

Kvantfysik Lecture Notes No. 18

In this lecture we will give a brief introduction to molecules. We give a fairly quantitative description of the H_2^+ molecule, a hydrogen molecule with one electron removed. We then discuss the H_2 molecule in a more qualitative fashion. We then describe the molecular spectra for general diatomic molecules.

1 The H_2^+ molecule

Suppose we have two hydrogen nuclei, *i.e.* protons, and a single electron. In this section we show that the presence of the electron leads to a binding between the nuclei, forming the simplest molecule. To proceed, we assume that the nuclei are separated by a distance R and that the motion of the nuclei can be ignored. This second assumption is very reasonable because the nuclei are so heavy that the total kinetic energy is dominated by the electron's motion. If a molecule forms, then there should be a finite separation R where the energy is minimized. We cannot do the calculation exactly, but here we describe a way to do it approximately.

Let us first discuss qualitatively why there could be a finite R which minimizes the energy. Suppose that $R \gg a_\mu$, where a_μ is the Bohr radius, the approximate size of a hydrogen atom. Then we would expect that the electron is bound to either one nucleus or the other, forming one hydrogen atom and leaving a free proton far away from the atom. Assuming that the electron is in the atomic ground state, the energy for this configuration is

$$E_H = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_\mu} = -\frac{1}{2} \frac{\hbar^2}{\mu a_\mu^2}.$$

If we consider the other extreme where $R = 0$ then it looks to the electron that there is a single nucleus with charge $+2e$, and so the electron energy is lowered to $4E_H$. From this point of view it would seem favorable to move the protons on top of each other. We can summarize this situation in terms of a function $E_e(R)$ where $E_e(\infty) = E_H$ and $E_e(0) = 4E_H$, which presumably decreases as R decreases. But this ignores the potential energy from proton-proton repulsion, which is $E_{pp}(R) = \frac{e^2}{4\pi\epsilon_0 R}$. So clearly, R cannot go to zero because $E_{pp}(R)$ would blow up. The radial force holding the nuclei together is

$$F(R) = -\frac{d}{dR}(E_e(R) + E_{pp}(R)),$$

so if $E_e(R)$ drops quickly enough for large R , then there should be a finite value of R where the force is balanced and thus the total energy is minimized. These arguments are summarized in figure 1.

We now describe how we can approximate $E_e(R)$ using the *variational method*. The Hamiltonian for the electron is given by

$$H = -\frac{\hbar^2}{2\mu} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}|} \quad (1)$$

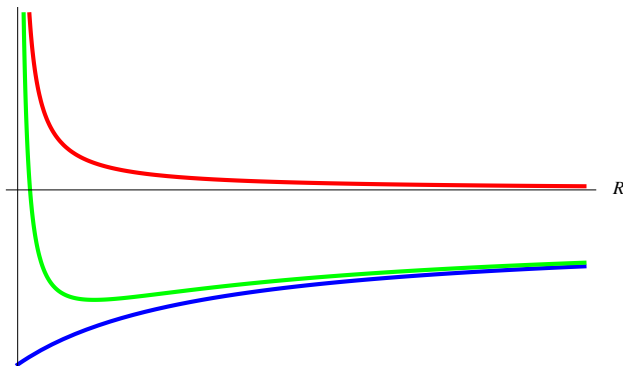


Figure 1: Schematic plots of $E_e(R)$ (blue), $E_{pp}(R)$ (red) and $E_e(R) + E_{pp}(R)$ (green) as functions of R . The minimum of the sum is where the net force is zero.

where we are assuming that one nucleus is located at $\vec{r} = 0$ and the other is at $\vec{r} = \vec{R}$, $R = |\vec{R}|$. If $R \gg a_\mu$, then wave function should be very close to being a linear combination of the two hydrogen atom ground state wave functions, with equal probability for the electron to be bound to one nucleus or the other. Hence, the wave-function can be approximated as

$$\psi(\vec{r}) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1+I}} \left(\psi_A(\vec{r}) + \psi_B(\vec{r}) \right), \quad (2)$$

where $\psi_A(\vec{r})$ and $\psi_B(\vec{r})$ are the two normalized ground state wave-functions

$$\psi_A(\vec{r}) = \frac{2}{\sqrt{4\pi}} \left(\frac{1}{a_\mu} \right)^{3/2} \exp\left(-\frac{r}{a_\mu}\right), \quad \psi_B(\vec{r}) = \frac{2}{\sqrt{4\pi}} \left(\frac{1}{a_\mu} \right)^{3/2} \exp\left(-\frac{|\vec{r} - \vec{R}|}{a_\mu}\right),$$

with each wave-function centered about its respective nucleus. The two wave-functions $\psi_A(\vec{r})$ and $\psi_B(\vec{r})$ are not exactly orthogonal to each other, so the normalized wave-function has the extra factor

$$I = \langle \psi_A | \psi_B \rangle = \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \psi_A(\vec{r}) \psi_B(\vec{r}).$$

We now assume that the wave-function keeps the form in (2) even if $R \sim a_\mu$ and we then make the estimate that

$$E_e(R) \approx \langle E \rangle = \langle \psi | H | \psi \rangle.$$

This approximation may or may not be a particularly good one, but we do know that the estimate we get for $E_e(R)$ must be greater than or equal to the true value. To see this we note that the expectation value of the energy $\langle E \rangle$ is greater than or equal to the ground state energy. To show this, suppose we label the true eigenstates of H as $|\psi_n\rangle$ with eigenvalues

$$H|\psi_n\rangle = E_n|\psi_n\rangle.$$

We denote the ground state, *i.e.* the lowest energy state, as $|\psi_0\rangle$ and the other states by positive integers n . We apply the quantum mechanics postulates and assume that the $|\psi_n\rangle$ form a complete set of states, meaning that any state $|\psi\rangle$ is a linear combination of the eigenstates:

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |\psi_n\rangle.$$

We make no claim to actually knowing what $|\psi_n\rangle$ and E_n are. The coefficients c_n satisfy

$$\sum_{n=0}^{\infty} |c_n|^2 = 1,$$

ensuring that $|\psi\rangle$ is properly normalized. Now, since $E_0 < E_n$ for $n \neq 0$, and since $|c_n^2| \geq 0$, we have

$$\langle E \rangle = \langle \psi | H | \psi \rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n \geq \sum_{n=0}^{\infty} |c_n|^2 E_0 = E_0 \sum_{n=0}^{\infty} |c_n|^2 = E_0.$$

Hence, no matter what state we choose for $|\psi\rangle$, we always know that $\langle E \rangle$ will be greater than or equal to E_0 , even if we don't actually know what E_0 is. Thus, if we find that our estimate for $E_e(R)$ leads to a minimum with finite R , the same must be true for $E_e^{(\text{true})}(R)$, the function we would have found had we used the true ground state.

For our particular choice of ψ we find

$$\langle E \rangle = \frac{1}{2(1+I)} \left(\langle \psi_A | H | \psi_A \rangle + \langle \psi_B | H | \psi_B \rangle + \langle \psi_A | H | \psi_B \rangle + \langle \psi_B | H | \psi_A \rangle \right). \quad (3)$$

We also use

$$\begin{aligned} \langle \psi_A | H | \psi_A \rangle &= \langle \psi_B | H | \psi_B \rangle \\ \langle \psi_A | H | \psi_B \rangle &= \langle \psi_B | H | \psi_A \rangle \end{aligned}$$

where the first equality follows from the symmetry of the problem and the second is because the wave-functions are real and H is Hermitian. We then note that

$$\begin{aligned} H|\psi_A\rangle &= \left(-\frac{\hbar^2}{2\mu} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}|} \right) |\psi_A\rangle = \left(E_H - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}|} \right) |\psi_A\rangle \\ H|\psi_B\rangle &= \left(-\frac{\hbar^2}{2\mu} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}|} \right) |\psi_B\rangle = \left(E_H - \frac{e^2}{4\pi\epsilon_0 r} \right) |\psi_B\rangle. \end{aligned}$$

Hence, to find our estimate for $E_e(R)$ it is enough to compute $I = \langle \psi_A | \psi_B \rangle$, $\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle$, and $\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_A \rangle$.

In the appendix we show that

$$\begin{aligned}
I &= \left(\frac{w^2}{3} + w + 1 \right) e^{-w} \\
\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle &= \frac{1}{a_\mu} (w + 1) e^{-w} \\
\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_A \rangle &= \frac{1}{w a_\mu} (1 - (1 + w) e^{-2w}) , \tag{4}
\end{aligned}$$

where we have introduced the dimensionless quantity $w \equiv R/a_\mu$. Inserting (4) into (3) we find for our estimate of $E_e(R)$,

$$\begin{aligned}
E_e(R) &= E_H - \frac{e^2}{4\pi a_\mu} \frac{1}{1 + (\frac{w^2}{3} + w + 1) e^{-w}} \left(\frac{1}{w} + (1 + w) e^{-w} - \left(\frac{1}{w} + 1 \right) e^{-2w} \right) \\
&= E_H + \frac{2E_H}{1 + (\frac{w^2}{3} + w + 1) e^{-w}} \left(\frac{1}{w} + (1 + w) e^{-w} - \left(\frac{1}{w} + 1 \right) e^{-2w} \right) .
\end{aligned}$$

Adding $E_{pp}(R)$ to this and subtracting the constant term we then get

$$E_e(R) + E_{pp}(R) - E_H = - \frac{2E_H}{1 + (\frac{w^2}{3} + w + 1) e^{-w}} \left(\left(\frac{1}{w} - \frac{2}{3} w \right) e^{-w} + \left(\frac{1}{w} + 1 \right) e^{-2w} \right) . \tag{5}$$

For $w \gg 1$ we can approximate (5) as

$$E_e(R) + E_{pp}(R) - E_H \approx \frac{4E_H}{3} w e^{-w} ,$$

and since $E_H < 0$, we see that this is negative and becomes more negative as w decreases. For this reason there is a net attraction. Notice that this term is due entirely to the overlap integrals $\langle \psi_A | \psi_B \rangle$ and $\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle$ and thus it is the overlap of the wave-functions that is responsible for the binding. For $w \ll 1$ the function in (5) is approximately

$$E_e(R) + E_{pp}(R) - E_H \approx - \frac{2E_H}{w} ,$$

which is blowing up to positive infinity as $w \rightarrow 0$, as we previously argued would occur. Hence, from these arguments there must be a finite value of w that minimizes the function in (5). It's not possible to find this minimum analytically, but it can be done numerically where one finds $w \approx 2.49$. This means that the nuclei are separated by about $R = 2.49 a_\mu = 1.3 \text{ \AA}$. Plugging this value of w back into (5) we find

$$E_e(2.59 a_\mu) + E_{pp}(2.59 a_\mu) - E_H \approx 0.13 E_H = -1.76 \text{ eV} .$$

This is the binding energy, in other words it takes 1.76 eV to pull the two nuclei away from each other.

We can compare our estimates to the experimental results, where the nuclear separation is measured to be 1.06 \AA , and the binding energy is -2.8 eV . As promised, the true result for the energy is less than our estimate. In fact, we can see that our estimate did not give a particularly good result for the binding energy. The reason for this is because, while ψ is close to the true ground state wave-function when $R \gg a_\mu$, it is not so close once R is on the order of a_μ . In fact, we can see that it is positively horrible for $R \ll a_\mu$, where ψ approaches the ground state wave-function of an electron about a hydrogen nucleus. But of course, there are two protons in the center, so the true ground state wave-function should approach the wave-function of an electron about a $Z = 2$ nucleus.

2 The H_2 molecule

In nature, two hydrogen atoms combine to make a hydrogen molecule with two electrons and two separated protons. The extra electron makes this more complicated than the H_2^+ molecule, so we will give a less quantitative description of the molecular bonding.

Let us call the positions of two electrons \vec{r}_1 and \vec{r}_2 and we again attempt to build a wave-function that will be at least qualitatively close to the true ground state wave-function. We expect that at very large separation the wave-function should reduce to that of two hydrogen atoms. Furthermore, the electrons are identical fermions and so the overall state should be antisymmetric under the exchange of the two electrons. Taking into account the electron spin, we then assume the spatial part of the wave-function has the form

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1 \pm I^2}} \left(\psi_A(\vec{r}_1) \psi_B(\vec{r}_2) \pm \psi_A(\vec{r}_2) \psi_B(\vec{r}_1) \right)$$

where $\psi_A(\vec{r})$, $\psi_B(\vec{r})$ and their overlap I are the same as in the last section. The \pm signs depend on the total spin state of the electrons. If the spin is $S = 0$ (singlet) then the spin part is antisymmetric and so the spatial part must be symmetric and the $+$ sign is used. If the spin is $S = 1$ (triplet) then the spin part is symmetric and so the spatial part must be antisymmetric and the $-$ sign is used.

The Hamiltonian for the electrons is given by

$$\mathcal{H} = H_1 + H_2 + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|},$$

where H_1 and H_2 are the Hamiltonian H in (1) with \vec{r} replaced by \vec{r}_1 and \vec{r}_2 respectively. The last term is due to the Coulomb repulsion between the electrons. We assume that the electrons' contribution to the energy, $E_{ee}(R)$ is

$$\begin{aligned}
\langle \psi | \mathcal{H} | \psi \rangle &= \frac{1}{1 \pm I^2} \left(\langle \psi_A | H | \psi_A \rangle \langle \psi_B | \psi_B \rangle + \langle \psi_B | H | \psi_B \rangle \langle \psi_A | \psi_A \rangle \right. \\
&\quad \left. \pm \langle \psi_A | H | \psi_B \rangle \langle \psi_B | \psi_A \rangle \pm \langle \psi_B | H | \psi_A \rangle \langle \psi_A | \psi_B \rangle \right) \\
&\quad + \langle \psi | \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} | \psi \rangle \\
&= \frac{2}{1 \pm I^2} \left(\langle \psi_A | H | \psi_A \rangle \pm \langle \psi_A | H | \psi_B \rangle I \right) + \langle \psi | \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} | \psi \rangle \\
&= 2E_H - \frac{e^2}{4\pi\epsilon_0} \frac{2}{1 \pm I^2} \left(\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_A \rangle \pm \langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle I \right) \\
&\quad + \langle \psi | \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} | \psi \rangle
\end{aligned}$$

We can use our results from the last section for the first set of terms, although we will now only make qualitative arguments. We notice that with a + sign, the overlap term $\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle$ contributes negatively to the energy and so it favors binding. With the minus sign it disfavors binding. If we now consider the last term we have

$$\begin{aligned}
\langle \psi | \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} | \psi \rangle &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{1 \pm I^2} \left(\int d^3 r_1 \int d^3 r_2 \frac{\psi_A^*(\vec{r}_1) \psi_A(\vec{r}_1) \psi_B^*(\vec{r}_2) \psi_B(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \right. \\
&\quad \left. \pm \int d^3 r_1 \int d^3 r_2 \frac{\psi_A^*(\vec{r}_1) \psi_B(\vec{r}_1) \psi_B^*(\vec{r}_2) \psi_A(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \right)
\end{aligned}$$

Unfortunately, these are not easy integrals to perform, so we won't do them. However, we can see that with a + sign the overlap integral coming from the electron repulsion increases the energy and with a minus sign the overlap decreases the energy. It turns out that the first set of overlap integrals wins out over the electron repulsion overlap, roughly speaking because each electron sees two protons and only one other electron. Consequently, binding requires a + sign and so it follows that the electrons that bind the two nuclei together are in an $S = 0$ state.

This is a general feature in the bonding of two atoms, namely an electron in one atom forms an $S = 0$ state with an electron in the other atom. However, in order for this to work the electron cannot be in a filled shell, since it is already part of an $S = 0$ state with another electron in the shell (you cannot antisymmetrize the spins of 3 electrons). Therefore, atoms with completely filled shells like He and Ar don't form bonds with other atoms, making them chemically inert. If the atoms making up the molecule are identical then the electrons will be equally shared. Such a bond is called *covalent*. However if the atoms are not the same, it is possible that the outer electrons have a higher probability to be about one atom than another. Bonds of this type are called *ionic*. Ordinary sodium chloride (NaCl), that is salt, is an example of this.

3 Molecular spectra

We have seen with the H_2^+ molecule that there is a favored separation between the nuclei where the energy is at a minimum. We can think of this energy as a potential $V(R)$ for the nuclear separation, where $V(R)$ takes into account all contributions from the electrons. We should expect the same for any other diatomic molecule, namely there should be a potential $V(R)$ that has a minimum at some $R = R_0$. This means that if we do a Taylor expansion of $V(R)$ about $R = R_0$ we would find

$$V(R) = V(R_0) + \frac{1}{2}(R - R_0)^2 \left. \frac{d^2V}{dR^2} \right|_{R=R_0} + O((R - R_0)^3)$$

where we used that $\left. \frac{dV}{dR} \right|_{R=R_0} = 0$ since $V(R_0)$ is a minimum.

In the previous sections we ignored the nuclear motion, but now let us include it. We effectively have a two body problem where R is the radial coordinate of the separation vector \vec{R} between the two nuclei, so we can describe this two body system by the Hamiltonian

$$H_{\text{diatom}} = -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 + V(R),$$

where M is the reduced mass for the two nuclei $M = \frac{M_A M_B}{M_A + M_B}$. Since we have a radially symmetric potential we can consider the radial wave-function $u_\ell(R)$ for the relative molecular motion with a radial Hamiltonian

$$H_{\text{diatom}} = -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \frac{\ell(\ell + 1)\hbar^2}{2MR^2} + V(R).$$

If we approximate $V(R) \approx V(R_0) + \frac{1}{2}k(R - R_0)^2$, where $k = \left. \frac{d^2V}{dR^2} \right|_{R=R_0}$, then we can approximate the effective Hamiltonian as

$$H_{\text{diatom}} = H_{\text{vib}} + H_{\text{rot}} + V(R_0).$$

H_{vib} is the vibrational part of H_{diatom}

$$H_{\text{vib}} \approx -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_0)^2$$

and H_{rot} is the rotational part

$$H_{\text{rot}} = \frac{\ell(\ell + 1)\hbar^2}{2MR^2}.$$

$V(R_0)$ is an overall constant so it can be dropped.

H_{vib} is the Hamiltonian for a harmonic oscillator and so the diatomic molecule will have vibrational modes with energies

$$E_{\text{vib}} = \hbar\omega(n + \frac{1}{2})$$

where $\omega = \sqrt{k/M}$. These modes can be seen when the molecule makes a transition from one vibrational mode to another, emitting a photon. To get an idea of the energy, recall from our discussion of the H_2^+ molecule that $V(R)$ is comparable to a typical atomic energy, so within an order of magnitude $V(R_0) \sim E_H$ and since $R_0 \sim a_\mu$, we expect $k \sim |E_H|/a_\mu^2$. Consequently, the typical vibrational energies should be

$$E_{\text{vib}} \sim \frac{\hbar}{a_\mu} \sqrt{\frac{|E_H|}{M}} \sim |E_H| \frac{\hbar}{a_\mu} \sqrt{\frac{1}{M|E_H|}} \sim |E_H| \frac{\hbar}{a_\mu} \sqrt{\frac{\mu a_\mu^2}{M\hbar^2}} \sim |E_H| \sqrt{\frac{\mu}{M}}$$

where we used that $|E_H| \sim \frac{\hbar^2}{\mu a_\mu^2}$. Hence the vibrational modes have frequencies which are on the order of typical atomic frequencies suppressed by a factor of $\sqrt{\mu/M} \leq 0.02$. This puts these modes in the far infrared. We also have that the rms size of the vibrations are

$$\sqrt{\langle (R - R_0)^2 \rangle} \sim \sqrt{\frac{\hbar}{M\omega}} \sim a_\mu \left(\frac{\mu}{M}\right)^{1/4}$$

which is small compared to $R_0 \sim a_\mu$.

To find the energies for the rotational modes, we observe that since the vibrational fluctuations are small compared to R_0 we can approximate H_{rot} by replacing R with R_0 . Hence the energies are approximately

$$E_{\text{rot}} \approx \frac{\ell(\ell+1)\hbar^2}{2MR_0^2} = \frac{\ell(\ell+1)\hbar^2}{2\mathcal{I}}$$

where we have written the energy in terms of the moment of inertia \mathcal{I} . To see why this is the moment of inertia, one can think of the molecule as being shaped like a dumbbell with the two nuclei at the ends. The moment of inertia for rotation about the center of mass is

$$\mathcal{I} = M_A \left(\frac{M_B}{M_A + M_B} R_0 \right)^2 + M_B \left(R_0 - \frac{M_B}{M_A + M_B} R_0 \right)^2 = MR_0^2.$$

To get an estimate of the rotational energies, we again assume that $R_0 \sim a_\mu$, hence the rotational energies are on the order of

$$E_{\text{rot}} \sim \frac{\hbar^2}{a_\mu^2 M} \sim |E_H| \frac{\mu}{M}.$$

Accordingly, the energies of the rotational modes come with an even larger suppression factor than the vibrational modes and the typical frequencies coming from transitions between different rotational energy levels are in the microwave range. Clearly, by measuring these frequencies one can get an accurate measurement of the internuclear distance simply by using

$$h\nu = \frac{\ell_i(\ell_i+1)\hbar^2}{2MR_0^2} - \frac{\ell_f(\ell_f+1)\hbar^2}{2MR_0^2} = \frac{(\ell_i - \ell_f)(\ell_i + \ell_f + 1)\hbar^2}{2MR_0^2},$$

where ℓ_i and ℓ_f are the initial and final angular momentum quantum numbers.

A Details for the inner products

Here we find the inner products given in section 1 of the text.

Without any loss of generality, we can assume that $\vec{R} = R\hat{z}$. Then, letting $y \equiv |\vec{r} - \vec{R}|$, we have

$$y^2 = r^2 - 2rR \cos \theta + R^2 .$$

Hence, for I we have

$$I = \frac{4(2\pi)}{4\pi a_\mu^3} \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta e^{-r/a_\mu} e^{-y/a_\mu} .$$

We can substitute the θ integral for an integral over y by observing that $y dy = rR \sin \theta d\theta$ for fixed r with y in the range $|r - R| \leq y \leq r + R$. Hence we can reexpress I as

$$\begin{aligned} I &= \frac{2}{Ra_\mu^3} \int_0^\infty r dr e^{-r/a_\mu} \int_{|r-R|}^{r+R} y e^{-y/a_\mu} dy \\ &= \frac{2}{Ra_\mu^3} \int_0^\infty r e^{-r/a_\mu} \left(a_\mu(|r-R| + a_\mu) e^{-|r-R|/a_\mu} - a_\mu(r+R+a_\mu) e^{-(r+R)/a_\mu} \right) dr \\ &= \frac{2}{Ra_\mu^2} \left(e^{-R/a_\mu} \int_0^R (R-r+a_\mu) r dr + e^{+R/a_\mu} \int_R^\infty (r-R+a_\mu) r e^{-2r/a_\mu} dr \right. \\ &\quad \left. - e^{-R/a_\mu} \int_0^\infty (r+R+a_\mu) r e^{-2r/a_\mu} dr \right) \\ &= \frac{2}{Ra_\mu^2} \left(e^{-R/a_\mu} \left(\frac{R^3}{2} - \frac{R^3}{3} + \frac{R^2 a_\mu}{2} \right) + e^{-R/a_\mu} \left(\frac{2a_\mu^3}{8} + \frac{a_\mu^3}{4} + \frac{Ra_\mu^2}{4} + \frac{Ra_\mu^2}{2} \right) \right. \\ &\quad \left. - e^{-R/a_\mu} \left(\frac{2a_\mu^3}{8} + \frac{a_\mu^2(R+a_\mu)}{4} \right) \right) = \left(\frac{w^2}{3} + w + 1 \right) e^{-w} . \end{aligned}$$

As a check, we see that $I = 1$ when $R = 0$ ($w = 0$), as expected since here ψ_B is the same normalized wave-function as ψ_A . We also see that the overlap between the two wave-functions falls off exponentially for large separations.

We next have

$$\begin{aligned} \langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_B \rangle &= \frac{4(2\pi)}{4\pi a_\mu^3} \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta e^{-r/a_\mu} \frac{1}{y} e^{-y/a_\mu} \\ &= \frac{2}{Ra_\mu^3} \int_0^\infty r dr e^{-r/a_\mu} \int_{|r-R|}^{r+R} e^{-y/a_\mu} dy \\ &= \frac{2}{Ra_\mu^2} \int_0^\infty r e^{-r/a_\mu} \left(e^{-|r-R|/a_\mu} - e^{-(r+R)/a_\mu} \right) dr \\ &= \frac{2}{Ra_\mu^2} e^{-R/a_\mu} \left(\frac{R^2}{2} + \frac{a_\mu^2}{4} + \frac{Ra_\mu}{2} - \frac{a_\mu^2}{4} \right) = \frac{1}{a_\mu} (w + 1) e^{-w} . \end{aligned}$$

The last integral is

$$\begin{aligned}
\langle \psi_A | \frac{1}{|\vec{r} - \vec{R}|} | \psi_A \rangle &= \frac{4(2\pi)}{4\pi a_\mu^3} \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta e^{-2r/a_\mu} \frac{1}{y} \\
&= \frac{2}{Ra_\mu^3} \int_0^\infty r dr e^{-2r/a_\mu} \int_{|r-R|}^{r+R} dy \\
&= \frac{2}{Ra_\mu^2} \int_0^\infty r e^{-2r/a_\mu} ((r+R) - |r-R|) dr \\
&= \frac{2}{Ra_\mu^2} \left(\left(\frac{2a_\mu^3}{8} + \frac{Ra_\mu^2}{4} \right) - \left(-\frac{a_\mu^3}{4} + \frac{Ra_\mu^2}{4} + e^{-2R/a_\mu} \left(\frac{a_\mu^3}{4} + \frac{Ra_\mu^2}{4} \right) \right) \right. \\
&\quad \left. - e^{-2R/a_\mu} \left(\frac{2a_\mu^3}{8} + \frac{Ra_\mu^2}{4} \right) \right) = \frac{1}{w a_\mu} (1 - (1+w)e^{-2w}) .
\end{aligned}$$