Hydrogen molecule H_2^+
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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.

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.

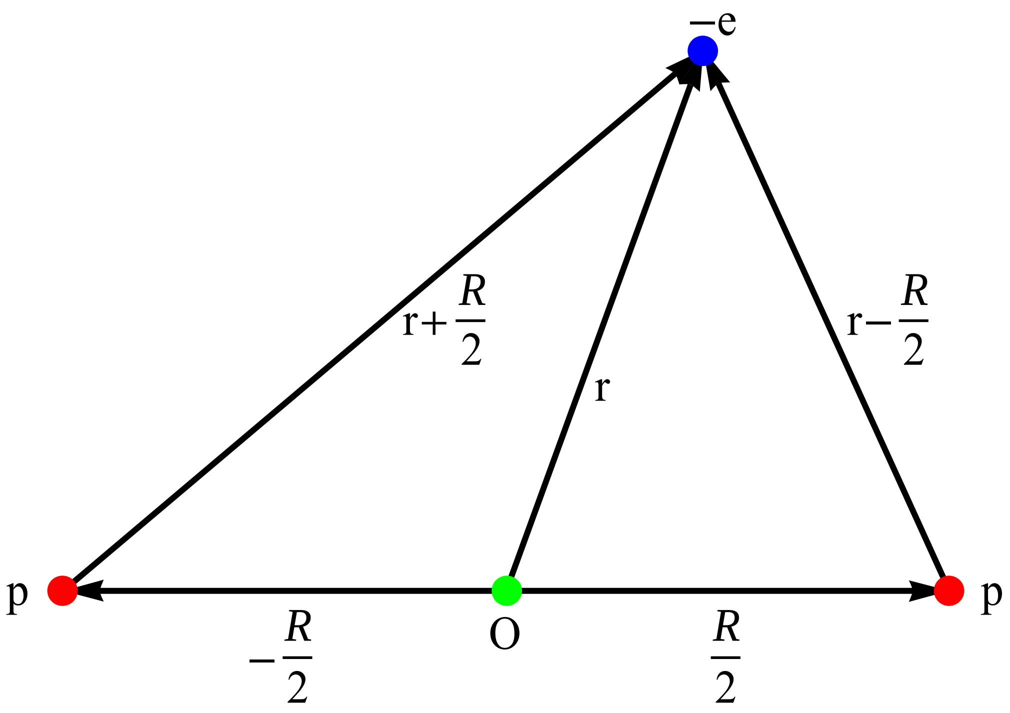

Fig. The co-ordinates of the two protons and one electron used in the discussion of hydrogen molecule ion. R is the distance between two protons.

(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.

$$E_0 = -13.6 \text{ eV}.$$

(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),

$$E_0 = -54.4 \text{ eV}.$$

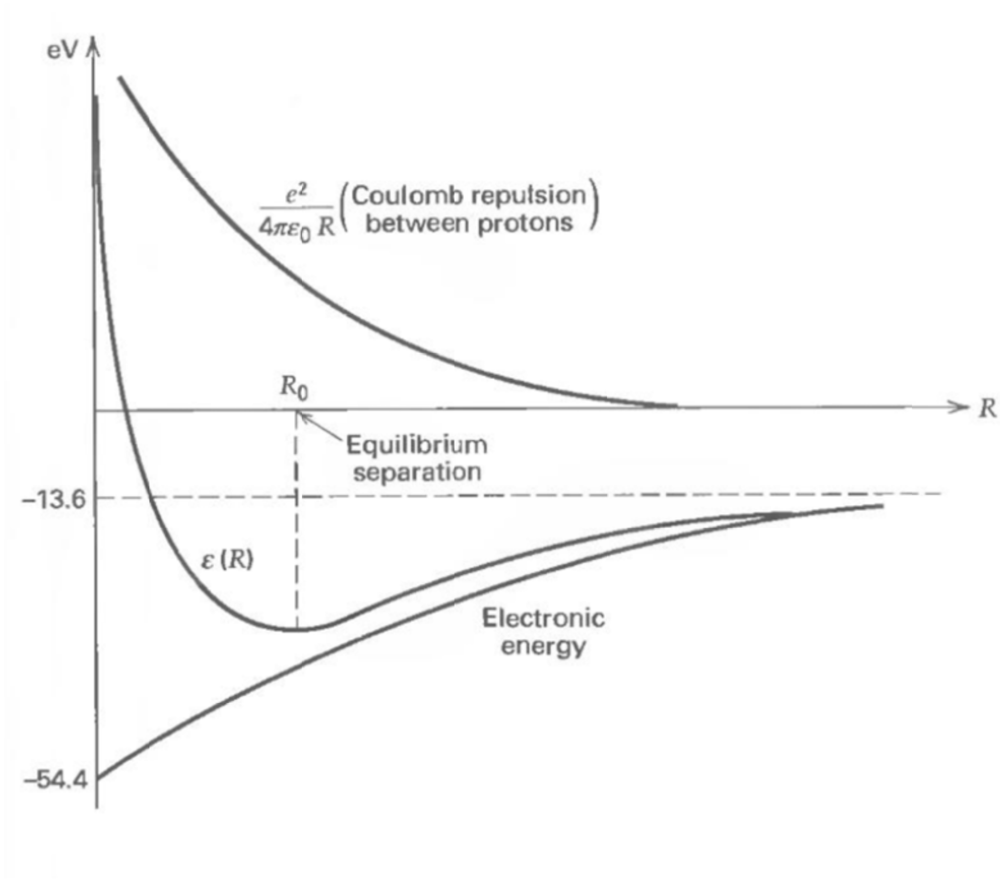

Fig. Rough prediction of E_0 vs R. R increases with increasing R from -54.4 eV at $R = 0$ to -13.6 eV at $R = \infty$.

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

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

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

where a_0 (=0.53 Å) is a Bohr radius,

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

and

$$\boldsymbol{r}_1 = \boldsymbol{r} - \frac{1}{2}\boldsymbol{R}, \qquad \boldsymbol{r}_2 = \boldsymbol{r} + \frac{1}{2}\boldsymbol{R}$$

The Hamiltonian of the system is given by

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

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

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

3. Even function and odd function

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

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

Since

$$\hat{\pi}^2 = \hat{1}$$

we get

$$\hat{\pi}^2|\psi\rangle = \lambda\hat{\pi}|\psi\rangle = \lambda^2|\psi\rangle = |\psi\rangle$$

leading to the eigenvalues $\lambda = \pm 1$. The eigenkets are given by

$$\hat{\pi}|\psi_e\rangle = |\psi_e\rangle \qquad (\lambda = 1); \qquad \text{(even parity)}$$

$$\hat{\pi}|\psi_o\rangle = -|\psi_o\rangle \qquad (\lambda = \text{-}1); \qquad \text{(odd parity)}$$

or

$$\psi_e(-\boldsymbol{r}) = \psi_e(\boldsymbol{r})$$

$$\psi_o(-\boldsymbol{r}) = -\psi_o(\boldsymbol{r})$$

4. 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 $|\psi_2\rangle$.

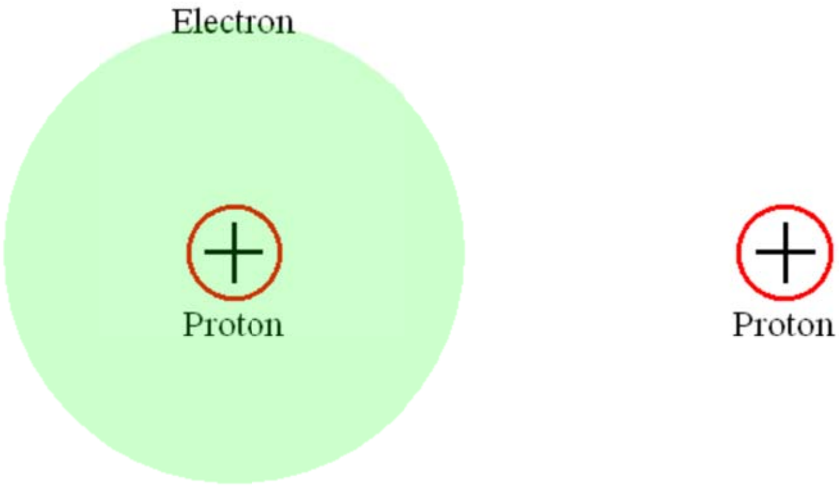

Fig. The state $|\psi_1\rangle$ for the two protons and electron

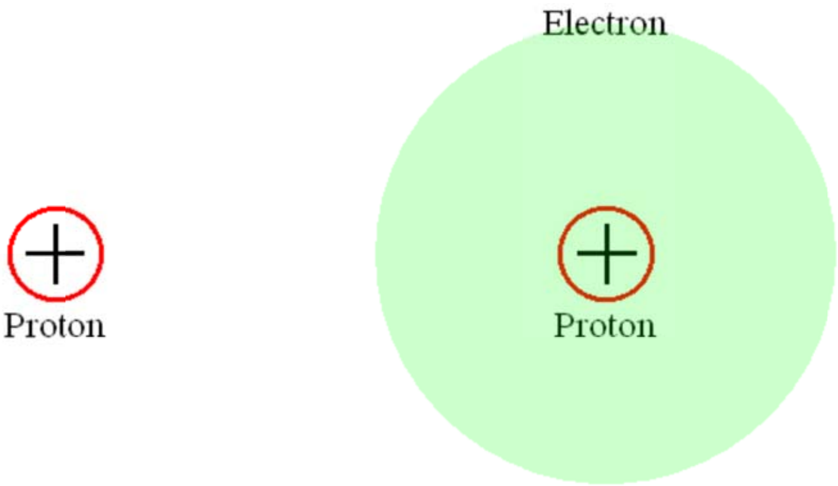

Fig. The state $|\psi_2\rangle$ for the two protons and electron

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

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

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

From the properties

$$\psi_1(-\boldsymbol{r}) = \psi_2(\boldsymbol{r}), \qquad \psi_2(-\boldsymbol{r}) = \psi_1(\boldsymbol{r})$$

we have

$$\langle -\boldsymbol{r}|\psi_1\rangle = \langle \boldsymbol{r}|\hat{\pi}|\psi_1\rangle = \langle \boldsymbol{r}|\psi_2\rangle, \qquad \langle -\boldsymbol{r}|\psi_2\rangle = \langle \boldsymbol{r}|\hat{\pi}|\psi_2\rangle = \langle -\boldsymbol{r}|\psi_1\rangle$$

or

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

From this relation we also have

$$\hat{\pi}(|\psi_1\rangle + |\psi_2\rangle) = (|\psi_1\rangle + |\psi_2\rangle), \qquad \hat{\pi}(|\psi_1\rangle - |\psi_2\rangle) = -(|\psi_1\rangle - |\psi_2\rangle)$$

leading to the even and odd functions, as follows.

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 state); eigenvalue (+1)

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

or

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

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

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

or

$$\psi_o(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi_o\rangle = C_0[\psi_1(\boldsymbol{r}) - \psi_2(\boldsymbol{r})]$$

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

We consider the correlation function

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

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

or

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

where

$$d^3\boldsymbol{r} = 2\pi r^2 dr \sin\theta d\theta$$

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.

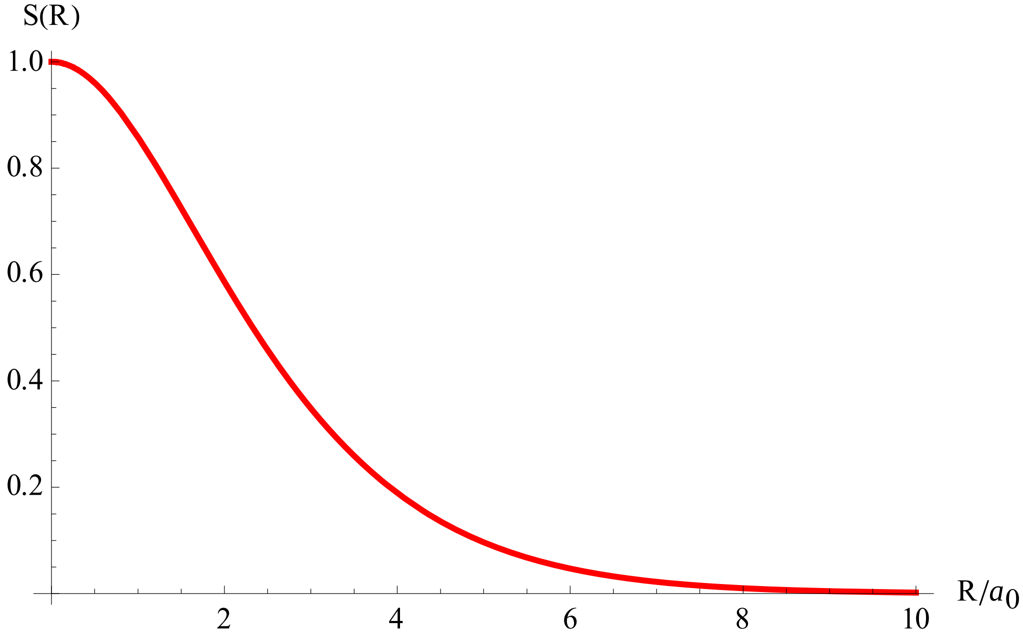

Fig. $S(R)$ vs R/a_0. a_0 = 0.53 Å. d$S(R)$/dR = 0 at R/a_0 = 1.61803 (i.e. R = 0.8575 Å).

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

```
Clear["Global`*"]; p1 = √(r^2 - 2 r R Cos[θ] + R^2);
f1 = 2 π Sin[θ] 1/(a0^3 π) Exp[-p1/a0];
f2 = Integrate[f1, {θ, 0, π}] //
   FullSimplify[#, {R > 0, a0 > 0, r > 0,
      (r - R)^2 > 0}] &;

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

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

a1 = Integrate[r^2 f21, {r, 0, R}] // Simplify;

a2 = Integrate[r^2 f22, {r, R, ∞}] //
    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 $\langle\psi_2|\psi_2\rangle = 1$

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

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

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

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

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

or

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

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 r^2/(a0^3 π) Exp[-2 r/a0];

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

1
```

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7. Claculation of the expectation

$$\begin{aligned}\langle\psi_e|\psi_e\rangle &= C_e{}^2(\langle\psi_1| + \langle\psi_2|)(|\psi_1\rangle + |\psi_2\rangle)\\ &= C_e{}^2[2 + \langle\psi_1|\psi_2\rangle + \langle\psi_2|\psi_1\rangle]\\ &= C_e{}^2[2 + 2S(R)]\end{aligned}$$

$$\begin{aligned}\langle\psi_o|\psi_o\rangle &= C_o{}^2(\langle\psi_1| - \langle\psi_2|)(|\psi_1\rangle - |\psi_2\rangle)\\ &= C_o{}^2[2 - \langle\psi_1|\psi_2\rangle - \langle\psi_2|\psi_1\rangle]\\ &= C_o{}^2[2 - 2S(R)]\end{aligned}$$

$$\begin{aligned}\langle \psi_e | \psi_o \rangle &= C_e C_o (\langle \psi_1 | + \langle \psi_2 |)(| \psi_1 \rangle - | \psi_2 \rangle) \\ &= C_e C_o [-\langle \psi_1 | \psi_2 \rangle + \langle \psi_2 | \psi_1 \rangle] \\ &= 0\end{aligned}$$

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

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

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

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

with

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

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

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

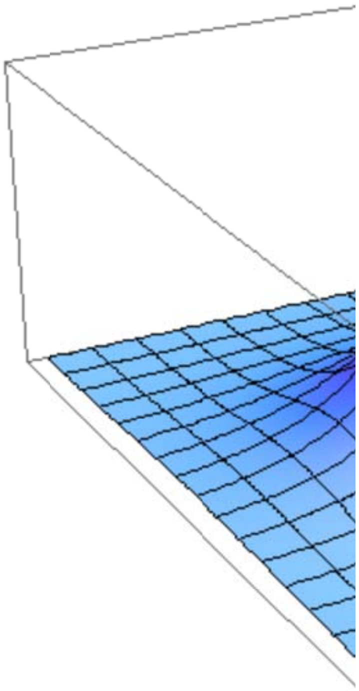

Fig. Plot3D of the wave funct