ICFP M2 Advanced Quantum Mechanics
Supplementary exercises, series #2

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1 The virial theorem

We consider the following Hamiltonian describing a single quantum particle in three–dimensional space:

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) , \tag{1}$$

where $\boldsymbol{r}$ is the position of the particle, $\boldsymbol{p}$ its conjugate momentum, and m its mass. The operator $V(\boldsymbol{r})$ is the external trapping potential. *Our aim is to obtain a relation between the expectation values, calculated in a stationary state of H, of the kinetic and potential energies under a hypothesis on the behaviour of $V(\boldsymbol{r})$ under scaling transformations.* Specifically, we assume that the potential energy is a homogeneous function of degree α:

$$\text{For any real number } \lambda, \quad V(\lambda\boldsymbol{r}) = \lambda^\alpha V(\boldsymbol{r}) . \tag{2}$$

1. We consider a stationary state $|\Phi\rangle$ of H.
   a) Show that, for any operator T, the expectation value $\langle\Phi|\,[H,T]\,|\Phi\rangle$ of the commutator $[H,T]$ is equal to 0.
   b) We now assume that T is a hermitian operator, and interpret it as the generator for a continuous unitary transformation[1] U_ν indexed by ν. In other words:

   $$\text{For small } \nu, \quad U_\nu = 1 - i\nu T . \tag{3}$$

   Calculate the expectation value $\langle\Phi|(1+i\nu T)H(1-i\nu T)|\Phi\rangle$ up to first order in ν, and interpret the property of question 1a in terms of the stationarity of the energy $E[\Psi]$ associated with Schrödinger's equation,

   $$E[\Psi] = \langle\Psi|H|\Psi\rangle = \int d^3r \left(-\frac{\hbar^2}{2m}\Psi^*\nabla^2\Psi + V(\boldsymbol{r})\,|\Psi(\boldsymbol{r})|^2\right) , \tag{4}$$

   near the stationary state $\Psi(\boldsymbol{r}) = \Phi(\boldsymbol{r})$.

We now focus on scaling transformations. We introduce the transformation U_ν, which maps the wavefunction $\Psi(\boldsymbol{r})$ onto the wavefunction $\Psi_\nu(\boldsymbol{r})$, defined by:

$$\Psi_\nu(\boldsymbol{r}) = \langle\boldsymbol{r}|U_\nu|\Psi\rangle = (1+\nu)^{3/2}\,\Psi((1+\nu)\boldsymbol{r}) . \tag{5}$$

2. Two properties of the transformation U_ν:
   a) Prove that U_ν is a unitary transformation.
   b) Show that the corresponding generator is $S = -(\boldsymbol{r}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{r})/(2\hbar)$, meaning that:

   $$\Psi_\nu(\boldsymbol{r}) = \Psi(\boldsymbol{r}) + i\nu\,\frac{\boldsymbol{r}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{r}}{2\hbar}\,\Psi(\boldsymbol{r}) . \tag{6}$$

3. Proof of the virial theorem:
   a) Calculate the commutator $[H,S]$:

   $$[H, S] = [H, -\frac{\boldsymbol{p}\cdot\boldsymbol{r} + \boldsymbol{r}\cdot\boldsymbol{p}}{2\hbar}] = i\left[2\,\frac{\boldsymbol{p}^2}{2m} - (\boldsymbol{r}\cdot\nabla)\,V(\boldsymbol{r})\right] . \tag{7}$$

[1] For example, for translations along x, $T = p_x/\hbar$ and $\nu = x$; for rotations of angle θ about the axis $\boldsymbol{e}_z$, $T = J_z/\hbar$ is the projection of the angular momentum along z and $\nu = \theta$.

b) Recast the homogeneity property of Eq. (2) into the form: $(\boldsymbol{r}\cdot\nabla)V(\boldsymbol{r}) = \alpha\, V(\boldsymbol{r})$.

c) Using questions 1a, 3a, and 3b, show that the expectation values, calculated in the stationary state $|\Phi\rangle$, of the kinetic energy and the potential energy satisfy:

$$2\,\langle\Phi|\,\frac{\boldsymbol{p}^2}{2m}\,|\Phi\rangle \quad = \quad \alpha\,\langle\Phi|V(\boldsymbol{r})|\Phi\rangle\ . \tag{8}$$

4. Applications of the virial theorem:

a) *For a three–dimensional harmonic oscillator* (which is not necessarily isotropic), show that the virial theorem states the equipartition of the total energy of any stationary state between the kinetic energy and the potential energy: $\langle\Phi|\boldsymbol{p}^2/(2m)|\Phi\rangle = \langle\Phi|V(\boldsymbol{r})|\Phi\rangle$.

b) *For the hydrogen atom,* we consider a discrete stationary state $|\phi_{n,l,m}\rangle$ with the energy $E_{n,l,m}$, labelled by the principal, angular, and magnetic quantum numbers n, l, m. Show that the expectation value of the kinetic energy only depends on n:

$$\langle\phi_{n,l,m}|\,\frac{\boldsymbol{p}^2}{2m}\,|\phi_{n,l,m}\rangle \quad = \quad -E_{n,l,m} \quad = \quad +\frac{\mathrm{Ry}}{n^2}\ , \tag{9}$$

where the Rydberg energy $\mathrm{Ry} = 13.6\,\mathrm{eV} = h \times 3.28 \times 10^{15}\,\mathrm{Hz}$ is the ionisation energy.

Further reading

- More details concerning continuous symmetry groups and their generators may be found in [1, chap. XIV, §9]. Reference [2, chap. 10] provides a more mathematically–oriented (but accessible) presentation.
- The virial theorem is not specifically quantum–mechanical. It also holds in classical mechanics, where the average is performed over time [3, §3.4]. An alternate derivation of the quantum–mechanical result may be given which closely follows the classical argument [4, chap. 3, §6]. It involves interpreting the result of question 1a in terms of the time–derivative of the expectation value $\langle\boldsymbol{p}\cdot\boldsymbol{r}\rangle$. However, it obfuscates both the stationary nature of the quantum result and the key role of scaling transformations.
- The quantum virial theorem may also be formulated in the context of the Gross–Pitaevskii equation [5, §11.3] There, the variational principle of question 1b is very useful.
- The virial theorem plays a key role in the statistical physics of gases because of its relation to the virial expansion [6, exercise 7.6 and chap. 10]. The link resides in the following equation, valid for a uniform gas described by classical or quantum physics:

$$\frac{3}{2}\,\frac{PV}{\langle K\rangle} \quad = \quad 1 + \frac{\langle\sum_i \boldsymbol{r}_i\cdot d\boldsymbol{p}_i/dt\rangle}{2\,\langle K\rangle}\ , \tag{10}$$

where P is the pressure, V is the total volume occupied by the gas, and $\langle K\rangle$ is the average kinetic energy (which reduces to $3Nk_{\mathrm{B}}T/2$ for N classical particles). Inside the average on the right–hand side of Eq. (10), the sum is taken over all particles in the system, whose positions and momenta are $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$. In the classical limit, and assuming the particles do not interact with each other, Eq. (10) reduces to the ideal gas law. The virial expansion characterises the deviation from the ideal case: it consists in expanding the fraction on the right–hand side of Eq. (10) in increasing powers of the density $n = N/V$.

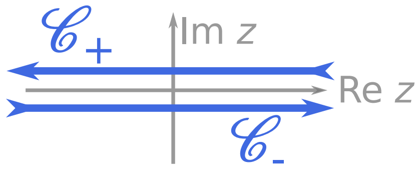

Figure 1 The contours $\mathscr{C}_+$ and $\mathscr{C}_-$ in the complex plane used in Eq. (14). Both are parallel to the real axis and infinitesimally close to it. The contour $\mathscr{C}_+$ is slightly above the real axis and oriented from right to left; $\mathscr{C}_-$ is slightly below the real axis and oriented from left to right.

2 Perturbation theory using the resolvent and projection operators

2.1 Evolution and resolvent operators

We consider a quantum system described by the Hamiltonian H. We introduce the resolvent operator $G(z)$, which is a function of the complex number z (homogeneous to an energy) defined by:

$$G(z) = \frac{1}{z - H} \; . \tag{11}$$

1. Recall the link between the bound states and continuous spectrum of H on the one hand, and the poles and branch cut of G on the other hand. Show the poles and the branch cut of G on a sketch of the complex plane.

We now turn to the evolution operator associated with H, which is a function $U(t)$ of the time t, defined by:

$$U(t) = \exp(-i\,H\,t/\hbar) \tag{12}$$

2. Show that $G(z)$ may be obtained from $U(t)$ through the following relation:

$$G(z) = -\frac{i}{\hbar}\int_0^{\eta\infty} e^{izt/\hbar}\, U(t)\, dt \; , \quad \text{where } \eta = \text{sign}(\text{Im}\, z) \text{ is the sign of the imaginary part of } z. \tag{13}$$

   Hint: Introduce a basis of states in which H is diagonal.

The inverse transformation, expressing $U(t)$ in terms of $G(z)$, requires more care. We call $\mathscr{C}_+$ the (open) contour in the complex plane which is parallel to the real axis and goes from $+\infty + i0^+$ to $-\infty + i0^+$, from right to left. Similarly, we call $\mathscr{C}_-$ the (open) contour which is parallel to the real axis and goes from $-\infty - i0^+$ to $+\infty - i0^+$, from left to right. The contours $\mathscr{C}_+$ and $\mathscr{C}_-$ are both shown on Fig. 1.

3. Show the following relations by completing $\mathscr{C}_+$ and $\mathscr{C}_-$ into two different closed contours in the complex plane:

$$\theta(t)e^{-iHt/\hbar} = \int_{\mathscr{C}_+} \frac{dz}{2\pi i}\, e^{-izt/\hbar}\, \frac{1}{z-H} \quad \text{and} \quad \theta(-t)e^{-iHt/\hbar} = \int_{\mathscr{C}_-} \frac{dz}{2\pi i}\, e^{-izt/\hbar}\, \frac{1}{z-H} \; , \tag{14}$$

   where $\theta(t)$ is the Heaviside step function: $\theta(t) = 0$ for $t < 0$ and $\theta(t) = 1$ for $t > 0$.

4. Combining the two parts of Eqs. (14), conclude as to the reciprocal transformation of Eq. (13):

$$U(t) = -\int_{-\infty}^{+\infty} \frac{dE}{2\pi i}\, e^{-iEt/\hbar}\, \left[G(E + i0^+) - G(E - i0^+)\right] \; . \tag{15}$$

2.2 Projection operators, linewidths and shifts

We write $H = H_0 + V$, all three operators in this equality being hermitian. We introduce a projector P (that is, a linear operator satisfying $P^2 = P$) which is orthogonal (i.e. hermitian: $P^\dagger = P$) and commutes with H_0: $PH_0 = H_0P$. We call $Q = 1 - P$ the projector on the supplementary subspace.

5. Show that $PH_0Q = QH_0P = 0$, meaning that H_0 has no "off–diagonal" elements in terms of P and Q.

6. Establish the following two identities:

$$P(z - H)PG(z)P - PVQG(z)P = P \quad \text{and} \quad -QVPG(z)P + Q(z-H)QG(z)P = 0 \tag{16}$$

   Hint: Start from the definition, $(z - H)G(z) = 1$, and think in terms of a matrix written by blocks corresponding to the subspaces represented by P and Q. One relation represents a diagonal block and the other an off–diagonal block.

7. Eliminate QGP between the two relations of Eq. (16) to obtain the key result:

$$PG(z)P = P\,\frac{1}{z - PHP - W(z)}\,P, \quad \text{where} \quad W(z) = PVQ\,\frac{1}{z - QHQ}\,QVP\ . \tag{17}$$

On which Hilbert space or subspace does the operator $W(z)$ operate?

We wish to calculate $PU(t)P$ using Eq. (15). Therefore, we specialise Eq. (17) to the two important cases $z = E \pm i0^+$. We recall the following identity relating the Cauchy principal value $\mathscr{P}$ to the Dirac peak δ:

$$\frac{1}{u \pm i0^+} = \mathscr{P}\frac{1}{u} \mp i\pi\delta(u)\ . \tag{18}$$

8. Justify the following relation between operators:

$$\frac{1}{E - QHQ \pm i0^+} = \mathscr{P}\frac{1}{E - QHQ} \mp i\pi\delta(E - H)\ . \tag{19}$$

9. Write $W(E \pm i0^+) = \Delta(E) \mp i\Gamma(E)/2$ in terms of the shift operator $\Delta(E)$ and the linewidth $\Gamma(E)$, both of which depend on E and are Hermitian:

$$\Delta(E) = PVQ\,\mathscr{P}\frac{1}{E - QHQ}\,QVP \quad \text{and} \quad \Gamma(E) = 2\pi\,PVQ\,\delta(E - QHQ)\,QVP\ . \tag{20}$$

Check that $\Gamma(E)$ is a positive operator: its average in any state $|\psi\rangle$ satisfies $\langle\psi|\Gamma(E)|\psi\rangle \geq 0$.

10. Justify that the expansions $\widetilde{W}(z)$, $\widetilde{\Delta}(E)$, $\widetilde{\Gamma}(E)$ of $W(z)$, $\Delta(E)$, and $\Gamma(E)$ to second order in V are obtained by replacing QHQ by H_0 in Eq. (20):

$$\widetilde{W}(z) = PVQ\frac{1}{z - H_0}QVP, \quad \widetilde{\Delta}(E) = PVQ\,\mathscr{P}\frac{1}{E - H_0}\,QVP, \quad \widetilde{\Gamma}(E) = 2\pi\,PVQ\,\delta(E - H_0)\,QVP\ . \tag{21}$$

2.3 The case where P projects onto a single eigenstate of H_0

From now on, we consider an eigenstate $|\phi_0\rangle$ of H_0 with the energy E_0. We choose the projector P which projects onto the unidimensional subspace spanned by $|\phi_0\rangle$, that is, $P = |\phi_0\rangle\langle\phi_0|$. Then, the operators $PG(z)P$, $W(z)$, $\Delta(E)$ and $\Gamma(E)$ reduce to the *functions* $\langle\phi_0|G(z)|\phi_0\rangle$, $\langle\phi_0|\Delta(E)|\phi_0\rangle$, and $\langle\phi_0|\Gamma(E)|\phi_0\rangle$. Equation (17) now reads:

$$\langle\phi_0|G(z)|\phi_0\rangle = \frac{1}{z - E_0 - \langle\phi_0|V|\phi_0\rangle - \langle\phi_0|W(z)|\phi_0\rangle} \tag{22}$$

11. Explain why replacing W by a perturbative approximation in Eq. (22) yields an approximation for $\langle\phi_0|G(z)|\phi_0\rangle$ which is non–perturbative, in the sense that it amounts to summing over an infinite number of terms in the perturbative expansion (but not over all terms).

    Hint: Rewrite Eq. (22) as the sum of a geometric series, which you may then interpret diagramatically.

Our final step in this section is to highlight the link between $\widetilde{\Delta}(E)$ and $\widetilde{\Gamma}(E)$. For that purpose, we now introduce a full basis $\{|\phi_a\rangle\}$ in which the *bare* Hamiltonian H_0 is diagonal: $H_0 = \sum_a E_a\,|\phi_a\rangle\langle\phi_a|$. The index $a = 0$ corresponds to the eigenstate $|\phi_0\rangle$ related to the projector $P = |\phi_0\rangle\langle\phi_0|$, so that $Q = 1 - P = \sum_{a\neq 0}|\phi_a\rangle\langle\phi_a|$.

12. Express the approximate shift $\widetilde{\Delta}(E)$ and linewidth $\widetilde{\Gamma}(E)$ in terms of the basis states $\{|\phi_a\rangle\}$:

$$\widetilde{\Delta}(E) = \mathscr{P}\sum_{a\neq 0}\frac{|\langle\phi_a|V|\phi_0\rangle|^2}{E - E_a} \quad \text{and} \quad \widetilde{\Gamma}(E) = 2\pi\sum_{a\neq 0}|\langle\phi_a|V|\phi_0\rangle|^2\delta(E - E_a)\ . \tag{23}$$

13. Deduce from Eq. (23) that the displacement $\widetilde{\Delta}(E)$ and the linewidth $\widetilde{\Gamma}(E)$ satisfy the following relation:

$$\widetilde{\Delta}(E) = \frac{1}{2\pi}\,\mathscr{P}\int dE'\,\frac{\widetilde{\Gamma}(E')}{E - E'}\ . \tag{24}$$

Equation (24) expresses the Kramers–Kronig relation connecting the dissipative effect of the perturbation V (i.e. the linewidth $\widetilde{\Gamma}(E)$ describing irreversible decay) to its reactive effect (i.e. the radiative shift $\widetilde{\Delta}(E)$).

14. In which other context have you encountered similar Kramers–Kronig relations?
    Identify the common point shared by the two theories.
    Hint: What is the theory underlying e.g. susceptibilities, refractive indices ... etc.?

Further reading

- A concise and rigorous presentation of the techniques associated with the resolvent may be found in Messiah's book [1]: §15–17 in chapter XVI, and §13 and §15 in chapter XXI, are especially relevant.

References

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