

1. This problem is from the May, 2004 Prelims. Hydrogen molecule. Consider the neutral hydrogen molecule, H_2 . Write down the Hamiltonian keeping only the kinetic energy terms and the Coulomb interactions of all the constituents and omitting terms which cause fine and hyperfine structure.

Solution

Clearly, the Hamiltonian contains four kinetic energy terms and six Coulomb terms. We let indices 1 and 2 be the protons and 3 and 4 be the electrons.

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_{i,j,i \neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

However, this is probably not the best way to write the Hamiltonian. The electrons, 2000 times less massive than the protons, can adjust their configuration to the configuration of the protons very rapidly. So a better idea is to write the Hamiltonian for the electrons separately.

$$H_e = \frac{p_3^2}{2m_e} + \frac{p_4^2}{2m_e} - \frac{e^2}{|\mathbf{r}_3 - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r}_3 - \mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_3|}.$$

Assuming the protons are at the fixed positions \mathbf{r}_1 , and \mathbf{r}_2 , the ground state of the electrons can be found with a total energy $U(|\mathbf{r}_1 - \mathbf{r}_2|)$. Then, the Hamiltonian for the protons may be approximated by

$$H_p = \frac{p_1^2}{2m_p} + \frac{p_2^2}{2m_p} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + U(|\mathbf{r}_1 - \mathbf{r}_2|).$$

Some things to notice are that when the protons are very far apart, the ground state of the electrons is that of two Hydrogen atoms with a binding energy of $2 \times 13.6 \text{ eV}$. When the protons are right on top of each other the ground state of the electrons is that of Helium with a binding energy of 79 eV . We expect that the electron ground state energy ($U(|\mathbf{r}_1 - \mathbf{r}_2|)$) monotonically decreases as the proton separation decreases. On the other hand, the Coulomb energy of the protons increases as their separation decreases. At some separation r_0 , the electron energy plus proton Coulomb energy is a minimum. This will be the equilibrium separation of the protons. We can make a Taylor expansion of the energy around the Equilibrium position and the result is a harmonic oscillator potential. So the Hamiltonian of the protons can be written

$$H_p = \frac{p_1^2}{2m_p} + \frac{p_2^2}{2m_p} + \frac{1}{2}k(|\mathbf{r}_1 - \mathbf{r}_2| - r_0)^2.$$

As rough guesses, we might take $r_0 \approx a$, the Bohr radius, and $k \approx e^2/a^3$.

We can separate off the center of mass motion which yields the following Hamiltonian for the motion of the protons, where r is the distance between the two protons.

$$H_p = \frac{p^2}{2\mu} + \frac{1}{2}k(r - r_0)^2,$$

and $\mu = m_p/2$ is the reduced mass of the protons. Finally, L^2 commutes with this Hamiltonian, so we write it in terms of the radial momentum,

$$H_p = \frac{p_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + \frac{1}{2}k(r - r_0)^2 .$$

Other considerations: The Hamiltonian for the entire system is even so all non-degenerate eigenstates are even or odd and degenerate eigenstates may be chosen to be even or odd. In particular the electron ground state assumed the electrons were in an even configuration, so they must be in a singlet spin configuration.

— End Solution —

- (a) What is the degeneracy of the ground state? Give all quantum numbers and symmetries of the ground state(s), including the electron and proton spin degrees of freedom.

— Solution —

Electrons are in a singlet state, $\mathbf{S}_e = 0$. The protons are in a singlet state, $\mathbf{S}_p = 0$. The degeneracy of the ground state is 1. The angular momentum quantum number for the protons is $l = 0$, and the vibrational quantum number is $\nu = 0$. This makes the spatial part of the state symmetric under interchange of the protons, which is why they must be in a singlet state. The electrons are in hydrogen-like ground state with orbital angular momentum 0 and principal quantum number $n = 1$. This makes the spatial part of the electron wave function symmetric which is why they must be in a singlet state.

— End Solution —

- (b) What is the degeneracy and what are all the quantum numbers of the first excited state of this H₂ molecule? Explain.

— Solution —

The first excited state will involve a change in the angular momentum of the protons. We can see this as follows. Electronic excitations are the order of e^2/a where $a = \hbar^2/me^2$ is the Bohr radius. Vibrational excitations are the order of $\hbar\omega$, where $\omega = \sqrt{k/\mu}$. Plugging in our guess for k , we find that the excitation energy of a vibrational mode is $(e^2/a)\sqrt{m_e/\mu}$ or about 1/30 times the electronic excitations. The rotational excitations will be the order of $\hbar^2/2\mu r_0^2 = \hbar^2/2\mu a^2 = (e^2/2a)(m_e\mu)$ or another factor of 1/30 down from the vibrational excitations. Since the spatial state must be even, the first excited state cannot be $l = 1$, but must be $l = 2$ which has a degeneracy of 5.

The spatial state must be even because we assume the nuclear spins stay in the singlet state. In fact, the nuclear spins couple very weakly to anything else, so transitions involving a change of the nuclear spin from singlet to triplet and vice versa are rare. If the nuclear spins were in the triplet state, then the spatial state would have to be anti-symmetric and the lowest energy state is the $l = 1$ state. Although simple radiative transitions do not couple this state to the ground state, one could take this as the first excited state. Then

the degeneracy is 9, 3 for $l = 1$ times 3 for the triplet spin state. The energy is the same order of magnitude as in part (c) below ($l(l + 1) = 2$ instead of 6).

End Solution

- (c) What is the energy difference between ground and first excited states? Estimate it first through a formula, in terms of properties of the molecule's ground state, and then in electron-Volts (eV).

Solution

From the solution to part (b), the formula is $l(l + 1)(e^2/2a)(m_e/(m_p/2))$ or about 0.08 eV.

End Solution

2. With Hund's rules, determine S , L , and J for nitrogen whose configuration is $1s^2 2s^2 2p^3$.

Solution

Rule number 1 says, S should be maximal which means $S = 3/2$ Rule number 2 says, L should be maximal. However, the spin state is symmetric, so the spatial state must be antisymmetric. With three $l = 1$ states, the possibilities are $L = 0, 1, 2, 3$. The easiest way to see which are allowed is to consider m_l for each electron. Can we find an antisymmetric state that adds up to $m_L = 0, 1, 2, 3$? So, we'll write out the states where the position from left to right corresponds to electrons 1, 2, 3. For example $|1, 1, 1\rangle$ means electron 1 has $m_l = 1$, electron 2 has $m_l = 1$, and electron 3 has $m_l = 1$. We need to antisymmetrize this state; we take all six permutations with the appropriate sign:

$$|1, 1, 1\rangle - |1, 1, 1\rangle + |1, 1, 1\rangle - |1, 1, 1\rangle + |1, 1, 1\rangle - |1, 1, 1\rangle = 0,$$

so we can't have $L = 3$. How about $L = 2$? To get $m_L = 2$, we would have to add up two $m_l = 1$ along with an $m_l = 0$. The state would be

$$|1, 1, 0\rangle - |1, 0, 1\rangle + |0, 1, 1\rangle - |0, 1, 1\rangle + |1, 0, 1\rangle - |1, 1, 0\rangle = 0,$$

so we can't have $L = 2$. How about $L = 1$? There are two ways we could come up with $m_L = 1$. We could add up two $m_l = 1$ along with an $m_l = 0$ or we could add an $m_l = 1$ along with two $m_l = 0$. In either case, two would be the same and there's no way to form a non-vanishing antisymmetrized state. How about $L = 0$? If we can't have this, then nitrogen can't exist! There are two ways to come up with $m_L = 0$. One way is all three $m_l = 0$. This can't lead to an antisymmetric state. Another way is $m_l = 1, m_l = 0$ and $m_l = -1$,

$$|1, 0, -1\rangle - |1, -1, 0\rangle + |-1, 1, 0\rangle - |-1, 0, 1\rangle + |0, -1, 1\rangle - |0, 1, -1\rangle \neq 0,$$

so $L = 0$ works! Then $J = S$ and the term is ${}^4S_{3/2}$.

End Solution

3. Two particles of mass m are confined to a rectangular box of sides $a < b < c$. They are in the lowest energy state compatible with the conditions in the cases below. For each of these cases, determine the lowest energy state and its energy and also use first order perturbation theory to determine the correction to the energy if there is an interaction between the particles of the form $V = (V_0(abc))\delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2)$.

(a) Two non-identical particles.

Solution

The single particle wave functions will be of the form

$$|n_a, n_b, n_c\rangle = \sqrt{\frac{8}{abc}} \sin \frac{\pi n_a x}{a} \sin \frac{\pi n_b y}{b} \sin \frac{\pi n_c z}{c},$$

with all quantum numbers greater than 0 and with energy

$$E_{n_a, n_b, n_c} = \frac{\hbar^2 \pi^2}{2m} \left(\left(\frac{n_a}{a} \right)^2 + \left(\frac{n_b}{b} \right)^2 + \left(\frac{n_c}{c} \right)^2 \right).$$

The lowest energy single particle state is $|1, 1, 1\rangle$ with energy

$$E_{1,1,1} = \frac{\hbar^2 \pi^2}{2m} \left(\left(\frac{1}{a} \right)^2 + \left(\frac{1}{b} \right)^2 + \left(\frac{1}{c} \right)^2 \right).$$

Since c is the largest side of the box, the next lowest energy single particle state is $|1, 1, 2\rangle$ with energy

$$E_{1,1,2} = \frac{\hbar^2 \pi^2}{2m} \left(\left(\frac{1}{a} \right)^2 + \left(\frac{1}{b} \right)^2 + \left(\frac{2}{c} \right)^2 \right).$$

We will write two particle states as $|n_a, n_b, n_c\rangle |n'_a, n'_b, n'_c\rangle$ where the first ket refers to particle 1 and the second to particle 2.

For the case at hand, non-identical particles, both particles can be placed in the lowest energy single particle state, so the state

$$\psi = |1, 1, 1\rangle |1, 1, 1\rangle,$$

with energy

$$E_{1,1,1,1,1,1} = 2E_{1,1,1} = 2 \frac{\hbar^2 \pi^2}{2m} \left(\left(\frac{1}{a} \right)^2 + \left(\frac{1}{b} \right)^2 + \left(\frac{1}{c} \right)^2 \right).$$

To take account of the “contact” interaction we need the product of three integrals like

$$\begin{aligned}\Delta_x &= \frac{4}{a^2} \int_0^a dx_1 \int_0^a dx_2 \sin^2 \frac{\pi n_a x_1}{a} \sin^2 \frac{\pi n'_a x_2}{a} (a\delta(x_1 - x_2)) \\ &= \frac{4}{a} \int_0^a dx \sin^2 \frac{\pi n_a x}{a} \sin^2 \frac{\pi n'_a x}{a} \\ &= 1 + \frac{1}{2} \delta_{n_a, n'_a}\end{aligned}$$

For this case, $n_a = n'_a = 1$, and the integral is $3/2$. Putting it all together, we find

$$\Delta E = V_0 \Delta_x \Delta_y \Delta_z = \frac{27}{8} V_0 .$$

End Solution

(b) Two identical particles of spin 0.

Solution

In this case, the wave function must be symmetric under the exchange of the two particles. Since spin 0 particles must necessarily be in a symmetric spin state, the spatial state must be symmetric. The state described in part (a) is symmetric so it works for this part. The state, the energy, and the contact interaction energy are the same as for part (a).

End Solution

(c) Two identical particles of spin 1/2 in the singlet state.

Solution

Now the wave function must be antisymmetric. Since the singlet state is antisymmetric, the spatial state must be symmetric. So the wave function, energy, and contact interaction energy are again, the same as in part (a).

End Solution

(d) Two identical particles of spin 1/2 in the triplet state.

Solution

The wave function must be antisymmetric under exchange of the two particles, the spin state is symmetric, so the spatial state must be antisymmetric. The lowest energy state is

$$\psi = \frac{1}{\sqrt{2}} (|1, 1, 1\rangle |1, 1, 2\rangle - |1, 1, 2\rangle |1, 1, 1\rangle) ,$$

with energy

$$E_{1,1,1,1,1,2} = E_{1,1,1} + E_{1,1,2} = \frac{\hbar^2 \pi^2}{2m} \left(2 \left(\frac{1}{a} \right)^2 + 2 \left(\frac{1}{b} \right)^2 + 5 \left(\frac{1}{c} \right)^2 \right) .$$

Now we need the matrix element of the perturbation for this state. The integrals for x and y will be the same as before. The integral for z is,

$$\begin{aligned}\Delta_z &= \frac{4}{c^2} \frac{1}{2} \int_0^c dz_1 \int_0^c dz_2 \left(\sin \frac{\pi z_1}{c} \sin \frac{2\pi z_2}{c} - \sin \frac{2\pi z_1}{c} \sin \frac{\pi z_2}{c} \right)^2 (c\delta(z_1 - z_2)) \\ &= \frac{2}{\pi} \int_0^\pi dz (\sin z \sin 2z - \sin 2z \sin z) \\ &= 0.\end{aligned}$$

Not surprisingly, the particles in the triplet state are prevented from being right on top of each other by the Pauli exclusion principle, so the contact interaction is zero.

End Solution

4. Beta decay rearrangement. Based on a problem in Schwabl. In β -decay, the nuclear charge number Z of a $Z - 1$ times ionized atom (so it's hydrogen-like!) changes suddenly to $Z + 1$. Calculate the probabilities for the transition of the electron to the $2s$ or $3s$ states given that the electron was in the ground state before the β -decay. Do you have any comments on energy conservation?

Solution

We use the sudden approximation, and we need to calculate the overlap integral between the $1s$ state of an electron orbiting a nucleus with charge Ze and the $2s$ and $3s$ states of an electron orbiting a nucleus of charge $(Z + 1)e$. We ignore everything but the Coulomb interaction. The angular part of the wave function is Y_{00} in all cases, so we don't need to worry about it. (Also, we can only wind up in an s -state since Y_{00} is orthogonal to all higher angular momentum states!) The radial part of the wave function before the decay and the two choices post decay are

$$\begin{aligned}R_{10} &= 2 \left(\frac{Z}{a} \right)^{3/2} e^{-Zr/a} \\ R_{20} &= 2 \left(\frac{Z+1}{2a} \right)^{3/2} \left(1 - \frac{(Z+1)r}{2a} \right) e^{-(Z+1)r/2a} \\ R_{30} &= 2 \left(\frac{Z+1}{3a} \right)^{3/2} \left(1 - \frac{2(Z+1)r}{3a} + \frac{2((Z+1)r)^2}{27a^2} \right) e^{-(Z+1)r/3a}.\end{aligned}$$

The amplitude to go to the $2s$ -state is

$$\begin{aligned}
 \langle 20 | 10 \rangle &= 2^{1/2} (Z(Z+1))^{3/2} \frac{1}{a^3} \int_0^\infty r^2 dr \left(1 - \frac{(Z+1)r}{2a} \right) e^{-(Z+1)r/2a - Zr/a} \\
 &= 2^{1/2} (Z(Z+1))^{3/2} \frac{1}{a^3} \int_0^\infty r^2 dr \left(1 - \frac{(Z+1)r}{2a} \right) e^{-(3Z+1)r/2a} \\
 &= 2^{7/2} \frac{(Z(Z+1))^{3/2}}{(3Z+1)^3} \int_0^\infty x^2 dx \left(1 - \frac{(Z+1)x}{3Z+1} \right) e^{-x} \\
 &= 2^{7/2} \frac{(Z(Z+1))^{3/2}}{(3Z+1)^3} \left(2 - 6 \frac{Z+1}{3Z+1} \right) \\
 &= -2^{11/2} \frac{(Z(Z+1))^{3/2}}{(3Z+1)^4}.
 \end{aligned}$$

Similarly, the amplitude to go to the $3s$ -state is,

$$\begin{aligned}
 \langle 30 | 10 \rangle &= \frac{4(Z(Z+1))^{3/2}}{3^{3/2}a^3} \int_0^\infty r^2 dr \left(1 - \frac{2(Z+1)r}{3a} + \frac{2((Z+1)r)^2}{27a^2} \right) e^{-(4Z+1)r/3a} \\
 &= \frac{4 \cdot 3^{3/2} (Z(Z+1))^{3/2}}{(4Z+1)^3} \int_0^\infty x^2 dx \left(1 - \frac{2(Z+1)x}{4Z+1} + \frac{2(Z+1)^2 x^2}{3(4Z+1)^2} \right) e^{-x} \\
 &= \frac{8 \cdot 3^{3/2} (Z(Z+1))^{3/2}}{(4Z+1)^3} \left(1 - \frac{6(Z+1)}{4Z+1} + \frac{8(Z+1)^2}{(4Z+1)^2} \right) \\
 &= -\frac{8 \cdot 3^{5/2} (Z(Z+1))^{3/2} (2Z-1)}{(4Z+1)^5}.
 \end{aligned}$$

So, the transition probabilities are

$$P_{1 \rightarrow 2} = \frac{2^{11} (Z(Z+1))^3}{(3Z+1)^8} \quad P_{1 \rightarrow 3} = \frac{2^6 \cdot 3^5 (Z(Z+1))^3 (2Z-1)^2}{(4Z+1)^{10}}.$$

As an example, we might consider the decay of tritium,



Tritium is just “extra-heavy hydrogen,” so $Z = 1$ and,

$$P_{1 \rightarrow 2} = \frac{1}{4} = 0.25 \quad P_{1 \rightarrow 3} = \frac{2^9 3^5}{5^{10}} = 0.01274.$$

With respect to the conservation of energy question: Again, consider tritium for a concrete example. Before the decay, the binding energy of the electron was -13.6 eV. After the decay, the electron in the $2s$ or $3s$ states has energy -13.6 eV (an accident of our example) or -6.0 eV, respectively. So, in the decay with the electron going into the $3s$ state, 7.6 eV has apparently been gained by the excited Helium atom left behind. Presumably, this means the decay products: the β , the $\bar{\nu}$, and the recoiling nucleus have 7.6 eV less kinetic energy than they otherwise would.

End Solution

5. Coulomb excitation. Somewhat based on a problem from Schwabl. Consider hydrogen in its ground state at $t = -\infty$. It's acted on by an electric field in the z -direction of the form

$$\mathbf{E}(t) = \frac{E_0 \mathbf{e}_z}{1 + t^2/\tau^2}.$$

This field can be represented by the potential $\phi = -E(t)z$. This is an approximation to what happens when a charge particle passes nearby. If it's not relativistic, we can ignore its magnetic field. What is the probability that the electron winds up in the $2p$ state at $t = +\infty$? Once you've produced a formula, make some reasonable assumptions and calculate a numerical estimate of the probability to see if a Coulomb collision is a reasonable way to excite an atom.

Solution

With a small extension (letting the perturbation start at $t = -\infty$ rather than $t = 0$) to what was discussed in lecture, the amplitude to go from state $|m\rangle$ to state $|n\rangle$ is

$$\langle n, +\infty | m, -\infty \rangle = \frac{1}{i\hbar} \int_{-\infty}^{+\infty} dt e^{i\omega_{nm}t} \langle n | V(t) | m \rangle,$$

where $\omega_{nm} = (E_n - E_m)/\hbar$ and where the perturbing potential is $V(t) = +eE(t)z$. (The potential can be thought of as acting on the electron.) Now, $z = r \cos \theta$. The $2p$ states involve $Y_{1,+1}$, $Y_{1,0}$, and $Y_{1,-1}$. For the $m = \pm 1$ states, the integral over ϕ will give 0. So, we need to evaluate

$$\int \sin \theta d\theta d\phi Y_{1,0}^*(\theta, \phi) \cos \theta Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{3}}.$$

The radial part requires the evaluation of

$$\int_0^\infty r^2 dr R_{21}(r) r R_{1,0}(r) = \frac{2^{15/2} a}{3^{9/2}}.$$

Next we need to evaluate the time integral which is really the Fourier transform of the potential at the frequency corresponding to the energy difference.

$$\int_{-\infty}^{+\infty} dt \frac{e^{i\omega_{nm}t} e E_0}{1 + t^2/\tau^2} = \pi e E_0 \tau e^{-|\omega_{nm}|\tau}.$$

We multiply the three results together to get the transition amplitude,

$$\langle n, +\infty | m, -\infty \rangle = \frac{2^{15/2} \pi e E_0 a \tau e^{-|\omega_{nm}|\tau}}{3^5 i \hbar},$$

and the transition probability is

$$P_{mn} = \frac{2^{15} \pi^2 (e E_0 a \tau)^2 e^{-2|\omega_{nm}|\tau}}{3^{10} \hbar^2}.$$

It will be interesting to make a numerical estimate of this probability. However, there are a lot of parameters! To proceed, we note that $\tau \exp(-\omega_{nm}\tau)$ is maximum when $\tau = 1/\omega_{nm}$. So, let's assume this. Also, suppose the field is caused by one unit of charge e passing at a distance of a (just grazing the atom). We note that $\hbar\omega_{nm} = (3/4)13.6 \text{ eV}$, so $\tau = 6.45 \times 10^{-17} \text{ s}$. The velocity of the incident particle is the order of a/τ which works out to about $0.003c$, so it's safely non-relativistic. Since the particle passed at a , the peak field is $E_0 = e/a^2$. Plugging it all in,

$$\begin{aligned}
 P_{nm} &= \frac{2^{15}\pi^2 e^{-2}}{3^{10}} \frac{(e^2/a)^2}{(\hbar\omega_{nm})^2} \\
 &= \frac{2^{15}\pi^2 \exp(-2)}{3^{10}} \frac{(e^2/a)^2}{((3/4)(e^2/2a))^2} \\
 &= \frac{2^{21}\pi^2 \exp(-2)}{3^{12}} \\
 &= 5.3,
 \end{aligned}$$

just a bit bigger than 1! Not to worry. The main reason to do this numerical calculation was to see if this is a viable way to excite an atom. The answer is yes! For the parameters we've chosen it appears that the collision is too violent for perturbation theory. However, if the colliding particle passed at $4a$ rather than a , the probability would be 0.33, perfectly reasonable.

End Solution
