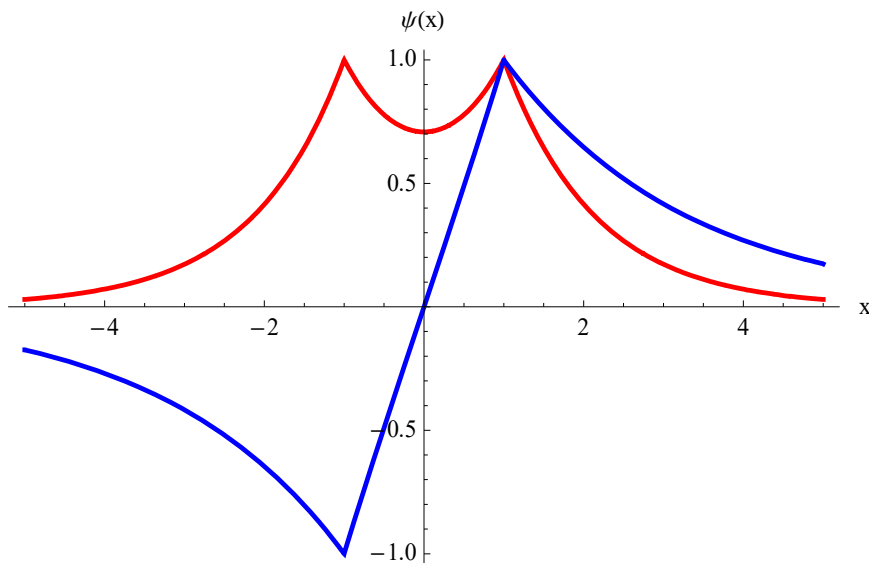

Fig. Even parity (red) and odd parity (blue) function for $y = \dfrac{2amV_0}{\hbar^2} = 1.5$ (fixed). $ka = 0.8792$ for the even parity, $ka = 0.4371$ for the odd parity. For simplicity we assume $a = 1$.

REFERENCES

R.P. Feynman, R.B. Leighton, and M. Sands, The Feynman Lectures on Physics (Addison-Wesley Publishing Company, Reading Ma, 1965).

J. Binney and D. Skinner, The Physics of Quantum Mechanics (Oxford University Press, 2013).

S. Tomonaga, *The Story of Spin* (University of Chicago Press, 1997).

APPENDIX   Green function method
Bound state under attractive double-delta potential

We discuss the eigenvalue (the bound state) problem for the Schrodinger equation for the attractive double-delta potential,

V(x)

Bound state

$-E\ (<0)$

$-V_0$
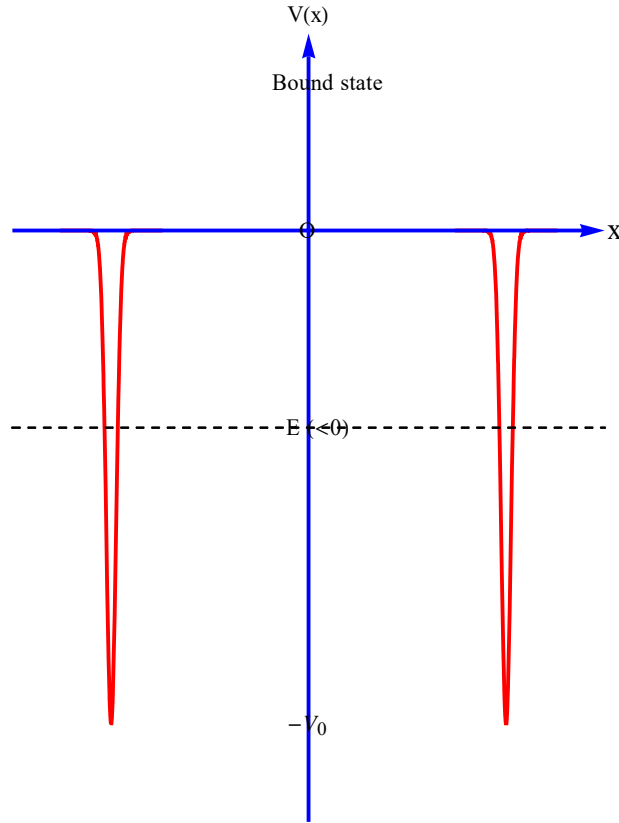
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) - V_0[\delta(x-a) + \delta(x+a)]\psi(x) = E\psi(x) = -\frac{\hbar^2\rho^2}{2m}\psi(x)$$

where the potential energy is an even function of x,

$$V(x) = V_0\ [\delta(x-a) + \delta(x+a)]$$

and the energy is given by

$$E = -\frac{\hbar^2\rho^2}{2m}\ (<0)$$

for the bound state. Then we get

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$$(\frac{d^2}{dx^2} - \rho^2)\psi(x) = L_x\psi(x) = -2\alpha[\delta(x-a) + \delta(x+a)]\psi(x) = -f(x)$$

where

$$\alpha = \frac{mV_0}{\hbar^2}.$$

Using the 1D Green's function (modified Helmholtz), the solution of this equation can be given by

$$\psi(x) = \int G(x,\xi)f(\xi)d\xi$$

$$= \int \frac{1}{2\rho}e^{-\rho|x-\xi|}2\alpha[\delta(x-a) + \delta(x+a)]\psi(\xi)d\xi$$

$$= \frac{\alpha}{\rho}[\psi(a)e^{-\rho|x-a|} + \psi(-a)e^{-\rho|x+a|}]$$

where

$$L_x G(x,\xi) = -\delta(x-\xi)$$

$$\left(\frac{d^2}{dx^2} - \rho^2\right)G(x,\xi) = -\delta(x-\xi)$$

$$\Downarrow$$

$$G(x,\xi) = \frac{1}{2\rho}e^{-\rho|x-\xi|} \qquad \text{(Green's function: modified Helmholtz equation).}$$

At $x = a$

$$\psi(a) = \frac{\alpha}{\rho}[\psi(a) + \psi(-a)e^{-2\rho a}]$$

At $x = -a$

$$\psi(-a) = \frac{\alpha}{\rho}[\psi(a)e^{-2\rho a} + \psi(-a)]$$

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We note that the wave function $\psi(x)$ is either an even function or an odd function of x.

(i)   Even parity for the wave function

$$\psi_e(-a) = \psi_e(a)$$

or

$$1 = \frac{\alpha}{\rho}(e^{-2\rho a} + 1)$$

or

$$\frac{\rho}{\alpha} = 1 + e^{-2\rho a}$$

For simplicity we put

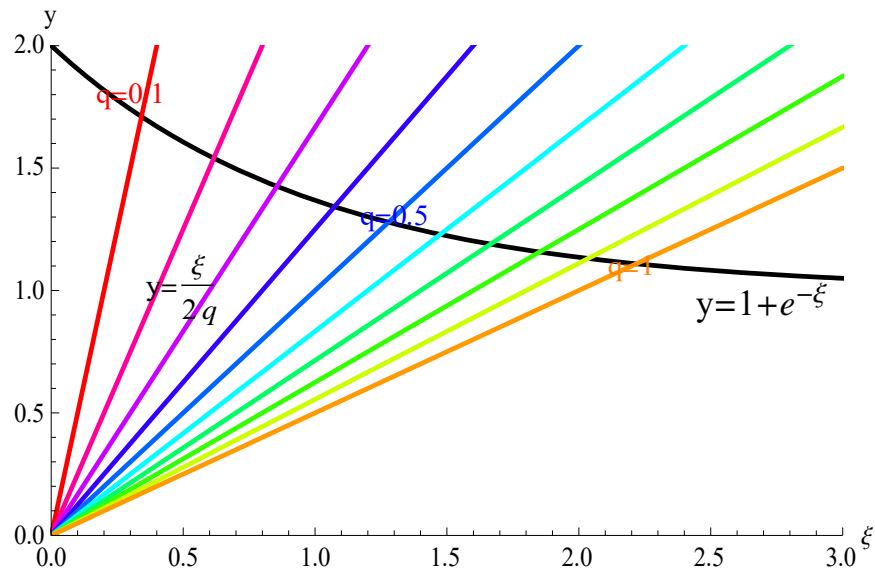$$x = 2\rho a$$

$$\frac{x}{2a\alpha} = 1 + e^{-x}$$

Fig. Even parity solution. Plot of $y = \dfrac{\xi}{2q}$ and $y = 1 + e^{-\xi}$ where q is changed as a parameter.

$\xi = 2\rho a$. $q = a\alpha$. The two curves intersect at a non-zero finite value of ξ. When $q = 1$, we have $\xi = 2.21772$. $y = 1.10886$.

The wave function (even parity) is given by

$$\frac{\psi_e(x)}{\psi_e(a)} = \frac{\alpha}{\rho}[e^{-\rho|x-a|} + e^{-\rho|x+a|}]$$

When $q = a\alpha = 1$, we have $x = 2\rho a = 2.21772$. For $a = 1$ and $\rho = 1.10886$, we make a plot of this function as a function of x. Clearly this function is an even function of x.
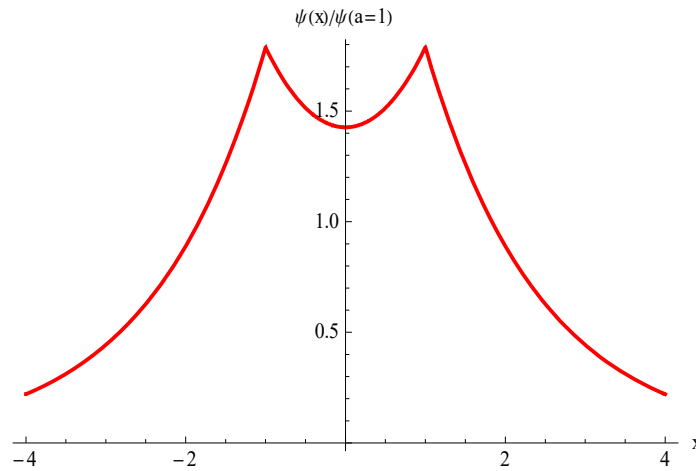

$\psi(x)/\psi(a=1)$

Fig. Plot of $\dfrac{\psi_e(x)}{\psi_e(a=1)}$ as a function of x. $\alpha = 1$. $a = 1$ and $\rho = 1.10886$.

(ii)   Odd parity for the wave function

$$\psi_o(-a) = -\psi_o(a)$$

or

$$1 = \frac{\alpha}{\rho}(-e^{-2\rho a} + 1)$$

or

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$$\frac{\rho}{\alpha} = -e^{-2\rho a} + 1$$

The value of ρ is obtained from the intersection of two curves

$$y = \frac{\xi}{2q}, \qquad y = 1 - e^{-\xi}$$
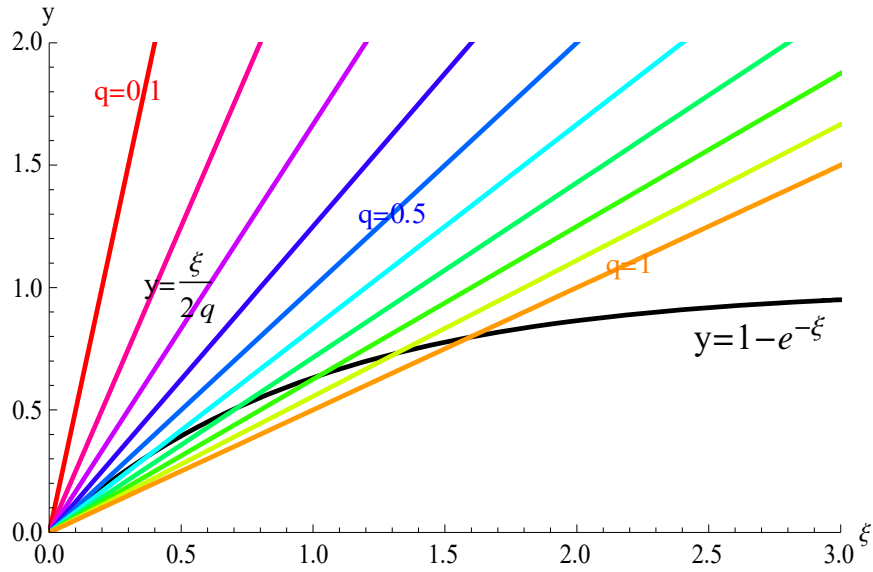
with $\xi = 2\rho a$ and $q = a\alpha$ (parameter).

Fig. Odd parity solution. Plot of $y = \frac{\xi}{2q}$ and $y = 1 - e^{-\xi}$ where q is changed as a parameter. $\xi = 2\rho a$. $q = a\alpha$. When $q > 0.5$, there are two solutions including $\xi = 0$. When $q < 0.5$, there is only one solution $\xi = 0$. When $q = 1$, we have $\xi = 1.59362$. $y = 0.796812$.

The wave function (odd parity) is given by

$$\frac{\psi_o(x)}{\psi_o(a)} = \frac{\alpha}{\rho}[e^{-\rho|x-a|} - e^{-\rho|x+a|}]$$

When $q = a\alpha = 1$, we have $\xi = 2\rho a = 1.59362$. For $a = 1$ and $\rho = 0.796812$, we make a plot of this function as a function of x. Clearly this function is an odd function of x.
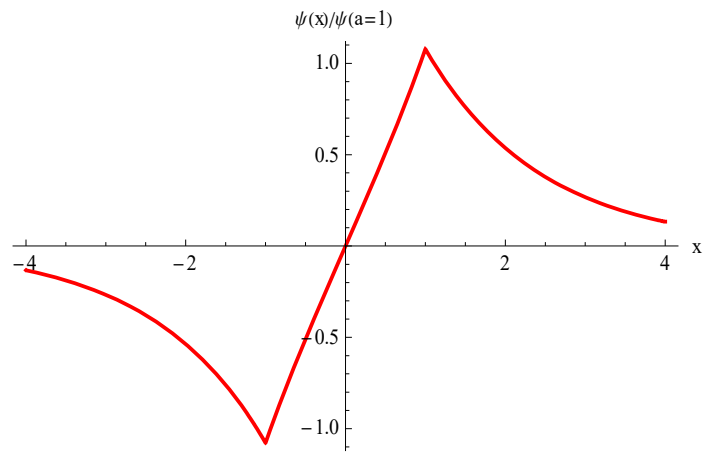
Fig. Plot of $\dfrac{\psi_o(x)}{\psi_o(a=1)}$ as a function of x. $\alpha = 1$. $a = 1$ and $\rho = 1.10886$.