

Emilio d'Emilio Luigi E. Picasso

Problems in Quantum Mechanics

with solutions

We present here, for promotional purposes, an excerpt of the book consisting of one problem from each chapter and the corresponding solution. The choice of the problems does not obey any particular criterion: they should only provide the reader with an idea of the style and the characteristics of the book. Obviously, both the problems and the solutions will gain in clarity within the context of the entire book due, for instance, to reference – even not explicit – to preceding problems.

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Contents

1 Classical Systems

Atomic models; radiation; Rutherford scattering; specific heats; normal modes of vibration.

Problems	1
Solutions	5

2 Old Quantum Theory

Spectroscopy and fundamental constants; Compton effect; Bohr–Sommerfeld quantization; specific heats; de Broglie waves.

Problems	13
Solutions	20

3 Waves and Corpuscles

Interference and diffraction with single particles; polarization of photons; Malus' law; uncertainty relations.

Problems	29
Solutions	37

4 States, Measurements and Probabilities

Superposition principle; observables; statistical mixtures; commutation relations.

Problems	47
Solutions	53

5 Representations

Representations; unitary transformations; von Neumann theorem; coherent states; Schrödinger and momentum representations; degeneracy theorem.

Problems	63
Solutions	74

6 One-Dimensional Systems

Nondegeneracy theorem; variational method; rectangular potentials; transfer matrix and S -matrix; delta potentials; superpotential; completeness.

Problems	93
Solutions	107

7 Time Evolution

Time evolution in the Schrödinger and Heisenberg pictures; classical limit; time reversal; interaction picture; sudden and adiabatic approximations.

Problems	139
Solutions	149

8 Angular Momentum

Orbital angular momentum: states with $l = 1$ and representations; rotation operators; spherical harmonics; tensors and states with definite angular momentum ($l = 1, l = 2$).

Problems	167
Solutions	173

9 Changes of Frame

Wigner's theorem; active and passive point of view; reference frame: translated, rotated; in uniform motion; in free fall, rotating.

Problems	185
Solutions	190

10 Two and Three-Dimensional Systems

Separation of variables; degeneracy theorem; group of invariance of the two-dimensional isotropic oscillator.

Problems	199
Solutions	204

11 Particle in Central Field

Schrödinger equation with radial potentials in two and three dimensions; vibrational and rotational energy levels of diatomic molecules.

Problems	213
Solutions	219

12 Perturbations to Energy Levels

Perturbations in one-dimensional systems; Bender–Wu method for the anharmonic oscillator; Feynman–Hellmann and virial theorems; “no-crossing theorem”; external and internal perturbations in hydrogen-like ions.

Problems	231
Solutions	243

13 Spin and Magnetic Field

Spin $\frac{1}{2}$; Stern and Gerlach apparatus; spin rotations; minimal interaction; Landau levels; Aharonov–Bohm effect.

Problems	263
Solutions	272

14 Electromagnetic Transitions

Coherent and incoherent radiation; photoelectric effect; transitions in dipole approximation; angular distribution and polarization of the emitted radiation; life times.

Problems	283
Solutions	291

15 Composite Systems and Identical Particles

Rotational energy levels of polyatomic molecules; entangled states and density matrices; singlet and triplet states; composition of angular momenta; quantum fluctuations; EPR paradox; quantum teleportation.

Problems	301
Solutions	309

16 Applications to Atomic Physics

Perturbations on the fine structure energy levels of the hydrogen atom; electronic configurations and spectral terms; fine structure; Stark and Zeeman effects; intercombination lines.

Problems	323
Solutions	333

Appendix A Physical Constants	347
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Appendix B Useful Formulae	349
---	------------

Index	351
--------------------	------------

Preface

This book stems from the experience the authors acquired by teaching Quantum Mechanics over more than two decades.

The necessity of providing students with abundant and understandable didactic material – i.e. exercises and problems good for testing “in real time” and day by day their comprehension and mastery of the subject – confronted the authors with the necessity of adapting and reformulating the vast number of problems available from the final examinations given in previous years. Indeed those problems, precisely because they were formulated as final exam problems, were written in a language appropriate for the student who is already a good step ahead in his preparation, not for the student that, instead, is still in the “middle of the thing”.

Imagining that the above necessity might be common to colleagues from other Departments and prompted also by the definite shortage, in the literature, of books written with this intent, we initially selected and ordered the 242 problems presented here by sticking to the presentation of Quantum Mechanics given in the textbook “Lezioni di Meccanica Quantistica” (ETS, Pisa, 2000) by one of us (LEP).

Over time, however, our objective drifted to become making the present collection of problems more and more autonomous and independent of any textbook. It is for this reason that certain technical subjects – as e.g. the variational method, the virial theorem, selection rules etc. – are exposed in the form of problems and subsequently taken advantage of in more standard problems devoted to applications.

The present edition – the first in English – has the advantage over the Italian one [“Problemi di Meccanica Quantistica” (ETS, Pisa 2003, 2009)] that all the material has by now been exhaustively checked by many of our students, which has enabled us to improve the presentation in several aspects.

A comment about the number of proposed problems: it may seem huge to the average student: almost certainly not all of them are necessary to have a satisfactory insight into Quantum Mechanics. However it may happen – particularly to the student who will take further steps towards becoming a

professional physicist – that he or she will have to come back, look at, and even learn again certain things ... well, we do not hide our intent: this book should not be just for passing exams but, possibly, for life.

Here are a few further comments addressed to students who decide to go through the book. Firstly, some of the problems (also according to our students) are easy, standard, and just recall basic notions learned during the lectures. Others are not so. Some of them are definitely difficult and complex, mainly for their conceptual structure. However, we had to put them there, because they usually face (and we hope clarify) questions that are either of outstanding importance or rarely treated in primers. The student should nonetheless try them using all his or her skill, and not feel frustrated if he or she cannot completely solve them. In the latter case the solution can be studied as a part of a textbook: the student will anyhow learn something new. Second, despite our effort, it may happen (seldom, we hope) that a symbol used in the text has not been defined in the immediately previous lines: it can be found in the Appendices. Our claim also is that all the problems can be solved by simple elementary algebra: the more complicated, analytic part of the calculation – when present – should take advantage of the proposed suggestions (e.g. any awkward, or even elementary, integral supposed to appear in the solution is given in the text) and should be performed in such a way as to reduce all the formulae to those given in the Appendices.

A last comment concerns the way numerical calculations are organized, particularly in the first chapters. We have written dimensionless numbers as the ratio of known quantities, e.g. two energies, two masses ... (so that a better dimensional control of what is being written is possible at a glance and at any step of the calculation – a habit the student should try hard to develop) and we have used the numerical values of these known quantities given in Appendix A: this is quicker and safer than resorting to the values of the fundamental constants.

Among the many persons – students, colleagues, families – who helped us over years in this work, three played a distinguished role. We are thankful to Pietro Menotti, maybe the only one of our colleagues with a more long-lasting didactic experience of the subject, for the very many comments and suggestions and for having been for one of us (EdE) a solid reference point along the twenty years of our didactic collaboration. Stephen Huggett helped us with our poor English. Bartolome Alles Salom, in addition to having gone through the whole book with an admirable painstaking patience, has a major responsibility for the appearance of the present English edition, having driven and convinced us with his enthusiasm to undertake this job.

Of course all that could have (and has not yet) been improved is the authors' entire responsibility.

Pisa, May 2011

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1.1 According to the model proposed by J.J. Thomson at the beginning of the 20th century, the atom consists of a positive charge Ze (Z is the atomic number) uniformly distributed inside a sphere of radius R , within which Z pointlike electrons can move.

- a) Calculate R for the hydrogen atom ($Z = 1$) from the ionization energy $E_I = 13.6 \text{ eV}$ (that is, the minimum work necessary to take the electron from its equilibrium position to infinity).
- b) If the electron is not in its equilibrium position, it performs harmonic oscillations within the sphere. Find the value of the period. Assuming it emits radiation with the same frequency, find the wavelength λ of the emitted radiation and say in which region of the electromagnetic spectrum it falls. (For visible radiation $3900 \text{ \AA} \leq \lambda \leq 7500 \text{ \AA}$, $1 \text{ \AA} = 10^{-8} \text{ cm}$.)
- c) Determine the polarization of the radiation observed in the direction of the unit vector \hat{n} if:
 - i) the electron oscillates in the direction of the z axis;
 - ii) the electron moves in a circular orbit in the plane $z = 0$.

1.1

- a) Inside a uniformly charged sphere, whose total charge is Ze , the electric field and the potential ($\varphi(\infty) = 0$) are:

$$\vec{E} = \frac{Ze}{R^3} \vec{r}, \quad \varphi = -\frac{Ze r^2}{2R^3} + \frac{3Ze}{2R}, \quad r \leq R.$$

The equilibrium position for the electron is the centre of the sphere, which is a position of stable equilibrium for negative charges; the minimum work to take the electron at infinity is $-(-e)\varphi(0)$, therefore:

$$\frac{3}{2} \frac{e^2}{R} = 13.6 \text{ eV} = 2.2 \times 10^{-11} \text{ erg} \quad \Rightarrow \quad R = 1.6 \times 10^{-8} \text{ cm} = 1.6 \text{ \AA}.$$

- b) The restoring force is harmonic, its angular frequency is $\omega = \sqrt{e^2/m_e R^3}$. Then, rewriting ω as $(c/R) \times \sqrt{r_e/R}$, ($r_e \equiv e^2/m_e c^2$ is the classical electron radius) one has:

$$T = \frac{2\pi}{\omega} = 2\pi \times \sqrt{\frac{R}{r_e}} \times \left(\frac{R}{c}\right) = 8 \times 10^{-16} \text{ s}$$

and the wavelength of the emitted radiation is $\lambda = cT = 2.4 \times 10^{-5} \text{ cm} \simeq 2400 \text{ \AA}$, in the ultraviolet region.

- c) In the dipole approximation, if $\vec{d}(t)$ stands for the dipole moment of the sources and $\ddot{\vec{d}}(t) = -\omega^2 \vec{d}(t)$ (harmonic oscillator), at large distances in the direction of the unit vector \hat{n} one has:

$$\vec{E}(\vec{r}, t) = \frac{\omega^2}{rc} (\vec{d} - (\vec{d} \cdot \hat{n}) \hat{n}), \quad \vec{d} \equiv \vec{d}(t - r/c)$$

and the polarization is given by the trajectory of the vector

$$\vec{e}(t) = \vec{d} - (\vec{d} \cdot \hat{n}) \hat{n}$$

which is the projection of the vector $\vec{d}(t)$ onto the plane orthogonal to the direction of observation \hat{n} . So, if $\vec{d} \parallel \hat{z}$, in every direction \hat{n} different from the direction of the z axis (where the electric field is vanishing), the radiation is linearly polarized in the plane containing \hat{n} and the z axis and is orthogonal to \hat{n} ; if the electron follows a circular trajectory in the $z = 0$ plane, the projection of the orbit onto the plane orthogonal to \hat{n} is an ellipse; the latter may degenerate into a segment, if the orbit is projected onto a plane orthogonal to the orbit itself, or may be a circumference, if the orbit is projected onto a plane parallel to it. In summary, the polarization is linear in all directions orthogonal to the z axis, circular in the z direction, elliptic in the remaining cases.

2.7 When a system with several degrees of freedom enjoys the possibility of the *separation of variables* – i.e. there exists a choice of q 's and p 's such that the Hamiltonian takes the form $H = H_1(q_1, p_1) + H_2(q_2, p_2) \cdots$ – it is possible to use the Bohr–Sommerfeld quantization rules $\oint p_i dq_i = n_i h$ for all $i = 1, \cdots$ relative to the individual degrees of freedom.

- a) Find the energy levels $E(n_1, n_2, n_3)$ of an *anisotropic* three-dimensional harmonic oscillator. Exploit the fact that its Hamiltonian can be written in the form:

$$H = \frac{p_1^2}{2m} + \frac{1}{2}m\omega_1^2 q_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}m\omega_2^2 q_2^2 + \frac{p_3^2}{2m} + \frac{1}{2}m\omega_3^2 q_3^2.$$

Consider now an *isotropic* three-dimensional harmonic oscillator. The number of states corresponding to a given energy level $E_n = n \hbar \omega$ (the “degeneracy” of the level) is the number of ways the three quantum numbers n_1, n_2, n_3 can be chosen such that $E(n_1, n_2, n_3) = E_n$.

- b) Compute the degeneracy of the energy levels for an isotropic three-dimensional harmonic oscillator and the number of states with energy $E \leq E_n$.
- c) Find the energy levels of a particle confined in a rectangular box with edges of lengths a, b, c .
- d) Still referring to the particle in the rectangular box (of volume $V = abc$), compute the number of states enclosed in the phase space volume:

$$V \times \left[(|p_1| \leq p_{n_1}) \times (|p_2| \leq p_{n_2}) \times (|p_3| \leq p_{n_3}) \right]; \quad p_{n_1} = \frac{n_1 h}{2a}, \quad \text{etc.}$$

and show that, just as in Problem 2.6, the volume-per-state is h^3 .

2.7

- a) As the Hamiltonian H is a separate variables one: $H = H_1 + H_2 + H_3$, its energy levels are:

$$E(n_1, n_2, n_3) = n_1 \hbar \omega_1 + n_2 \hbar \omega_2 + n_3 \hbar \omega_3 .$$

- b) In the case of an isotropic oscillator $\omega_1 = \omega_2 = \omega_3 \equiv \omega$ and

$$E(n_1, n_2, n_3) = (n_1 + n_2 + n_3) \hbar \omega \equiv n \hbar \omega , \quad n = n_1 + n_2 + n_3 .$$

Choosing $n_1 = n - k$, ($k = 0, \dots, n$), n_2 and n_3 may be chosen in $k + 1$ ways: $n_2 = k$, $n_3 = 0$; $n_2 = k - 1$, $n_3 = 1$; \dots $n_2 = 0$, $n_3 = k$. So the degeneracy of the level E_n is

$$g_n = \sum_0^n (k + 1) = \frac{(n + 1)(n + 2)}{2}$$

and the number of states with energy $E \leq E_n$ is

$$\begin{aligned} \sum_0^n g_k &= \frac{1}{2} \sum_0^n (k^2 + 3k + 2) = \\ &= \frac{1}{2} \left(\frac{n(n + 1)(2n + 1)}{6} + 3 \frac{n(n + 1)}{2} + 2(n + 1) \right) = \frac{(n + 1)(n + 2)(n + 3)}{6} . \end{aligned}$$

Compare this result – that will be confirmed by quantum mechanics – with what has been found in question d) of Problem 2.6.

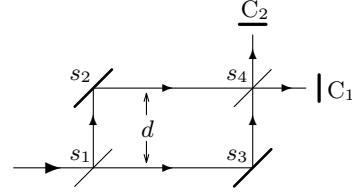
- c) Also in the case of a particle in a box the Hamiltonian is a separate variables one: $H = p_1^2/2m + p_2^2/2m + p_3^2/2m$, therefore:

$$E(n_1, n_2, n_3) = \frac{n_1^2 h^2}{8ma^2} + \frac{n_2^2 h^2}{8mb^2} + \frac{n_3^2 h^2}{8mc^2} = \frac{h^2}{8m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) .$$

- d) Due to $p_{n_1} = n_1 h/2a$, $p_{n_2} = n_2 h/2b$, etc. the required volume is given by $V \times 2^3 p_{n_1} p_{n_2} p_{n_3} = n_1 n_2 n_3 h^3$ and, since the number of states with quantum numbers less or equal to n_1, n_2, n_3 is $n_1 n_2 n_3$, the result follows.

3.4 The Bonse–Hart interferometer for neutrons is similar to the Mach–Zehnder interferometer for light (the mirrors are silicon crystals by which neutrons are reflected à la Bragg).

Neutrons (mass $m_n = 1.7 \times 10^{-24}$ g), whose de Broglie wavelength is $\lambda = 1.4 \text{ \AA}$, are sent horizontally in a Bonse–Hart interferometer positioned in such a way that their paths are in a vertical plane. The difference in height between the paths $s_2 \rightarrow s_4$ and $s_1 \rightarrow s_3$ is d (see figure). Assume the propagation of the neutrons between the mirrors is rectilinear.



- Let $k \equiv 2\pi/\lambda$ be the neutron wavenumber and g the gravitational acceleration. Neglecting terms of order g^2 , calculate the difference $\Delta k \equiv k - k'$ between the wavenumbers in the paths $s_1 \rightarrow s_3$ and $s_2 \rightarrow s_4$ due to the difference in potential energy.
- Assume the paths $s_1 \rightarrow s_3$ and $s_2 \rightarrow s_4$ both have length L and that also the paths $s_1 \rightarrow s_2$ and $s_3 \rightarrow s_4$ are identical. Calculate the phase difference φ between the de Broglie waves that arrive at s_4 via the ‘low’ path ($s_1 \rightarrow s_3 \rightarrow s_4$) and via the ‘high’ path ($s_1 \rightarrow s_2 \rightarrow s_4$). Calculate φ when $d = 3 \text{ cm}$, $L = 7 \text{ cm}$.

The interferometer is rotated around the direction of the incident beam (the direction $s_1 \rightarrow s_3$) in such a way that the difference in height between the paths $s_2 \rightarrow s_4$ and $s_1 \rightarrow s_3$ is varied.

- Calculate the number of maxima in the countings at C_1 (‘number of fringes’) for a rotation from -30° to $+30^\circ$ with respect to the vertical plane.

3.4

- a) If p is the momentum of the incident neutrons and p' is the momentum at height d , one has:

$$\frac{p^2}{2m_n} = \frac{p'^2}{2m_n} + m_n g d \quad \Rightarrow \quad p - p' \simeq \frac{m_n^2 g d}{p}$$

and, using the Broglie relation $p = h/\lambda = \hbar k$, one obtains $\Delta k \simeq \frac{m_n^2 g d}{\hbar^2 k}$.

- b) $\varphi = kL - k'L = \Delta k \times L = \frac{m_n^2 g d L}{\hbar^2 k} = \frac{2\pi \lambda m_n^2 g A}{h^2} = 120 \text{ radians}$

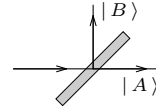
$A = d \times L$ is the area enclosed by $s_1 \rightarrow s_2 \rightarrow s_4 \rightarrow s_3 \rightarrow s_1$.

Indeed, to the first order in g , the result does not depend on the shape of the circuit $s_1 \rightarrow s_2 \rightarrow s_4 \rightarrow s_3 \rightarrow s_1$, but only on the enclosed area, as can be shown by observing that $\varphi = \hbar^{-1} \oint \vec{p} \cdot d\vec{q}$ and by using Stokes theorem: since only the horizontal parts of the circuit are relevant, we can define the vector field $\vec{p}(x, z)$ as $p_x(x, z) = (p^2 - 2m_n^2 g z)^{1/2}$, $p_z(x, z) = 0$. Then, paying attention to the sign of the circulation,

$$-(\text{curl } \vec{p})_y = -\frac{\partial p_x}{\partial z} = \frac{m_n^2 g}{\sqrt{p^2 - 2m_n^2 g z}} = \frac{m_n^2 g}{p} + O(g^2).$$

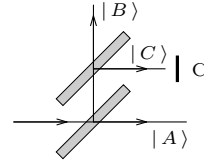
- c) Let θ denote the angle by which the interferometer is rotated with respect to the vertical plane: one has $A \rightarrow A \cos \theta$, then $\varphi \rightarrow \varphi \cos \theta$. In the range $-30^\circ \leq \theta \leq +30^\circ$ the phase φ varies from $120 \times \cos 30^\circ = 104$ to 120 and then again to 104: so there is an excursion of 32 radians and one observes $32/2\pi \simeq 5$ maxima ('fringes'). The result has been confirmed by several experiments performed between 1975 and 1987.

4.10 A photon crosses a semi-transparent mirror, whose reflection and transmission coefficients are equal. Let $|A\rangle$ represent the transmitted state, $|B\rangle$ the reflected state, $\langle A|A\rangle = 1$, $\langle B|B\rangle = 1$, $\langle A|B\rangle = 0$ (see figure).



- Say whether the state of the emerging photon is described either by the pure state $\frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$ or by the statistical mixture $\{|A\rangle, \frac{1}{2}; |B\rangle, \frac{1}{2}\}$.
- If a counter C, whose efficiency is 100%, is placed in the path of the reflected state, what is the state of the emerging photon in those cases when the counter does not reveal the photon?

Let us now consider the device consisting of two semi-transparent mirrors and the counter C as in the figure to the right.



- Write the state of a photon that emerges from the device when the counter does not click.

4.10

- a) The state of the emerging photon is a pure state. Indeed, it is possible to recombine the reflected component with the transmitted one in such a way as they can interfere (this is not possible when the state is a statistical mixture): it is sufficient to add two reflecting mirrors and a semi-transparent mirror to build up the Mach-Zehnder interferometer (see Problem 3.1).
- b) The fact that the counter C does not record the arrival of the photon is, in any event, the result of a measurement: the measurement of the observable that gives “yes or no” as answer (dichotomic variable). Owing to the measurement postulate, the state is $|A\rangle$.
- c) The state of the photon just before reaching the counter is

$$|X\rangle = \frac{1}{\sqrt{2}}|A\rangle + \frac{1}{2}|B\rangle + \frac{1}{2}|C\rangle.$$

Then, if the counter C does not record the arrival of the photon (answer ‘no’), the state after the measurement is the projection of $|X\rangle$ onto the space orthogonal to $|C\rangle$, that is (N is the normalization factor)

$$N\left(\frac{1}{\sqrt{2}}|A\rangle + \frac{1}{2}|B\rangle\right) = \sqrt{\frac{2}{3}}|A\rangle + \sqrt{\frac{1}{3}}|B\rangle.$$

Applying the measurement postulate only to the part of the state reflected by the first mirror is wrong: in this case one would be led to the conclusion that $\frac{1}{2}(|B\rangle + |C\rangle) \rightarrow \frac{1}{\sqrt{2}}|B\rangle$ and that the state after the measurement should be $\frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$. If the latter conclusion were correct, one should observe, after letting many photons in the device, that equal numbers of photons emerge in the states $|A\rangle$ and $|B\rangle$. It is instead evident that 50% emerge in the state $|A\rangle$, 25% in the state $|B\rangle$ and 25% in the state $|C\rangle$.

5.19 A particle in one dimension is in the state:

$$|A\rangle = |A_0\rangle + e^{i\varphi} U(a) |A_0\rangle$$

where $U(a) = e^{-ip a/\hbar}$ is the translation operator and $|A_0\rangle$ is the state with wavefunction $\psi_0(x) = (2\pi\Delta^2)^{-1/4} e^{-x^2/4\Delta^2}$, $\langle A_0 | A_0 \rangle = 1$.

- a) What condition must a and Δ satisfy in order that $\langle A_0 | U(a) | A_0 \rangle$ be negligible? Calculate $\langle A_0 | U(a) | A_0 \rangle$ for $a = 10\Delta$.

From now on we shall assume that $\langle A_0 | U(a) | A_0 \rangle$ is negligible.

- b) Determine the probability density $\rho(x)$ for the position of the particle. Within the approximation $\langle A_0 | U(a) | A_0 \rangle \simeq 0$, is it possible to determine the phase φ by means of position measurements?
- c) Determine the probability density $\tilde{\rho}(k)$ for the momentum of the particle.
- d) Say what is the required precision for momentum measurements in order to distinguish the state $|A\rangle$ from the statistical mixture

$$\{|A_0\rangle, \nu_1 = \tfrac{1}{2}; U(a)|A_0\rangle, \nu_2 = \tfrac{1}{2}\}.$$

5.19

- a) As $\psi_0(x)$ is a Gaussian function appreciably different from zero in a region whose amplitude is 4Δ and the wavefunction of $U(a)|A_0\rangle$ is $\psi_0(x-a)$, $|A_0\rangle$ and $U(a)|A_0\rangle$ are practically orthogonal if $a \gg \Delta$. If $a = 10\Delta$ one has:

$$\begin{aligned}\langle A_0 | U(a) | A_0 \rangle &= \frac{1}{\sqrt{2\pi}\Delta} \int_{-\infty}^{+\infty} e^{-x^2/4\Delta^2} e^{-(x-a)^2/4\Delta^2} dx \\ &= \frac{1}{\sqrt{2\pi}\Delta} \int_{-\infty}^{+\infty} e^{-(x+a/2)^2/4\Delta^2} e^{-(x-a/2)^2/4\Delta^2} dx = e^{-a^2/8\Delta^2} \simeq 4 \times 10^{-6}.\end{aligned}$$

- b) The normalized state $|A\rangle$, in the approximation $\langle A_0 | U(a) | A_0 \rangle \simeq 0$, is

$$\frac{1}{\sqrt{2}}(|A_0\rangle + e^{i\varphi} U(a)|A_0\rangle) \xrightarrow{\text{SR}} \frac{1}{(8\pi\Delta^2)^{1/4}} (e^{-x^2/4\Delta^2} + e^{i\varphi} e^{-(x-a)^2/4\Delta^2})$$

(the approximation concerns the normalization coefficient). Taking into account that the product of $\psi_0(x)$ and $\psi_0(x-a)$ is negligible,

$$\rho(x) = \frac{1}{\sqrt{8\pi\Delta^2}} (e^{-x^2/2\Delta^2} + e^{-(x-a)^2/2\Delta^2}).$$

Since φ does not appear in the expression of $\rho(x)$, it is not possible to determine it by means of position measurements.

- c) In the momentum representation (see Problem 5.14):

$$|A_0\rangle \rightarrow \varphi_0(k) = \left(\frac{2\Delta^2}{\pi\hbar^2}\right)^{1/4} e^{-k^2\Delta^2/\hbar^2}; \quad U(a)|A_0\rangle = e^{-ip a/\hbar} |A_0\rangle \Rightarrow$$

$$\varphi_A(k) = \frac{1}{\sqrt{2}} \left(\frac{2\Delta^2}{\pi\hbar^2}\right)^{1/4} e^{-k^2\Delta^2/\hbar^2} (1 + e^{i\varphi} e^{-ik a/\hbar}) \Rightarrow$$

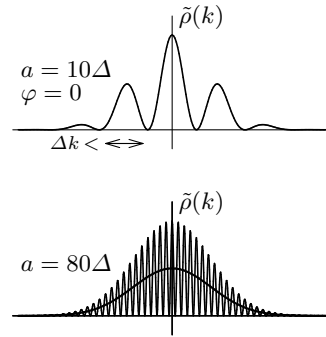
$$\tilde{\rho}(k) = \sqrt{\frac{2\Delta^2}{\pi\hbar^2}} e^{-2k^2\Delta^2/\hbar^2} (1 + \cos(ka/\hbar - \varphi)).$$

- d) In order to distinguish the state $|A\rangle$ from the statistical mixture:

$$\{|A_0\rangle, \nu_1 = \frac{1}{2}; U(a)|A_0\rangle, \nu_2 = \frac{1}{2}\}$$

it is necessary that the momentum measurements one performs be able to reveal the interference term $\cos(ka/\hbar - \varphi)$ that, on a period $2\pi\hbar/a$, has a vanishing average. Therefore the precision must be $\Delta k < 2\pi\hbar/a = h/a$ (see the figure). Note that $\tilde{\rho}(k)$ (not by any chance!) coincides with the interference pattern generated by two

‘Gaussian’ slits of width $\simeq \Delta$ separated by a distance a : if $a \gg \Delta$, the fringes are too close to each other and if the resolving power of the device that measures the momentum is not sufficiently high, only the average intensity is observed, i.e. the thick curve in the second figure.



6.6 It is known that a particle in one dimension subject to a rectangular potential well of depth V_0 and width $2a$ admits as many bound states as the least integer greater or equal to $\sqrt{2m V_0 a^2 / \hbar^2} / (\pi/2) = \sqrt{8m V_0 a^2 / \pi^2 \hbar^2}$. By exploiting the results of Problem 6.5:

- a) Find the minimum number n_b of bound states that the following potentials admit:

$$V(x) = -3 \frac{\hbar^2}{m b^2} e^{-x^2/b^2}; \quad V(x) = -4 \frac{\hbar^2}{m b^2} e^{-x^2/b^2}.$$

- b) Find the value of λ such that the potential:

$$V(x) = -\frac{\lambda}{x^2 + b^2}, \quad \lambda > 0$$

admits at least N bound states.

- c) Find the number of bound states admitted by the potential:

$$V(x) = -\frac{\lambda}{|x| + b}, \quad \lambda > 0, \quad b > 0.$$

6.6

- a) The potential well of width $2a$ inscribed in the Gaussian potential $V(x) = -\lambda e^{-x^2/b^2}$ has the depth $V_0 = \lambda e^{-a^2/b^2}$. In order to obtain the best estimate, we must determine a in such a way that $V_0 a^2$ be a maximum: this happens for $a = b$: so $V_0 a^2 = \lambda b^2/e$. The number of bound states of the potential well with $\lambda = 3\hbar^2/m b^2$ is the minimum integer greater or equal to:

$$\sqrt{(8m/\pi^2\hbar^2) \times (3\hbar^2/m b^2) b^2/e} = \sqrt{24/(\pi^2 \times e)} = 0.95 \Rightarrow n_b \geq 1.$$

Likewise, if $\lambda = 4\hbar^2/m b^2$,

$$\sqrt{(8m/\pi^2\hbar^2) \times (4\hbar^2/m b^2) b^2/e} = \sqrt{32/(\pi^2 \times e)} = 1.09 \Rightarrow n_b \geq 2.$$

- b) As in point a) above, one must determine the maximum of the function $a^2|V(a)| = \lambda a^2/(a^2 + b^2)$: this function attains its maximum – equal to λ – for $a = \infty$, so it must happen that:

$$\frac{8m\lambda}{\pi^2\hbar^2} \geq (N-1)^2 \Rightarrow \lambda \geq (N-1)^2 \frac{\pi^2\hbar^2}{8m}.$$

- c) The function $\lambda a^2/(a + b)$ grows indefinitely as a grows, so the number of bound states is infinite for any $\lambda > 0$ and for any b .

7.4 The Hamiltonian of a particle of mass m in one dimension is

$$H = \frac{p^2}{2m} + V(x) + V(a - x)$$

where $V(x)$ is an attractive potential with compact support and a is large enough so that $V(x)$ and $V(a - x)$ have disjoint supports (double well potential: see Problem 6.21). Let us assume, in addition, that $V(x)$ has only one bound state whose energy is $E_0 \equiv -\hbar^2 \kappa_0^2 / 2m$.

- a) Show that H commutes with the space inversion operator $I_{\bar{x}}$, the inversion being performed with respect to a suitable point \bar{x} . If I_0 is the space inversion operator with respect to the origin ($I_0 q I_0^{-1} = -q$, $I_0 p I_0^{-1} = -p$), how is the operator $I_{\bar{x}}$ expressed in terms of I_0 ?

If $\kappa_0 a$ is large enough (distant wells) the Hamiltonian H has two bound states with energies E_1, E_2 (see Problem 6.21). Let $E_1 < E_2$.

- b) Having suitably chosen the phases of the vectors $|E_1\rangle$ and $|E_2\rangle$ (see Problem 5.5), determine the states $|L\rangle$ and $|R\rangle$, among the superpositions of $|E_1\rangle$ and $|E_2\rangle$, in which the mean value of q is respectively a minimum and a maximum.

At time $t = 0$ the particle is ‘localized in the left well’, i.e. it is in the state $|L\rangle$ in which the mean value of q is a minimum.

- c) Find the state $|L, t\rangle$ at time t , show that the state $|L, t\rangle$ evolves in a periodic way and find its period. Find the instant when, for the first time, the particle is localized in the right well. Does this result have a classical analogue?
- d) Let us assume that we do not know $|E_1\rangle$ and $|E_2\rangle$, but that we know the bound state $|E_0, l\rangle$ of the single left well $V(x)$. How is the bound state $|E_0, r\rangle$ of the single right well $V(a - x)$ obtained? What is the best approximation for the eigenstates $|E_1\rangle$ and $|E_2\rangle$ of H in terms of $|E_0, l\rangle$ and $|E_0, r\rangle$?

7.4

- a) The Hamiltonian is invariant under the space inversion ($\bar{x} = a/2$):

$$\begin{cases} (q - \frac{1}{2}a) \rightarrow -(q - \frac{1}{2}a) \\ p \rightarrow -p \end{cases} \Leftrightarrow \begin{cases} q \rightarrow -q + a \\ p \rightarrow -p \end{cases} \Rightarrow$$

$$V(x) + V(a - x) \rightarrow V(a - x) + V(x).$$

Let $U(a) = e^{-i p a / \hbar}$ denote the translation operator: $U(-a) q U^{-1}(-a) = q + a$; then one has $I_{\bar{x}} = I_0 U(-a)$ (or also $I_{\bar{x}} = U(a) I_0$ as well as other equivalent expressions), indeed:

$$I_0 U(-a) q U^{-1}(-a) I_0^{-1} = I_0 (q + a) I_0^{-1} = -q + a,$$

$$I_0 U(-a) p U^{-1}(-a) I_0^{-1} = I_0 p I_0^{-1} = -p.$$

- b) The states $|E_1\rangle$ (ground) and $|E_2\rangle$ (the first excited) respectively are even and odd under $I_{\bar{x}}$. Putting $\tilde{q} = q - \frac{1}{2}a$, one has $\langle E_1 | \tilde{q} | E_1 \rangle = \langle E_2 | \tilde{q} | E_2 \rangle = 0$ (selection rule on parity: see Problem 6.1), then the mean value of \tilde{q} in the state $\alpha |E_1\rangle + \beta |E_2\rangle$ ($|\alpha|^2 + |\beta|^2 = 1$) has the value $2 \Re(\alpha^* \beta \langle E_1 | \tilde{q} | E_2 \rangle)$. Since, in analogy with Problem 5.5, we are allowed to choose the phases of $|E_1\rangle$ and $|E_2\rangle$ in such a way that $\langle E_1 | \tilde{q} | E_2 \rangle$, if nonvanishing (see below), is real and positive, the mean value of \tilde{q} , as well as of q , is either a maximum or a minimum respectively for $\alpha = \pm \beta = 1/\sqrt{2}$. Then:

$$|L\rangle = \frac{1}{\sqrt{2}}(|E_1\rangle - |E_2\rangle), \quad \langle L | q | L \rangle = \frac{1}{2}a - \langle E_1 | \tilde{q} | E_2 \rangle$$

$$|R\rangle = \frac{1}{\sqrt{2}}(|E_1\rangle + |E_2\rangle), \quad \langle R | q | R \rangle = \frac{1}{2}a + \langle E_1 | \tilde{q} | E_2 \rangle.$$

The matrix element $\langle E_1 | \tilde{q} | E_2 \rangle$ is nonvanishing: indeed $\psi_{E_1}(x)$ is real and has no zeroes, i.e. it has a constant sign, $\psi_{E_2}(x)$ has its only zero in $x = \frac{1}{2}a$, so also the product $\psi_{E_1}(x)(x - \frac{1}{2}a)\psi_{E_2}(x)$ has constant sign and its integral is nonvanishing.

- c) $|L, t\rangle = \frac{1}{\sqrt{2}} e^{-i E_1 t / \hbar} (|E_1\rangle - e^{-i (E_2 - E_1) t / \hbar} |E_2\rangle)$

so the period of the state is $\tau = \hbar / (E_2 - E_1)$; after half a period the particle is in the state $|R\rangle$ and then it keeps on oscillating between the two wells. The result has no classical analogue: a particle localized in one of the two wells has a negative energy and, as a consequence, cannot cross the classically forbidden region that separates them. When $\kappa_0 a \rightarrow \infty$, $\tau \propto e^{\kappa_0 a} \rightarrow \infty$ (see Problem 6.21).

- d) $|E_0, r\rangle = I_{\bar{x}} |E_0, l\rangle$.

The state $|E_1\rangle$ is even under $I_{\bar{x}}$, whereas $|E_2\rangle$ is odd; in the subspace generated by $|E_0, l\rangle$ and $|E_0, r\rangle$, the only even and odd states are:

$$N_{\pm} (|E_0, l\rangle \pm |E_0, r\rangle); \quad N_{\pm} = (2 \pm 2 \langle E_0, l | E_0, r \rangle)^{-1/2}$$

with N_{\pm} standing for normalization factors. In the limit $a \rightarrow \infty$, $E_1 = E_2 = E_0$ (see Problem 6.21), whence all the linear combinations of $|E_0, l\rangle$ and $|E_0, r\rangle$ are exact eigenstates of H , i.e. stationary states.

8.6 The spherical harmonics $Y_{l,m}(\theta, \phi)$, if expressed in terms of the Cartesian coordinates, may be written as $r^{-l} \times$ (homogeneous polynomial of degree l in x, y, z). The orthonormality of spherical harmonics is expressed by:

$$\int Y_{l',m'}(\theta, \phi)^* Y_{l,m}(\theta, \phi) d\Omega = \delta_{l'l} \delta_{m'm}, \quad d\Omega \equiv \sin \theta d\theta d\phi.$$

- a) Is it true that all the states represented by the wavefunctions:

$$\psi(x, y, z) = \frac{1}{r^2} \times (\text{homogeneous polynomial of degree 2}) \times f(r)$$

are eigenstates of the angular momentum with $l = 2$?

Are all the states, represented by the wavefunctions:

$$\psi(x, y, z) = \frac{1}{r} \times (\text{homogeneous polynomial of degree 1}) \times f(r),$$

eigenstates of \vec{L}^2 belonging to $l = 1$?

- b) Only two among the following functions are (nonnormalized) spherical harmonics. Which ones?

$$\cos^2 \theta e^{2i\phi}, \quad \sin^2 \theta e^{2i\phi}, \quad \sin \theta \cos \theta e^{2i\phi}, \quad \sin \theta \cos \theta e^{i\phi}.$$

- c) Write the most general homogeneous polynomial of degree 2 that, multiplied by a radial function, gives rise to states with $L_z = 0$. Exploit the orthogonality of spherical harmonics with different values of l to find the one belonging to $l = 2$.
- d) Make use of the space inversion with respect to the plane $y = 0$ to show that, up to a phase factor, $Y_{l,-m}(\theta, \phi) = Y_{l,m}(\theta, -\phi)$ and write, both in polar and in Cartesian coordinates, all the normalized spherical harmonics $Y_{l=2,m}(\theta, \phi)$.

8.6

- a) No: the independent homogeneous polynomials of degree 2 are 6: $x_i x_j$ ($i, j = 1, 2, 3$), whereas the spherical harmonics with $l = 2$ are 5; indeed $r^{-2}(x^2 + y^2 + z^2)f(r) = f(r)$ is the wavefunction of a state with $l = 0$. Instead the polynomials $\alpha x + \beta y + \gamma z$ give rise to states with $l = 1$ (see Problem 8.1).

- b) One has $z = r \cos \theta$, $(x + iy) = r \sin \theta e^{i\phi}$ whence:

$$\begin{aligned} \cos^2 \theta e^{2i\phi} &= \frac{1}{r^2} \left(z^2 \cdot \frac{(x + iy)^2}{x^2 + y^2} \right) \\ &\neq \frac{1}{r^2} \times (\text{homogeneous polynomial of degree 2}). \end{aligned}$$

Likewise $\sin \theta \cos \theta e^{2i\phi} = r^{-2} \left(z(x + iy)^2 / \sqrt{x^2 + y^2} \right)$. Instead:

$$\sin^2 \theta e^{2i\phi} = \frac{(x + iy)^2}{r^2}; \quad \sin \theta \cos \theta e^{i\phi} = \frac{z(x + iy)}{r^2}.$$

The degree of the polynomial says that in both cases $l = 2$, while the dependence on ϕ says that the first is proportional to $Y_{2,2}(\theta, \phi)$ and the second to $Y_{2,1}(\theta, \phi)$.

- c) The polynomial one is after must be invariant under rotations around the z axis, so it has the form $a(x^2 + y^2) + bz^2$. The one that gives rise to $Y_{2,0}(\theta, \phi)$ must be orthogonal to $Y_{0,0}(\theta, \phi)$, which is a constant, so:

$$\begin{aligned} 0 &= \int \frac{a(x^2 + y^2) + bz^2}{r^2} d\Omega = 2\pi \int_{-1}^{+1} (a \sin^2 \theta + b \cos^2 \theta) d \cos \theta \\ &= 2\pi \left(2a + \frac{2}{3}(b - a) \right) \Rightarrow b = -2a \\ &\Rightarrow Y_{2,0}(\theta, \phi) \propto \frac{x^2 + y^2 - 2z^2}{r^2} = 1 - 3 \cos^2 \theta. \end{aligned}$$

- d) If I_y stands for the space inversion with respect to the plane $y = 0$: $x \rightarrow x$, $y \rightarrow -y$, $z \rightarrow z$, one has $I_y L_z I_y^{-1} = -L_z$, $I_y \tilde{L}^2 I_y^{-1} = \tilde{L}^2 \Rightarrow I_y |l, m\rangle = |l, -m\rangle$ therefore, as $y \rightarrow -y \Rightarrow \phi \rightarrow -\phi$, $Y_{l,-m}(\theta, \phi) = Y_{l,m}(\theta, -\phi)$, up to a phase factor that is usually chosen equal to ± 1 : we shall put it equal to 1.

Due to b) and c) and to the above result (the calculation of the normalization factors requires the calculation of elementary integrals):

$$\begin{aligned} Y_{2,\pm 2}(\theta, \phi) &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}} \frac{(x \pm iy)^2}{r^2} \\ Y_{2,\pm 1}(\theta, \phi) &= \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} = \sqrt{\frac{15}{8\pi}} \frac{z(x \pm iy)}{r^2} \\ Y_{2,0}(\theta, \phi) &= \sqrt{\frac{5}{16\pi}} (1 - 3 \cos^2 \theta) = \sqrt{\frac{5}{16\pi}} \frac{r^2 - 3z^2}{r^2}. \end{aligned}$$

9.7 Consider a one-dimensional harmonic oscillator of mass m and angular frequency ω , whose centre of oscillation moves with uniform velocity v .

- a) Write the Hamiltonian of the system both in the laboratory frame and in the moving frame where the centre of oscillation is at rest.
- b) If, in the moving frame, the oscillator is in the ground state, which is its wavefunction in the frame of the laboratory?
- c) Assume that the wavefunction in the laboratory $\psi(x, 0)$ is known at time $t = 0$. Find the wavefunction $\psi(x, t)$ at time t . Explicitly verify that $\psi(x, t)$ satisfies the time dependent Schrödinger equation.

9.7

- a) Since in the moving frame the centre of oscillation is at rest, the Hamiltonian is

$$\tilde{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2.$$

In the laboratory frame the abscissa of the centre of oscillation is $x = vt$, therefore:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 (q - vt)^2.$$

Note that (see Problem 9.6) $\tilde{H} = G^\dagger(v, t) H G(v, t) + i\hbar \dot{G}^\dagger(v, t) G(v, t)$.

- b) Any state $|A\rangle$ of the oscillator in the moving frame is seen from the laboratory as the state $|A^{\text{tr}}\rangle$ obtained by transforming the state $|A\rangle$: so, as in the moving frame $|0\rangle \xrightarrow{\text{SR}} \psi_0(x) = (m\omega/\pi\hbar)^{1/4} e^{-(m\omega/2\hbar)x^2}$, in the laboratory (see Problem 9.6):

$$|0^{\text{tr}}\rangle \xrightarrow{\text{SR}} \psi_{0^{\text{tr}}}(x, t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-(m\omega/2\hbar)(x-vt)^2} e^{imvx/\hbar}$$

(the phase factor $e^{-imv^2t/2\hbar}$ is inessential).

- c) First we solve the problem in the frame where the centre of the oscillator is at rest (moving frame), then we go back to the laboratory frame. In the moving frame the wavefunction $\tilde{\psi}(x, 0)$ at time $t = 0$ is

$$\tilde{\psi}(x, 0) = \psi(x, 0) e^{-imvx/\hbar} \equiv \sum_n a_n \psi_n(x), \quad a_n = \int \psi_n^*(x) \tilde{\psi}(x, 0) dx$$

where $\psi_n(x)$ are the usual eigenfunctions of the Hamiltonian of the harmonic oscillator (i.e. of \tilde{H}); then:

$$\tilde{\psi}(x, t) = \sum_n a_n e^{-i(n+\frac{1}{2})\omega t} \psi_n(x) \Rightarrow$$

$$\psi(x, t) = \sum_n a_n e^{-i(n+\frac{1}{2})\omega t} \psi_n(x - vt) e^{imvx/\hbar}.$$

Let us verify that the single terms in the sum satisfy the Schrödinger equation (the phase factor $e^{-imv^2t/2\hbar}$ is reinserted):

$$\begin{aligned} & \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2(x-vt)^2 \right) \psi_n(x-vt) e^{imvx/\hbar} e^{-i(n+\frac{1}{2})\omega t} e^{-imv^2t/2\hbar} \\ &= \left(-\frac{\hbar^2}{2m} \psi_n''(x-vt) - i\hbar v \psi_n'(x-vt) + \frac{1}{2}m v^2 \psi_n(x-vt) \right. \\ & \quad \left. + \frac{1}{2}m\omega^2(x-vt)^2 \psi_n(x-vt) \right) \times e^{imvx/\hbar} e^{-i(n+\frac{1}{2})\omega t} e^{-imv^2t/2\hbar} \\ &= \left((E_n + \frac{1}{2}m v^2) \psi_n(x-vt) - i\hbar v \psi_n'(x-vt) \right) \\ & \quad \times e^{imvx/\hbar} e^{-i(n+\frac{1}{2})\omega t} e^{-imv^2t/2\hbar} \\ & \text{that is the same as } i\hbar \frac{\partial}{\partial t} \left(e^{-i(n+\frac{1}{2})\omega t} e^{-imv^2t/2\hbar} \psi_n(x-vt) \right) e^{imvx/\hbar}. \end{aligned}$$

10.5 A particle is subject to the potential $V = V(q_1^2 + q_2^2, q_3)$.

- a) Show that the Hamiltonian $H_0 = \vec{p}^2/2m + V$ commutes with the angular momentum operator $L_z = q_1 p_2 - q_2 p_1$.
- b) Use the degeneracy theorem to show that there exist degenerate energy levels.
- c) Say whether and how the degeneracy is removed if the system is on a platform rotating around the z axis with constant angular velocity ω .

10.5

- a) Both the kinetic energy and the potential are invariant under rotations around the z axis, therefore they commute with L_z .
- b) The Hamiltonian H commutes also with the operator I_x , the inversion with respect to the plane $x = 0$ (as a matter of fact, thanks to the invariance under rotations, H commutes also with the inversion with respect to any plane containing the z axis), but I_x and L_z do not commute, so there must exist degenerate levels. Since $I_x L_z I_x^{-1} = -L_z$, if one considers the simultaneous eigenstates of H and L_z : $|E, m'\rangle$, one has $I_x |E, m'\rangle \propto |E, -m'\rangle$, and, as a consequence, all the energy levels with $m' \neq 0$ are at least twice degenerate. This result holds true whatever the potential, provided it is invariant under rotations around some axis and depends only on the q 's: the invariance under reflections follows from these assumptions.
- c) In the rotating frame the Hamiltonian is (see Problem 9.10):

$$H = \frac{\vec{p}^2}{2m} + V(q_1^2 + q_2^2, q_3) - \omega L_z \equiv H_0 - \omega L_z$$

that still commutes with L_z , but does no longer commute with the inversions (in the present case $V - \omega L_z$ no longer depends only on the q 's), so the existence of degenerate levels cannot be guaranteed: indeed the states $|E_0, m'\rangle$ and $|E_0, -m'\rangle$ (eigenstates of H_0 and L_z , therefore of H and L_z) respectively have energies $E_0 \mp m' \hbar \omega$.

11.10 Consider a particle of mass m in three dimensions subject to the central potential $V(r) = -\lambda/r^s$, with $\lambda > 0$.

- a) Find how the normalization factor N depends on a for the states represented by the trial functions $\psi(r; a)$ depending on r and a only through the ratio r/a : $\psi(r; a) = N f(r/a)$, $a > 0$. Do the same for the mean values of the kinetic energy and of the potential energy.
- b) Use the above result and prove that, if $s > 2$, the spectrum of the Hamiltonian is not bounded from below.
- c) Use the method of the ‘inscribed well’ exposed in Problem 6.4 (see also Problem 6.6) and prove that, if $0 < s < 2$, the system admits an infinite number of bound states. In the latter case, where is it relevant that the potential has the asymptotic behaviour r^{-s} – for $r \rightarrow 0$ or, instead, for $r \rightarrow \infty$?

11.10

$$\text{a) } 1 = N^2 \int |\psi(r; a)|^2 r^2 dr d\Omega = N^2 a^3 \int |f(\xi)|^2 \xi^2 d\xi d\Omega \Rightarrow N \propto a^{-3/2}.$$

Having in mind that $d^2 f(\xi)/dr^2 = a^{-2} d^2 f(\xi)/d\xi^2$, one has:

$$\frac{\overline{p^2}}{2m} = -\frac{\hbar^2}{2m} N^2 \int f^*(\xi) \xi^{-1} \frac{1}{a^2} \frac{d^2(\xi f(\xi))}{d\xi^2} a^3 \xi^2 d\xi d\Omega = \frac{c_1}{a^2}, \quad c_1 > 0.$$

Likewise:

$$\overline{V(r)} = -\lambda N^2 \int |f(\xi)|^2 a^{-s} \frac{1}{\xi^s} a^3 \xi^2 d\xi d\Omega = -\frac{c_2}{a^s}, \quad c_2 > 0.$$

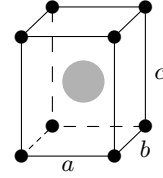
- b) The mean value of the Hamiltonian in the states of wavefunction $\psi(r; a)$ is

$$\overline{H} \equiv h(a) = \frac{c_1}{a^2} - \frac{c_2}{a^s}, \quad c_1, c_2 > 0$$

and, when $s > 2$, for a sufficiently small, $h(a)$ takes arbitrarily large negative values. This means that the spectrum of the operator H when $s > 2$ extends to $-\infty$: this situation, lacking of any physical significance, is described as “fall of the particle in the centre” (see also Problem 12.11).

- c) To start, let us limit ourselves to the case of the energy levels with $l = 0$: the Schrödinger equation for the reduced radial function $u(r)$ is that of a particle in one dimension subject to the potential $V(x) = -\lambda/x^s$ for $x > 0$ and $V(x) = \infty$ for $x \leq 0$ and, thanks to the condition $u(0) = 0$, the levels are the odd levels of a particle subject to the potential $V(x) = -\lambda/|x|^s$ for $-\infty < x < \infty$. Since $V(x) < 0$ and $V(x) \rightarrow 0$ for $x \rightarrow \infty$, for $E < 0$ the Hamiltonian may only have discrete eigenvalues; furthermore, the inscribed rectangular well of width $2a$ has depth $V_0 = \lambda/a^s$ and, owing to the fact that $V_0 a^2 = \lambda a^{2-s}$ grows indefinitely with the growing of a , the number of bound states is infinite for any $\lambda > 0$, $0 < s < 2$. What is relevant for the above result is the growing of λa^{2-s} with a , therefore the behaviour of the potential for $r \rightarrow \infty$: so the same result obtains for the states with $l > 0$, because for $s < 2$ the centrifugal potential does not change the asymptotic behaviour of $V(r)$.

12.16 A hydrogen atom is at the centre of the cell of a crystal consisting of equal atoms forming a rectangular parallelepiped lattice with edges a, b, c parallel to the axes $\hat{x}, \hat{y}, \hat{z}$.



- a) Exploit the symmetry of the crystal lattice and write the expansion of the electrostatic potential energy $V(x, y, z)$ generated by the lattice on the atom, up to the second order in $(x, y, z) \equiv \vec{r} = \vec{r}_e - \vec{r}_p$.

Consider the three cases: *i*) $a = b = c$, *ii*) $a = b \neq c$, *iii*) $a \neq b \neq c \neq a$. Approximate $V(x, y, z)$ with its expansion $V^{(2)}$ to the second order in x, y, z (being the potential energy $V(x, y, z)$ electrostatic, one has $V(0) = 0$).

- b) For each of the above cases say which, among the following observables, are constants of motion: $L_x, L_y, L_z, \vec{L}^2, I_x$ (the space inversion with respect to the plane $x = 0$), I_y, I_z and what can be concluded, as a consequence, on the degeneracy of the energy levels of the hydrogen atom.

Consider now $V^{(2)}(x, y, z)$ as a perturbation.

- c) Calculate its first order effect on the levels $n = 1$ and $n = 2$ when a, b, c are all different (case *iii*): for the states with $n = 2, l = 1$ it is convenient the use of the Cartesian basis (see Problem 8.2) or, which is the same thing, the basis of the simultaneous eigenvectors of I_x, I_y, I_z . Use the identity given in the text of Problem 12.14 and:

$$\langle 2, 1, 0 | z^2 | 2, 1, 0 \rangle = \frac{3}{5} \langle 2, 1, 0 | r^2 | 2, 1, 0 \rangle.$$

Let now $a = b = c$ (cubic crystal), and do not approximate $V(x, y, z)$ by $V^{(2)}$ any more.

- d) Is it possible that $V(x, y, z)$ completely removes the degeneracies of the energy levels of the hydrogen atom?

12.16

- a) The lattice is invariant under the inversion of the single axes, so:

$$V^{(2)}(x, y, z) = \alpha x^2 + \beta y^2 + \gamma z^2.$$

If $a = b$, the lattice is invariant under rotations by 90° around the z axis, therefore $\alpha = \beta$; if $a = b = c$, then $\alpha = \beta = \gamma$.

- b) If $\alpha = \beta = \gamma$ all the observables given in the text are constants of motion: in the latter case $V^{(2)}$ is a central potential and the eigenvectors of H can be classified as $|E, l, m\rangle$. The degeneracy on l of the hydrogen atom is removed and only the degeneracy $2l + 1$ on m is guaranteed.

If $\alpha = \beta \neq \gamma$, the observables L_z, I_x, I_y, I_z are constants of motion; the eigenstates of the Hamiltonian can be classified as $|E, m\rangle$, degenerate with $|E, -m\rangle$ ($I_x L_z = -L_z I_x$).

If $\alpha \neq \beta \neq \gamma$, only I_x, I_y, I_z are constants of motion commuting with one another, so the eigenstates of the Hamiltonian can be classified by means of the eigenvalues w_x, w_y, w_z of these operators ($w_i = \pm 1$) and one must expect that all the energy levels are nondegenerate.

- c) In the s (i.e. $l = 0$) states: $\overline{x^2} = \overline{y^2} = \overline{z^2} = \frac{1}{3}\overline{r^2}$, so that:

$$\begin{aligned} \Delta E_{1s}^{(1)} &= \langle 1, 0, 0 | V^{(2)} | 1, 0, 0 \rangle = \frac{1}{3}(\alpha + \beta + \gamma) \langle 1, 0, 0 | r^2 | 1, 0, 0 \rangle \\ &= (\alpha + \beta + \gamma) a_B^2. \end{aligned}$$

Level $n = 2$: $V^{(2)}$ has no nonvanishing matrix element between the state $2s$ ($|2, 0, 0\rangle$) and the states $2p$ ($|2, 1, m\rangle$), that have opposite parity, so:

$$\Delta E_{2s}^{(1)} = \frac{1}{3}(\alpha + \beta + \gamma) \langle 2, 0, 0 | r^2 | 2, 0, 0 \rangle = 14(\alpha + \beta + \gamma) a_B^2.$$

The states $2p$, classified by w_x, w_y, w_z , are:

$$|+, +, -\rangle = |n = 2, l = 1, m_z = 0\rangle,$$

$$|+, -, +\rangle = |n = 2, l = 1, m_y = 0\rangle,$$

$$|-, +, +\rangle = |n = 2, l = 1, m_x = 0\rangle$$

and in this basis the perturbation is diagonal (the terms w_x, w_y, w_z are all different). In the state with $m_z = 0$ one has $\overline{x^2} = \overline{y^2}$, so:

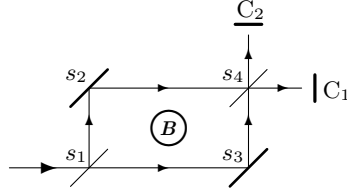
$$\begin{aligned} \Delta E_{2p, m_z=0}^{(1)} &= \alpha \overline{x^2} + \beta \overline{y^2} + \gamma \overline{z^2} = \frac{1}{2}(\alpha + \beta) (\overline{x^2} + \overline{y^2}) + \gamma \overline{z^2} \\ &= \frac{1}{2}(\alpha + \beta) (\overline{r^2} - \overline{z^2}) + \gamma \overline{z^2} = [6(\alpha + \beta) + 18\gamma] a_B^2; \end{aligned}$$

likewise:

$$\Delta E_{2p, m_y=0}^{(1)} = [6(\alpha + \gamma) + 18\beta] a_B^2; \quad \Delta E_{2p, m_x=0}^{(1)} = [6(\beta + \gamma) + 18\alpha] a_B^2.$$

- d) The Hamiltonian $H_0 + V$ commutes with all the transformations that leave the cube invariant: as the group of the cube is noncommutative (indeed it contains the group of the square: see Problem 10.2), due to the degeneracy theorem there must exist degenerate energy levels.

13.13 It is possible to realize an interferometer for electrons similar to that of Bonse–Hart for neutrons (see Problem 3.4). At the centre of the interferometer a long solenoid, of radius a and with the axis orthogonal to the plane containing the trajectories of the electrons, is present. The interferometer is tuned in such a way that, when the magnetic field inside the solenoid is vanishing, all the electrons arrive at the counter C_1 . Let I be the intensity of the beam of electrons (of energy E), \vec{B} the magnetic field inside the solenoid, $\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \wedge \vec{r}$ the vector potential inside the solenoid.



- a) Show that the vector potential outside the solenoid (where $\vec{B} = 0$) is

$$\vec{A}(\vec{r}) = \frac{a^2}{2(x^2 + y^2)} \vec{B} \wedge \vec{r} = \frac{a^2 B}{2(x^2 + y^2)} (-y, x, 0), \quad \hat{z} \parallel \vec{B}.$$

Calculate the line integral of $\vec{A}(\vec{r})$ along the closed circuit $s_1 \rightarrow s_3 \rightarrow s_4 \rightarrow s_2 \rightarrow s_1$.

- b) Show that the wavefunction along each of the two paths $\gamma_1 = s_1 \rightarrow s_3 \rightarrow s_4$ and $\gamma_2 = s_1 \rightarrow s_2 \rightarrow s_4$ is given by:

$$\psi(x, y, z) = \exp\left(i \int (\vec{k} + (e/\hbar c) \vec{A}) \cdot d\vec{l}\right), \quad k = \sqrt{2m_e E}/\hbar$$

where the integral is taken from the point where the electrons enter the interferometer up to the point (x, y, z) , of the path it belongs to.

- c) Calculate the difference of phase φ between the two components of the electron wavefunction that arrive at s_4 from the paths γ_1 and γ_2 ; calculate (see Problem 13.6) the intensities I_1 , I_2 of the electrons detected by the counters C_1 and C_2 .

[The above effect has been predicted by Aharonov and Bohm in 1959.]

13.13

- a) \vec{A} is continuous on the surface of the solenoid and, out of it, $\text{curl } \vec{A} = 0$. Thanks to Stokes theorem, the line integral of \vec{A} is given by the flux of \vec{B} through the surface, namely $\pi a^2 B$.
- b) Along each of the two paths the problem is one-dimensional, with Hamiltonian $H = (p + (e/c)A_t)^2/2m$ (A_t is the component of \vec{A} along the path), so it is identical with the problem discussed in question a) of Problem 13.7. Alternatively: since the region where $\text{curl } \vec{A} = 0$ is not simply connected, out of the solenoid $\vec{A}(\vec{r})$ is the gradient of a multivalued function Φ ($\Phi = a^2 B \phi/2\sqrt{x^2 + y^2}$, where ϕ is the azimuth angle around the axis of the solenoid); however, limiting to simply connected regions, as the two single circuits γ_1 and γ_2 , the function Φ is one valued (Φ_1 on γ_1 , Φ_2 on γ_2) and, as a consequence, the problem is the same as the three-dimensional one discussed in 13.7.
- c) The difference in phase φ is given by:

$$\begin{aligned}\varphi &= \int_{\gamma_1} (\vec{k} + (e/\hbar c) \vec{A}) \cdot d\vec{l}_1 - \int_{\gamma_2} (\vec{k} + (e/\hbar c) \vec{A}) \cdot d\vec{l}_2 \\ &= \frac{e}{\hbar c} \oint \vec{A}(\vec{r}) \cdot d\vec{l} = \frac{\pi a^2 e B}{\hbar c}\end{aligned}$$

(the line integral of \vec{k} is vanishing because, by assumption, the interferometer is well calibrated). It is remarkable that the phase difference is proportional to the flux of \vec{B} , even if only regions where $\vec{B} = 0$ are accessible to the electrons: this fact, known as Aharonov–Bohm effect, has been experimentally verified. One has (see Problem 13.6):

$$I_1 = \frac{I}{2}(1 + \cos \varphi), \quad I_2 = \frac{I}{2}(1 - \cos \varphi).$$

14.6 Inside a cavity atoms with two nondegenerate energy levels E_a and E_b , $E_a < E_b$, are in thermal equilibrium with the radiation (*black body radiation*).

- a) At which temperature \bar{T} of the cavity does the transition probability between the two states of energies E_a , E_b , induced by the radiation in the cavity, equal the probability of spontaneous emission $E_b \rightarrow E_a$? Make the numerical calculation in the case $E_b - E_a = 1 \text{ eV}$.

The black body temperature typical of a lamp used in the laboratory to induce transitions in an atomic system is about $T_L = 3000 \text{ K}$.

- b) What is the value of the ratio between the spectral intensity $I(\omega_{ba}, T)$ ($\omega_{ba} = (E_b - E_a)/\hbar$) of a black body at the temperature \bar{T} determined in a) and the spectral intensity $I(\omega_{ba}, T_L)$ of a lamp at the temperature $T_L = 3000 \text{ K}$?

14.6

- a) Let $W_{b \leftarrow a} = W_{a \leftarrow b} \equiv W_{ab}$ be the probability for the induced transition between the two states and w_{ab} the spontaneous emission probability (integrated over the angles). The condition of thermal equilibrium among radiation and matter (the atoms we are considering) entails that:

$$N_a \times W_{ab} = N_b \times (W_{ab} + w_{ab}), \quad \frac{N_a}{N_b} = e^{(E_b - E_a)/k_B T}$$

so the condition $W_{ab} = w_{ab}$ requires $N_a/N_b = 2 \Rightarrow (E_b - E_a)/k_B \bar{T} = \log 2 \Rightarrow \bar{T} = 1.67 \times 10^4 \text{ K}$.

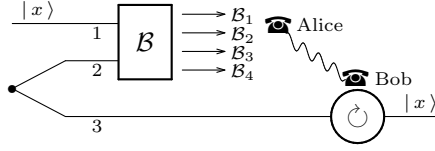
- b) The intensity is proportional to the energy density:

$$u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\hbar \omega / k_B T} - 1)} \Rightarrow$$

$$\frac{I(\omega_{ba}, \bar{T})}{I(\omega_{ba}, T_L)} = \frac{e^{\hbar \omega_{ba} / k_B T_L} - 1}{e^{\hbar \omega_{ba} / k_B \bar{T}} - 1} = \frac{2^{\bar{T}/T_L} - 1}{2 - 1} = 46 \simeq \left(\frac{N_a}{N_b} \right)_{T_L}.$$

Therefore, since $w_{ab}/W_{ab} = N_a/N_b - 1$, in ‘normal’ conditions ($T_L \simeq 10^3 \text{ K}$) the spontaneous emissions prevails on the induced one.

15.17 Two particles of spin $\frac{1}{2}$ (particles 2 and 3) are produced in a singlet state and move apart in different directions. Another particle of spin $\frac{1}{2}$ (particle 1), in an unknown spin state $|x\rangle$, travels along with particle 2. The spin state of the three particles is therefore $(\sigma_z |\pm\rangle = \pm |\pm\rangle)$:



$$|A\rangle = \frac{1}{\sqrt{2}} |x\rangle_1 (|+\rangle_2 |-\rangle_3 - |-\rangle_2 |+\rangle_3), \quad |x\rangle = \alpha |+\rangle + \beta |-\rangle.$$

On particles 1 and 2 Alice measures a nondegenerate observable \mathcal{B} , whose eigenstates (“Bell states”) are:

$$|\mathcal{B}_1\rangle = \frac{1}{\sqrt{2}} (|+\rangle_1 |+\rangle_2 + |-\rangle_1 |-\rangle_2),$$

$$|\mathcal{B}_2\rangle = \frac{1}{\sqrt{2}} (|+\rangle_1 |+\rangle_2 - |-\rangle_1 |-\rangle_2),$$

$$|\mathcal{B}_3\rangle = \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2),$$

$$|\mathcal{B}_4\rangle = \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2).$$

- a) Find the probability of the four possible results and for each of the obtained results find the state of particle 3 after the measurement.

The result of the measurement is communicated to Bob who, far from Alice, receives particle 3.

- b) For each of the possible results of the measurement on particles 1 and 2, which rotation must Bob perform on the spin state of particle 3 in order that this is transformed back in the state $|x\rangle$ in which particle 1 was initially? (*Quantum teleportation* of an unknown state $|x\rangle$.)

Assume now that the spin state of the three particles is

$$|B\rangle = |x\rangle_1 |+\rangle_2 |-\rangle_3.$$

- c) Calculate the probabilities of the four possible results of the observable \mathcal{B} and find the state of particle 3 after the measurement. Is it possible, in this case, to transform the state of particle 3 in the state $|x\rangle$ only knowing the result of the measurement of \mathcal{B} on particles 1 and 2?

15.17

a) One has:

$$\begin{aligned}
 |A\rangle &= \frac{1}{2} \left(\alpha(|\mathcal{B}_1\rangle + |\mathcal{B}_2\rangle) |-\rangle_3 - \alpha(|\mathcal{B}_3\rangle + |\mathcal{B}_4\rangle) |+\rangle_3 \right. \\
 &\quad \left. + \beta(|\mathcal{B}_3\rangle - |\mathcal{B}_4\rangle) |-\rangle_3 - \beta(|\mathcal{B}_1\rangle - |\mathcal{B}_2\rangle) |+\rangle_3 \right) \\
 &= \frac{1}{2} |\mathcal{B}_1\rangle (\alpha |-\rangle_3 - \beta |+\rangle_3) + \frac{1}{2} |\mathcal{B}_2\rangle (\alpha |-\rangle_3 + \beta |+\rangle_3) \\
 &\quad + \frac{1}{2} |\mathcal{B}_3\rangle (-\alpha |+\rangle_3 + \beta |-\rangle_3) + \frac{1}{2} |\mathcal{B}_4\rangle (-\alpha |+\rangle_3 - \beta |-\rangle_3)
 \end{aligned}$$

so the four results all have probability 1/4 and, for each of them, the state of the third particle after the measurement is

$$\begin{aligned}
 |\mathcal{B}_1\rangle : |b_1\rangle_3 &\equiv \alpha |-\rangle_3 - \beta |+\rangle_3; & |\mathcal{B}_2\rangle : |b_2\rangle_3 &\equiv \alpha |-\rangle_3 + \beta |+\rangle_3; \\
 |\mathcal{B}_3\rangle : |b_3\rangle_3 &\equiv \alpha |+\rangle_3 - \beta |-\rangle_3; & |\mathcal{B}_4\rangle : |b_4\rangle_3 &\equiv \alpha |+\rangle_3 + \beta |-\rangle_3.
 \end{aligned}$$

b) In the basis $|+\rangle, |-\rangle$ (the index 3 is hereafter omitted) one has:

$$|b_1\rangle \rightarrow \begin{pmatrix} -\beta \\ \alpha \end{pmatrix}; \quad \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} -\beta \\ \alpha \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow |x\rangle = -i\sigma_y |b_1\rangle.$$

Likewise $|x\rangle = \sigma_x |b_2\rangle, |x\rangle = \sigma_z |b_3\rangle, |x\rangle = |b_4\rangle$. The operator that performs the rotation of angle ϕ around the direction \hat{n} on the spin states of a particle of spin $\frac{1}{2}$ is (see Problem 13.2):

$$U(\hat{n}, \phi) = e^{\frac{1}{2}i\phi \vec{\sigma} \cdot \hat{n}} = \cos(\phi/2) + i\vec{\sigma} \cdot \hat{n} \sin(\phi/2)$$

so, up to phase factors, $\sigma_x, \sigma_y, \sigma_z$ implement rotations by 180° respectively around the x, y, z axes. If the result is \mathcal{B}_4 no rotation must be performed.

$$c) |x\rangle_1 |+\rangle_2 |-\rangle_3 = \frac{1}{\sqrt{2}} \left(\alpha(|\mathcal{B}_1\rangle + |\mathcal{B}_2\rangle) |-\rangle_3 + \beta(|\mathcal{B}_3\rangle - |\mathcal{B}_4\rangle) |-\rangle_3 \right)$$

so the probabilities respectively are $\frac{1}{2}|\alpha|^2, \frac{1}{2}|\alpha|^2, \frac{1}{2}|\beta|^2, \frac{1}{2}|\beta|^2$. Particle 3 always is in the state $|-\rangle$ that does not contain information about the state $|x\rangle$ so, in this case, teleportation of the state $|x\rangle$ is not possible.

16.12 Spectroscopic analysis has established that a certain atom, whose identity is unknown, has the following energy levels in eV (E_0 is the lowest energy level):

$$E_0 = 0, \quad E_1 = 1.7 \times 10^{-2}, \quad E_2 = 4 \times 10^{-2}, \quad E_3 = 7 \times 10^{-2}$$

separated by about 0.3 eV from the next higher level. It is therefore reasonable to assume that the levels $E_0 \cdots E_3$ constitute a fine structure multiplet. Even if the Landé interval rule ($E_{LS,J} - E_{LS,J-1} = A_{LS} J$) is not expected to hold with good accuracy, some pieces of information may however be obtained from it, both in qualitative and in quantitative character.

- a) Establish whether one is dealing with a direct multiplet ($A_{LS} > 0$) or, rather, with an inverted one ($A_{LS} < 0$). Say which is the value of the total spin S and the minimum value the orbital angular momentum L may have. Are the values of the total angular momentum J integers or half-integers?
- b) Having established whether J is integer or half-integer, determine the value J_0 of the total angular momentum of the lowest energy level that gives rise to the best approximation to the Landé rule. Find L .
- c) Taking into account all the configurations p^{n_1} and d^{n_2} for the electrons external to the filled shells, say which is the only configuration compatible with the found results. Knowing that the orbitals have to be filled according to the following order: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, \dots$, say which is the first atom exhibiting the found configuration.

16.12

- a) As the distance between adjacent levels increases, one is dealing with a “direct multiplet”. The number of levels of a fine structure multiplet is the least between $2S+1$ and $2L+1$ ($|L-S| \leq J \leq L+S$): as the levels are 4 and $2L+1$ is odd, it follows that $4 = 2S+1$, so $S = 3/2$, $L > S \Rightarrow L \geq 2$. The values of J are half-integers.

- b) One may proceed in several ways. It is convenient to eliminate A_{LS} by taking ratios:

$$\frac{E_3 - E_2}{E_1 - E_0} = \frac{J_0 + 3}{J_0 + 1} = \frac{3}{1.7}, \quad \frac{E_2 - E_1}{E_1 - E_0} = \frac{J_0 + 2}{J_0 + 1} = \frac{2.3}{1.7} \Rightarrow$$

$$1.3 J_0 - 2.1 = 0 \Rightarrow J_0 = 1.6; \quad 0.6 J_0 - 1.1 = 0 \Rightarrow J_0 = 1.8$$

whence it follows (but the method of the least squares could be used as well) that the half-integer that best solves both equations is $J_0 = 3/2$, then $L - S = 3/2 \Rightarrow L = 3$ (spectral term 4F).

- c) As $S = 3/2$, the number of electrons must be odd and ≥ 3 ; in addition, the multiplet being direct, the outer orbital must be filled for less than its half (p^3 with $L = 3$ and $S = 3/2$ is excluded also because it is a completely symmetric state; d^5 because Hund’s rule would require $S = 5/2$). There remains the configuration d^3 . The first atom with such a configuration has $Z = 23$: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^3$, so it is vanadium.

Appendix A

Physical Constants

Electronvolt	eV	1.6×10^{-12} erg
Speed of light	c	3×10^{10} cm/s
Elementary charge	e	4.8×10^{-10} esu = 1.6×10^{-19} C
Electron mass	m_e	0.91×10^{-27} g = 0.51 MeV/ c^2
Hydrogen mass	m_H	1.7×10^{-24} g = 939 MeV/ c^2
Planck constant	h	6.6×10^{-27} erg s = 4.1×10^{-15} eV s
Reduced Planck constant	$\hbar = \frac{h}{2\pi}$	1.05×10^{-27} erg s = 0.66×10^{-15} eV s
Boltzmann constant	k_B	1.38×10^{-16} erg/K $\simeq \frac{1}{12000}$ eV/K
Avogadro constant	N_A	6.03×10^{23} mol $^{-1}$
Fine structure constant	$\alpha = \frac{e^2}{\hbar c}$	$7.3 \times 10^{-3} \simeq \frac{1}{137}$
Bohr radius	$a_B = \frac{\hbar^2}{m_e e^2}$	$0.53 \text{ \AA} = 0.53 \times 10^{-8}$ cm
Bohr magneton	$\mu_B = \frac{e\hbar}{2m_e c}$	0.93×10^{-20} erg/G = 5.8×10^{-9} eV/G
Rydberg constant	$R_\infty = \frac{e^2}{2a_B \hbar c}$	109737 cm^{-1}
Compton wavelength	$\lambda_c = \frac{h}{m_e c}$	0.024 \AA
Classical electron radius	$r_e = \frac{e^2}{m_e c^2}$	2.8×10^{-13} cm
Atomic unit of energy	$\frac{e^2}{a_B} = \alpha^2 m_e c^2$	27.2 eV
A useful mnemonic rule	$h c$	12400 eV \AA

Appendix B

Useful Formulae

Normalized Gaussian wavefunctions:

$$\begin{aligned} |A\rangle &\xrightarrow{\text{SR}} \psi_A(x) = (\pi a^2)^{-1/4} e^{-x^2/2a^2}; \\ |A\rangle &\xrightarrow{\text{MR}} \varphi_A(p) = (\pi \hbar^2/a^2)^{-1/4} e^{-p^2 a^2/2\hbar^2} \\ \overline{x^2} &= \tfrac{1}{2} a^2, \quad \overline{x^4} = \tfrac{3}{4} a^4; \quad \overline{p^2} = \hbar^2/2a^2, \quad \overline{p^4} = 3\hbar^2/4a^4. \end{aligned}$$

Normalized eigenfunctions of the harmonic oscillator:

$$\begin{aligned} \psi_n(x) &= \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} H_n(\sqrt{m\omega/\hbar} x) e^{-(m\omega/2\hbar) x^2} \\ H_0(\xi) &= 1, \quad H_1(\xi) = 2\xi, \quad H_2(\xi) = 4\xi^2 - 2. \end{aligned}$$

$$\text{Spherical harmonics:} \quad \int |Y_{l,m}(\theta, \phi)|^2 d\Omega = 1, \quad d\Omega = \sin\theta d\theta d\phi$$

$$\begin{aligned} Y_{0,0}(\theta, \phi) &= \sqrt{\frac{1}{4\pi}} \\ Y_{1,\pm 1}(\theta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi} = \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r} \\ Y_{1,0}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \\ Y_{2,\pm 2}(\theta, \phi) &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}} \frac{(x \pm iy)^2}{r^2} \\ Y_{2,\pm 1}(\theta, \phi) &= \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi} = \sqrt{\frac{15}{8\pi}} \frac{z(x \pm iy)}{r^2} \\ Y_{2,0}(\theta, \phi) &= \sqrt{\frac{5}{16\pi}} (1 - 3\cos^2\theta) = \sqrt{\frac{5}{16\pi}} \frac{x^2 + y^2 - 2z^2}{r^2}. \end{aligned}$$

Energy levels of hydrogen-like ions: (infinite nuclear mass)

$$E_n = -Z^2 \frac{m_e c^4}{2\hbar^2 n^2} = -Z^2 \frac{e^2}{2n^2 a_B} = -Z^2 \frac{\alpha^2 m_e c^2}{2n^2} = -Z^2 \frac{R_\infty h c}{n^2} = -Z^2 \frac{13.6}{n^2} \text{ eV}.$$

Radial functions for hydrogen-like ions:

$$\int_0^\infty |R_{n,l}(\rho)|^2 \rho^2 d\rho = 1, \quad \rho = Z r / a_B$$

$$R_{1,0}(\rho) = 2 e^{-\rho}$$

$$R_{2,0}(\rho) = \frac{1}{\sqrt{2}} \left(1 - \frac{1}{2}\rho\right) e^{-\rho/2}$$

$$R_{2,1}(\rho) = \frac{1}{2\sqrt{6}} \rho e^{-\rho/2}$$

$$R_{3,0}(\rho) = \frac{2}{3\sqrt{3}} \left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right) e^{-\rho/3}$$

$$R_{3,1}(\rho) = \frac{8}{27\sqrt{6}} \rho \left(1 - \frac{1}{6}\rho\right) e^{-\rho/3}$$

$$R_{3,2}(\rho) = \frac{4}{81\sqrt{30}} \rho^2 e^{-\rho/3}$$

$$\text{Note: } \int_0^\infty \left| \left(\frac{Z}{a_B}\right)^{3/2} R_{n,l}(Zr/a_B) \right|^2 r^2 dr = 1.$$

Pauli matrices:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Index

- Aharonov–Bohm (see Effect)
- Angular Momentum
- Cartesian basis 8.2, 8.3, 8.11; 12.15, 12.16
 - centre of mass 15.1–15.3
 - commutation rules 4.12
 - composition 15.8–15.10
 - orbital 8.5, 8.7, 8.9, 8.10; 15.10
 - selection rules 8.8; 12.14
 - spherical basis 8.1, 8.3
 - spherical harmonics 8.1, 8.6, 8.7
 - states with $l = 1$ 8.1, 8.2, 8.4, 8.6
 - states with $l = 2$ 8.6, 8.11
- Anharmonic corrections 6.2, 6.3; 12.6, 12.7
- Bender–Wu method for $g x^4$ 12.9
- Anomaly
- μ -meson 13.11
 - electron 13.9
- Approximation
- adiabatic 7.17
 - dipole (see radiation)
 - impulse 7.14–7.16
 - strong field 16.2
 - sudden 7.17
 - weak field 16.2
- Baker–Campbell–Hausdorff identity 4.13; 5.8; 7.8
- Bessel equation/function 11.6, 11.7
- Bohr magneton 2.4, 2.9; 13.3
- Bohr–Sommerfeld quantization 2.6–2.10
- Bragg reflection 2.14; 7.9
- Classical limit 5.17; 7.2, 7.3, 7.6
- Coherence
- length 3.3
 - time 5.25
- Coherent states 5.9–5.11, 5.15; 7.5, 7.16, 7.17
- Completeness 5.18; 6.17, 6.19
- Crystal (one-dimensional) 1.8–1.10
- De Broglie wavelength 2.14, 2.15; 3.4, 3.5; 13.7
- Density matrix (see Statistical mixture)
- Deuterium 2.3; 11.13
- Deuteron (n - p bound state) 2.5; 15.15
- Diffraction 3.6, 3.7, 3.12
- Dirac delta
- potential (see Potentials)
 - normalization 5.14, 5.23; 6.17, 6.19
- Effect
- Aharonov–Bohm 13.13
 - Compton 2.4
 - Hanbury Brown–Twiss 15.14
 - photoelectric 14.3
 - Sagnac 3.5
 - Stark 12.13; 14.8; 16.3, 16.4
 - Zeeman 13.12; 16.2, 16.6

- Einstein–Podolsky–Rosen paradox 15.16
- Electromagnetic transitions 2.1
 - coherent radiation 14.1, 14.2
 - incoherent radiation 14.1, 14.2
 - in black body radiation 14.6, 14.7
- Electronic configuration 16.8–16.11
- Entangled states 13.5; 15.4, 15.16
- Exchange degeneracy 12.3, 16.7
- Exchange integral 12.3; 15.12; 16.7
- Exotic atoms 2.4, 2.5; 12.19
- Fall in the centre 11.10; 12.11
- Fermi energy/temperature 2.13
- Fine structure
 - constant 2.2; 12.20; 14.1, 14.11
 - multiplet 16.8–16.10, 16.12, 16.14, 16.15
- Forbidden line 16.15
- Gauge transformation (see Transformation/s, gauge)
- Gyromagnetic factor 13.9
- Gaussian wavefunctions (see also Coherent states) 5.17, 5.19; 7.6, 7.7, 7.9; 9.4, 9.5, 9.9
- Harmonic oscillator
 - one-dimensional 2.6
 - coherent states 5.10, 5.11; 7.5, 7.16, 7.17
 - eigenfunctions 5.14
 - forced 7.15–7.17
 - mean values 4.14, 4.15; 5.7, 5.12
 - perturbations 12.5–12.9
 - retarded Green’s function 7.15, 7.16
 - time evolution 7.1, 7.5
 - variational method 6.7
 - with center uniformly moving 9.7
 - three-dimensional 2.6, 2.7; 11.4; 14.1, 14.2, 14.4, 14.5
 - two-dimensional 10.1, 10.6–10.8; 11.4
- Helicity 13.11
- Helium atom and Helium-like ions 1.3; 12.19; 16.4–16.7
- Hydrogen atom and Hydrogen-like ions
 - electromagnetic transitions 14.3, 14.7, 14.8, 14.10
 - energy levels 5.6; 7.3; 11.9; 12.10, 12.20
 - external perturbations 12.13–12.16; 14.7, 14.8; 16.2, 16.3
 - internal perturbations 12.17, 12.18, 12.20; 16.1
 - isotopic shift 2.3
 - lifetime 1.2; 14.12
 - radial wavefunctions 11.9
 - relativistic effects 12.20
 - scale transformations 5.6; 11.9; 12.11
 - variational method 11.8
- Hund’s rule 16.11, 16.12
- Identical particles 15.12, 15.13
- Interaction representation 7.11–7.13
- Intercombination line 16.15
- Interference
 - of neutron/s (Bonse–Hart) 3.4, 3.5; 13.6, 13.13
 - of photon/s (Mach–Zehnder) 3.1–3.3
 - two slits (Young) 3.7, 3.9, 3.12, 3.13; 4.11
 - visibility 3.1, 3.9; 4.1
- Invariance group
 - of the cube 12.16
 - of the equilateral triangle 5.24
 - of the square 10.2
 - of the two-dimensional isotropic harmonic oscillator 10.7, 10.8
- Landau levels 2.9; 13.9, 13.10
- Landé (see Spin–orbit interaction)
- Level repulsion (see Theorem, no-crossing)
- Lifetime 1.2; 2.4; 3.3, 3.14; 14.5, 14.7, 14.11, 14.12; 16.15
- Malus’ law 3.8

- Minimal
 - substitution 13.8
 - for two-particle systems 13.12
- Minimum uncertainty 5.9; 6.16; 7.16
- Muonium (see Exotic atoms)
- Normal modes of vibration 1.3, 1.8–1.10
- Observables
 - as measurement devices 4.3, 4.4
 - compatible 4.4, 4.5
 - representation 5.1
- Particle constrained
 - in a segment 2.6, 2.8, 2.10, 2.12; 7.2; 10.2; 11.2; 12.1
 - in a sphere 11.2
 - in a square 10.2
 - in a triangle 10.3
- Pauli principle 2.13; 15.13, 15.15; 16.13
- Perturbations
 - in hydrogen-like ions 12.13–12.20; 16.1–16.3
 - in one-dimensional systems 12.1–12.9
 - third and fourth order formulae 12.5
- Polarization
 - state (see also Statistical mixture) 3.8–3.11; 4.2, 4.3; 5.4
 - degree 5.2, 14.10
 - in electromagnetic transitions 1.1; 14.4, 14.10, 14.13
 - photons 3.8–3.11; 4.2, 4.3; 5.4
- Positronium (see Exotic atoms)
- Potential/s
 - in one dimension
 - Dirac delta 6.18, 6.19, 6.23–6.26; 12.1, 12.2
 - double well 6.21, 6.23–6.25; 7.4
 - anharmonic $ax^4 (+bx^2)$ 6.2, 6.3, 6.8
 - infinite potential well 2.6, 2.8, 2.10; 6.11; 7.2, 7.3
 - rectangular 6.9–6.13
 - reflectionless ($\propto \cosh^{-2}(x/a)$) 6.17
 - $\propto (x/a)^{2k}$ 2.8
 - radial in two dimensions 11.4, 11.6, 11.7
 - radial in three dimensions 11.2, 11.5, 11.8–11.10; 12.11
 - $\propto r^{-s}$ 11.10; 12.11
 - superpotential 6.22
- Probability density 5.19, 5.21, 5.22; 6.16; 10.4; 15.11
- Quantum fluctuations (see Effect, Hambury Brown–Twiss)
- Radiation in the dipole approximation
 - angular distribution 14.4, 14.10, 14.13
 - polarization 1.1; 14.4, 14.8–14.10, 14.13
- Radiation of classical systems 1.1–1.3
- Reduced radial function 11.1–11.6, 11.9, 11.12
- Reference frame 9.2, 9.3
 - in free fall 9.9
 - in translational motion 9.8
 - in uniform motion 5.8; 9.6, 9.7
 - rotated 9.5
 - rotating 9.10; 10.5; 11.11; 15.3
 - translated 9.4
- Reflection and transmission coefficients 6.12, 6.14, 6.15, 6.17, 6.19
- Representation/s
 - of states and observables 5.1, 5.3, 5.5
 - momentum 5.14, 5.15, 5.20; 6.18
 - Schrödinger 5.13–5.16, 5.18, 5.20; 6.18
- Relativistic effects (see Hydrogen atom)
- Rotational levels of polyatomic molecules 15.2, 15.3
- Rotation operators 8.3, 13.2
- Scattering
 - Rutherford 1.4, 1.5
 - matrix 6.15
 - states 6.17, 6.19

- Schrödinger equation
 - in polar coordinates 11.1, 11.3
 - in dimensionless form 6.2, 6.3
- Selection rules
 - parity 6.1; 12.15
 - angular momentum 8.8; 12.14
 - n (harmonic oscillator) 12.6
- Separation of variables 2.7; 10.1–10.4, 10.6
- Singlet and triplet states 15.5–15.7
- Slater determinant 16.9, 16.10
- Specific heats 1.6, 1.7; 2.11
- Spectral terms (see Electronic configuration)
- Spectroscopy and fundamental constants 2.1–2.5
- Spin $\frac{1}{2}$
 - states 13.1, 13.4
 - rotations 13.2, 13.6
- Spin–orbit interaction 16.9
 - Landé interval rule 16.8, 16.9, 16.12
 - Landé factor 16.15
 - LS coupling 16.8, 16.10, 16.12
 - jj coupling 16.13, 16.14
- Statistical mechanics
 - classical 1.6, 1.7
 - quantum 2.11–2.13
- Statistical mixture/operator 4.6–4.9, 4.14; 5.2, 5.19; 14.10, 14.13; 15.4–15.7, 15.16
- Stern–Gerlach (apparatus) 13.3–13.5; 15.7
- Superposition principle 4.1
- Superpotential (see Potential/s)
- Teleportation 15.17
- Theorem
 - degeneracy 5.24; 6.1; 10.5; 11.11; 12.3, 12.16
 - Feynman–Hellmann 12.10, 12.11
 - no-crossing 12.12
 - nondegeneracy 6.1
 - virial 5.7; 12.11
 - von Neumann 5.6, 5.8; 10.8
 - Wigner 9.1
- Thomson’s atomic model 1.1–1.5
- Time reversal 5.20; 7.10
- Transfer matrix 6.14, 6.19–6.21
- Transformation/s
 - canonical 5.7, 5.8, 5.24; 8.8; 9.4, 9.8, 9.10; 10.1; 13.7, 13.8, 13.12
 - Galilei 5.8; 9.6
 - gauge 13.7–13.9
 - of states and observables 9.2, 9.3
 - scale 5.6, 5.23; 6.2; 11.9; 12.11; 16.5
- Translation operators 5.8
- Triplet states (see Singlet and triplet states)
- Tunnel effect 6.13; 7.4
- Two-level system 2.11; 7.13
- Uncertainty relations 3.12–3.14; 4.12; 5.9
- Variational method 1.8; 6.4–6.8, 6.24; 11.5, 11.8, 11.10
- Vibrational and rotational levels of linear molecules 11.12, 11.13
- von Neumann postulate (wavefunction collapse) 3.3; 4.5, 4.10; 5.25; 8.9
- Waveguide 10.4; 11.7
- Zeeman multiplet 13.12; 16.2



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