

Introduction to Quantum Mechanics

PVK - Solutions

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1 The Wave Function and the Schrödinger Equation

1.1 Quick Checks

- (T) F $\Psi(x, t)$ has no direct physical meaning.
- T (F) According to the uncertainty principle, if σ_x is very large, then the momentum is well determined.
- T (F) Any solution of the T.I.S.E. can be normalized.
- (T) F To obtain the T.I.S.E. from the T.D.S.E., we had to assume that the potential energy function was time-independent.
- (T) F If we confine an electron inside a finite volume with $V(x) = 0$, its ground state energy can never be exactly zero.
- (T) F Stationary states have a probability density that does not change with time.
- T (F) If a particle is described by a wave packet, its energy is always well defined.
- T (F) $\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0$ arises only for unphysical solutions to the 1D SE.
- (T) F $\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0$ arises only for unphysical solutions to the 1D SE.
- T (F) It holds $\langle H^2 \rangle = (\sum_i |c_i|^2 E_i)^2$.
- (T) F It holds $\langle H^2 \rangle = (\sum_i |c_i|^2 E_i^2)$.

1.2 Exercises

1. See Final Exam 2013, Exercise 1d.
2. See Problem Set 2, Exercise 2.
3. See Problem Set 2, Exercise 4.
4. See Final Exam 2013, Exercise 4.
5. See Final Exam 2013, Exercise 1c.
6. See Extra Questions 5.

2 Formalism

2.1 Quick Checks

- T (F) The momentum operator \hat{p} is not Hermitian, since $\hat{p} \neq \hat{p}^*$.
- (T) F The Dirac Delta function is not in Hilbert space.
- T (F) The function $f(x) = \sin(x)$ is in Hilbert space.
- T (F) The function $f(x) = e^{-x} \sin(x)$ is in Hilbert space.
- (T) F The function $f(x) = e^{-x^4} \sin(x)$ is in Hilbert space.
- (T) F Every classical observable can be represented in QM by a Hermitian Operator.
- (T) F The operator $\hat{A} = \text{diag}(4, 4, 2)$ is Hermitian.
- T (F) The operator $\hat{A} = \text{diag}(4, 4, i)$ is Hermitian.
- (T) F For a free particle, the separable solutions to the SE are not in Hilbert space.

2.2 Exercises

- See Problem Set 4, Exercise 2.
- (a) Since there are three independent states we can use 3D vectors:

$$\psi_1 \rightarrow \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \psi_2 \rightarrow \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \psi_3 \rightarrow \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}.$$

The general wavefunction is then

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3$$

or

$$|\psi\rangle = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix},$$

where $|c_1|^2 + |c_2|^2 + |c_3|^2 = 1$.

- (b) For the stationary states we know that

$$\hat{H}\psi_n = E_n\psi_n.$$

Thus,

$$\hat{H} = \frac{\hbar^2\pi^2}{2ma^2} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 9 \end{bmatrix}.$$

3 Measurements

3.1 Quick Checks

- T (F) In quantum mechanics, all measurements are probabilistic.
- T (F) Two Hermitian operators always commute.
- (T) F If a particle is in a non-stationary state, the measurement of its energy must yield one of several values.
- T (F) If a quantum mechanical observable is measured, one possible result is always the expectation value of the observable.
- (T) F An uncertainty relation will exist for any two observables that have operators that do not commute.
- (T) F \hat{p}_x and \hat{p}_y are compatible observables.
- T (F) Since $\hat{V} = V(\hat{x})$ and $[\hat{x}, \hat{p}] \neq 0$, the operators \hat{p} and \hat{V} never commute.

3.2 Exercises

1. See Final Exam 2013, Exercise 3.
2. $[a_-, a_+] = 1$.
3. See Problem Set 4, Exercise 5.
4. See Extra Questions 5.
5. We need to solve

$$\frac{\partial}{\partial x} f_q = q f_q.$$

Using separation of variables we obtain

$$\int \frac{1}{f} df = \int q dx,$$

which leads to

$$f_q(x) = C \exp(qx).$$

Thus, any complex number q is eigenvalue of \hat{Q} with eigenfunction $f_q = C \exp(qx)$. Since

$$\int_{-\infty}^{+\infty} |f_q|^2 dx = \infty,$$

none of the eigenfunctions can be normalized, i.e. they are not in Hilbert space.

4 Quantum Mechanics in 3D

4.1 Quick Checks

- (T) F Given a specific shell in a hydrogenic atom, all of the subshells have the same energy.
- (T) F The orbital shapes that we know from chemistry (s, p, d , etc.) come from the solutions to the angular equation of the hydrogen atom.
- (T) F For a single-particle system with a spherically symmetric potential, the eigenfunctions of \hat{H} will involve the spherical harmonics.
- (T) F In our mathematical treatment of the hydrogen atom, the potential energy function only affected the radial equation.
- T (F) Each spin eigenstate can be represented as a two-dimensional vector.
- (T) F For an atom with two electrons we can solve the TISE exactly (using separation of variables) if we ignore the interaction between the particles.
- T (F) For an one-electron atom with the potential $V(r, t) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \cos(\omega t)$ we can solve the TISE exactly.
- T (F) For an electron, the value of s can be $\pm\frac{1}{2}$.
- (T) F \hat{L}_x and \hat{L}^2 are compatible observables .
- T (F) The electron has a spin angular momentum because it is rotating in space.
- T (F) If we excite an electron in a hydrogen atom, we can change both its s and l .
- T (F) If we state that the spin of an electron is “up” with respect to the z axis, this means its spin-angular-momentum vector is pointing parallel to the z axis.
- T (F) An electron cannot be both “spin up” and “spin down”.

4.2 Exercises

- See Final Exam 2013, Exercise 1b.
- See Problem Set 7, Exercise 1.
- See Problem Set 7, Exercise 5.
- (a) Since $\hat{L}_z Y_l^{m_l} = \hbar m_l Y_l^{m_l}$ the possible values are $-2\hbar, -\hbar, 0, \hbar, 2\hbar$. The expectation of L_z is

$$\langle L_z \rangle = \frac{2}{7}\hbar + \frac{2}{7}(-\hbar) + \frac{1}{14}0 + \frac{1}{14}(-2\hbar - \hbar + 0 + \hbar + 2\hbar) = 0.$$

(b) Since $\hat{L}^2 Y_l^{m_l} = \hbar^2 l(l+1) Y_l^{m_l}$ the possible values are $0, 2\hbar^2, 6\hbar^2$. The expectation of L_z is

$$\langle L^2 \rangle = \frac{2}{7}2\hbar^2 + \frac{2}{7}2\hbar^2 + \frac{1}{14}0 + \frac{1}{14}(6\hbar^2 + 6\hbar^2 + 6\hbar^2 + 6\hbar^2 + 6\hbar^2) = \frac{16 + 0 + 30}{14}\hbar^2 = \frac{46}{14}\hbar^2.$$
- See Problem Set 7, Exercise 2.

5 Systems with Multiple Particles

5.1 Quick Checks

Circle True or False.

- T F In a multielectron atom with two electrons in 2p orbital the possible values of L are 0, 1, 2.
- T F Given a system of two identical particles, the exchange operator \hat{P} always commute with the Hamiltonian operator \hat{H} .
- T F The Pauli exclusion principle applies to both fermions and bosons.
- T F In quantum mechanics, an electron and proton are always distinguishable.
- T F Quantum mechanics allows us to determine the length of the orbital angular momentum vector.
- T F The Pauli's principle applies to particles with $s = \frac{3}{2}$.
- T F The electron configuration of an atom (e.g. $1s^2 2s^2 2p^2$) is enough information to describe its exact energy.
- T F In multielectron atoms, the $3p$ orbitals are lower in energy than the $4s$ orbitals.
- T F In multielectron atoms, the $3d$ orbitals are lower in energy than the $4s$ orbitals.
- T F It is possible to have the following term symbol for a multielectron atomic state: 1D_1 .
- T F The term symbol for $J = 2, L = 1$, and $S = 1$ is 1D_1 .
- T F For multielectron atoms, the energy of the single-particle states only depends on n .

5.2 Exercises

- (a)
 - $n = 3, l = 2, m_l = 1, m_s = 0$.
 - $n = 2, l = 0, m_l = 0, m_s = -1/2$.
 - $n = 7, l = 2, m_l = -2, m_s = 1/2$.
 - $n = 3, l = -3, m_l = -2, m_s = -1/2$.
 - $n = 0, l = 0, m_l = 0, m_s = 1/2$.
 (b) See Problem Set 9, Exercise 1b.
2. See Problem Set 9, Exercise 1c.
3. See Final Exam 2013, Exercise 2b.
4. See Final Exam 2013, Exercise 2c and Exercise 2d.
5. (a) In the box ($0 \leq x \leq a$) the Hamiltonian reads

$$\hat{H} = -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|x_1 - x_2|} + \frac{1}{|x_2 - x_3|} + \frac{1}{|x_1 - x_3|} \right),$$

where m_e denotes the mass of the electron. Outside of the box the potential is infinity.

(b) The simplified Hamiltonian reads

$$\hat{H} = -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right).$$

(c) Due to Pauli's Principle the two electrons will have $n = 1$ and one electron $n = 2$. Thus, the ground state energy is

$$E_0 = \frac{\hbar^2 \pi^2}{2m_e a^2} + \frac{\hbar^2 \pi^2}{2m_e a^2} + \frac{2^2 \hbar^2 \pi^2}{2m_e a^2} = \frac{6\hbar^2 \pi^2}{2m_e a^2}.$$

Remark. Since the electrons do not interact the TISE can be separated. By doing that, we obtain the classic 1D harmonic oscillator with one electron. The wave function is then the multiplication of the three wave function and the energy is the sum of the three energies.

(d) The Pauli's principle does not applies to electrons and proton (since they are distinguishable). Thus, the proton will be in $n = 1$. The ground state energy is

$$E_0 = \frac{6\hbar^2 \pi^2}{2m_e a^2} + \frac{\hbar^2 \pi^2}{2m_p a^2} = \frac{7\hbar^2 \pi^2}{2m_e a^2}.$$

(e) The fourth electron will have $n = 2$. Thus,

$$E_0 = \frac{6\hbar^2 \pi^2}{2m_e a^2} + \frac{2^2 \hbar^2 \pi^2}{2m_p a^2} = \frac{6\hbar^2 \pi^2}{2m_e a^2} + \frac{4\hbar^2 \pi^2}{2m_p a^2},$$

where m_p denotes the mass of the proton.

6. (a) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1| + |\vec{r}_2| + 1$ is symmetric;
 (b) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1| + 2|\vec{r}_2|$ is neither symmetric nor antisymmetric;
 (c) $f(\vec{r}_1, \vec{r}_2) = -|\vec{r}_1| + |\vec{r}_2| + 1$ is neither symmetric nor antisymmetric;
 (d) $f(\vec{r}_1, \vec{r}_2) = -|\vec{r}_1| + |\vec{r}_2|$ is antisymmetric;
 (e) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1|^2 + |\vec{r}_2|^3$ is neither symmetric nor antisymmetric;
 (f) $f(\vec{r}_1, \vec{r}_2) = (|\vec{r}_1| - |\vec{r}_2|)^2$ is symmetric;
 (g) $f(\vec{r}_1, \vec{r}_2) = \sin(|\vec{r}_1| - |\vec{r}_2|)$ is antisymmetric.

6 Solids

6.1 Quick Checks

Circle True or False.

- T F Electronic bands exist in semiconductor and insulators, but not metals.
- F In metals at $T = 0\text{K}$, the electronic states are filled up to the Fermi level.
- F Doping is used to enhance the conductivity of solids.
- F If we add more electrons to a crystalline metallic solid, such that additional electronic states are occupied, the Fermi energy rises.
- F Bloch's theorem applies to systems that have a potential-energy function that is periodic in space.
- F The electronic density of states at the Fermi energy affects the ability of a solid to conduct electricity.
- T F Semiconductors have band gaps, but insulators do not.
- T F Bloch's theorem states that the wave function in a solid is the same for each atom in the solid.

6.2 Exercises

1. See Problem Set 10, Exercise 2.
2. See Problem Set 10, Exercise 5.

7 Approximate Methods

7.1 Quick Checks

- T (F) The variational principle can be used to estimate the ground state wave function.
- T (F) Perturbation theory is mostly concerned with the calculation of the ground state energy.
- (T) F To get a good solution with the variational principle, we should make a good guess at a trial and add many adjustable parameters.
- T (F) The variational principle allows one to minimize the ground state energy by varying \hat{H}' .
- T (F) If your trial function has many adjustable parameters, the variational principle guarantees the exact ground state energy.
- T (F) Perturbation theory assumes non-degenerate states.
- (T) F The ground state energy is lower-bounded by the minimum of the potential energy V_{\min} .
- T (F) Any function can be used as trial function for the variational principle.
- (T) F In general, the accuracy of perturbation theory increases as the “strength” of the perturbation decreases.
- T (F) Perturbation theory is an alternative way to find the exact solution to the TISE.

7.2 Exercises

1. See Final Exam 2013, Exercise 5.
2. See Problem Set 11, Exercise 2.
3. See Problem Set 11, Exercise 3.