

PHY 304, II-Semester 2023/24, Tutorial 4 solution

Stage 1 Variational method for atomic and molecular physics:

- (a) Discuss why (or under which conditions) the variational wavefunction:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z_{\text{eff}}^3}{\pi a_0^3} e^{-Z_{\text{eff}}(r_1+r_2)/a_0}, \quad (1)$$

could be a good Ansatz for the Helium Hamiltonian.

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2}) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad (2)$$

(see section 7.5.1)

Solution: This variational wavefunction makes sense because it is essentially the wavefunction of two non-interacting electrons under a Hydrogen potential with $e^2 \rightarrow Ze^2$ and $a_0 \rightarrow a_0/Z$ but now with a pre-factor Z_{eff}^2 also to account for electron screening.

- (b) Propose at least one wavefunction that adds an extra parameter to variationally take into account electron-electron repulsion?

Solution:

We will include the variable $r_{12}(= |\mathbf{r}_1 - \mathbf{r}_2|)$, involving the inter-electron separation in the wavefunction to variationally take into account electron-electron repulsion.

$$\psi'(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1, \mathbf{r}_2) f(r_{12}) \quad (3)$$

$$= \psi_0(\mathbf{r}_1, \mathbf{r}_2) (1 + \alpha r_{12}) \quad (4)$$

Here, α is the additional parameter. The second term in Eq. 4 increases the probability of finding two electrons further apart and reduces the probability of finding two electrons in regions with $r_1 \approx r_2$.

- (c) Discuss why (or under which conditions) the variational wavefunction:

$$\psi_0(\mathbf{r}) = \frac{\mathcal{N}}{\sqrt{2}} (\phi_{100}(\mathbf{r}) + \phi_{100}(\mathbf{r}')) = \frac{\mathcal{N}}{\sqrt{2\pi a_0^3}} (e^{-r/a_0} + e^{-r'/a_0}), \quad (5)$$

could be a good Ansatz for the H_2^+ Hamiltonian.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r} + \frac{1}{r'} - \frac{1}{R} \right). \quad (6)$$

(see section 7.5.2)

Solution: Let's consider the problem with a very large R first. In that case, if the electron is near one of them, the second proton should not

be felt much, hence a Hydrogen ground-state should be a good guess for the wavefunction of the electron. However the problem is symmetric under exchange of the protons, hence the state in Eq. (5) is a reasonable guess. One can essentially think of it as guessing that the electron is in a superposition of "sitting at the site of either proton".

- (d) Using this, what is the essence of a covalent molecular bond that we discover?

Solution: Minimizing the energy functional for the LCAO ansatz and plotting the $E_{gs} = \langle \hat{H}(R) \rangle = -E_1 F(\frac{R}{a_0})$ (see Eqn (7.116) in lecture notes), one finds that the molecular potential has a local minimum because of which it is possible to have bound states. This is the essence of why covalent bonding takes places. At the right distance R , there is excess charge exactly between the protons weakening their mutual repulsion and lowering the overall energy.

- (e) Propose one or two physically motivated ways how the Ansatz (5) could be made more powerful by introducing variational parameters.

Solution: One could try to introduce tuneable parameters for example as in

$$\psi_0^{var}(\mathbf{r}) = \mathcal{N} \left[e^{-\alpha(r+r')} + p \left(e^{-\beta r} + e^{-\beta r'} \right) \right], \quad (7)$$

and then try to minimize the energy functional to find the optimal parameters α , β , p . Prior to that we would have to find the correct normalisation \mathcal{N} for all choices of α , β , p and R .

The physical motivation for the first term, would be that it allows the electron to be even more strongly localised in between the protons (exactly in between the two protons, $r + r'$ takes its smallest value. The parameter p then is some mixing amplitude between this new contribution, and the second part which we discussed in the lecture. For the latter, we now also made the width of each Hydrogen ground-state an optimisable parameter.

Stage 2 WKB approximation

- (i) Discuss in your team what constitutes the WKB approximation, what is the basic idea, and how one can estimate whether it will be valid.

Solution: See section 7.6

- (ii) Based on your summary, inspect Fig. 1 below and discuss for each case whether WKB will be good and why, where it won't be good or why it won't be good.

Solution: **Case(a):** yes, we can read off the potential that for the most part, over the scale of one λ (one oscillation of $\phi(x)$), the fractional change of $E - V(x)$ is small compared to the value of $E - V(x)$ itself. **Case(b):** no. In contrast to (a), over the scale of one wavelength, the change of

$E - V(x)$ is of the order of typical values of $E - V(x)$ itself. **Case(c):** yes, see (a). **Case(d):** tricky but yes. You'd think the delta-function potential is the total opposite of a slowly varying potential. However that affects "only $x = 0$ ", everywhere else $V(x)$ is constant, hence the WKB solution for the classically forbidden region (since $E < V(x) = 0$) actually completely captures Eq. (2.103). **Case(e):** no, this potential and energy combination gives rise to many points with $E = V$ near which WKB breaks down, we thus expect this to be littered with problems. **Case(f):** no, see (b). WKB generally works worst for ground-states.

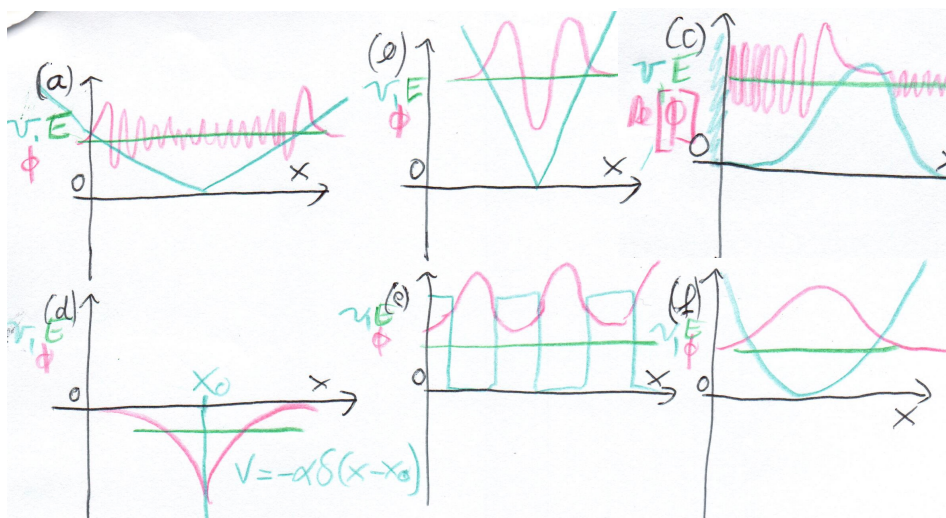


Figure 1: (**stage 2**) Potentials $V(x)$ (cyan) and energies E (green) are drawn on the same scale. Wavefunctions $\phi(x)$ are arbitrarily scaled and drawn with $\phi = 0$ on the green line (except in [d], where $\phi = 0$ is the black line).

- (iii) In Fig. 2, draw your own guess at the WKB wavefunction for the energies indicated, and discuss within your team. Take into account the given values for V , E (dimensionless units) and assume $\hbar = 1$ and importantly a mass $m = 1/320$.

Solution: See drawing in Fig. 2. To draw these we did the following: First estimate the local de Broglie wavelength near the global minimum for the lowest energy state drawing in green (which we take as having energy $E = 10$). At the minimum $p(x) = \sqrt{2mE}$ and $\lambda(x) = \hbar/p(x)$ is thus roughly $\lambda \approx 4$. Then we have drawn an oscillation with that wavelength and continued it to the turning point, while increasing the wavelength and the amplitude. After reaching the classical turning point we drew an exponential decay. We do not claim that these estimates have the correct numbers of nodes etc., but they give a reasonably qualitative idea on how the wave functions ought to look like.

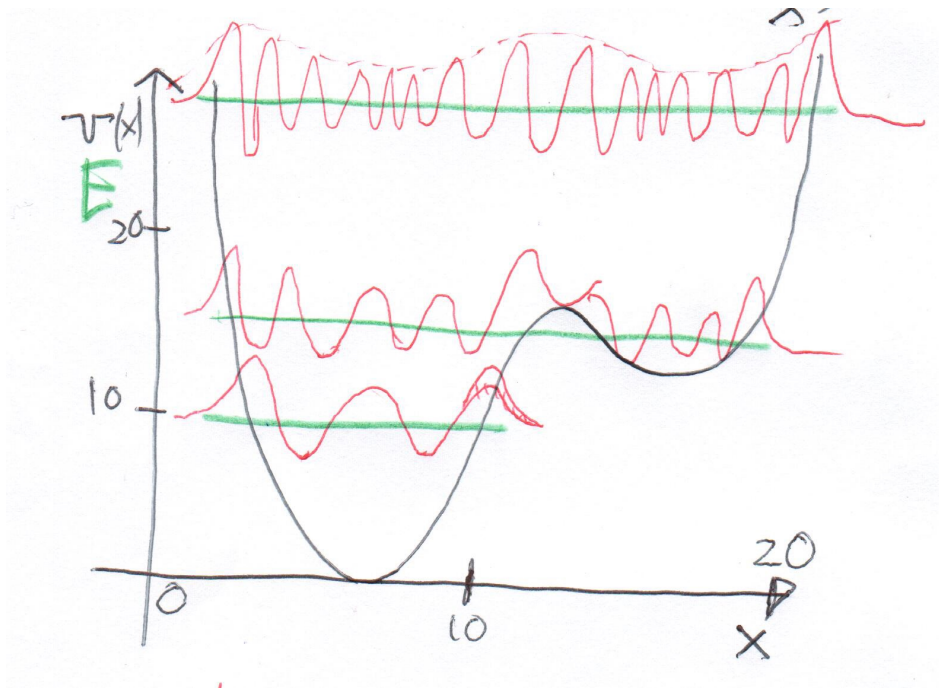


Figure 2: (**stage 2**) Rough guess at WKB approximations $\phi_{WKB}(x)$ (red) for the three energies shown in green. As usual the zero of the y-axis for the wavefunction is the green line near the wavefunction.

- (iv) With drawings and discussions, elaborate on how one arrives at the WKB connection formula Eq. (7.139) and what its uses are.

Solution: See figure on page 194 of lecture notes. While we cannot use the basic WKB idea near the classical turning point, since $\lambda(x)$ diverges there, we CAN approximate the potential as linear (thanks to its Taylor expansion), and thus use the solution of the TISE in a linear potential. We had seen in QM-I assignment 4, that the normalisable solution of this is an Airy function of the first kind. We thus patch together the WKB solution in the classically forbidden region, with the Airy function near the classical turning point, and then on the other side patch the Airy function with the WKB solution in the classically allowed region. Patching together means we adjust the free constants in the solution such that the overall wavefunction and its derivative are everywhere continuous). The formula is most important when we want to know quantised energies for bound-states.