Introduction to Quantum Mechanics, 3rd edition
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New Errata, October 26, 2023

- Page 3, Eq. 1.2: "1.054573" → "1.054572".
- Page 5, line 4 of item 2: "what is to be measured" → "what has to be measured".
- Page 7, footnote 11: "*Nature* **40**" → "*Nature* **401**".
- Page 26, second equation in footnote 3: "+" → "−".
- Page 53, Figure 2.7(b): on the vertical axis, "0.06" → "0.08".
- Page 57, footnote 42, line 3: "Equation 2.102" → "Equation 2.103".
- Page 71, Eq. 2.154: "$(0 < x < a)$" → "$(-a < x < a)$"; "$(x < 0)$" → "$(x < -a)$".
- Page 75, Problem 2.43(c): "Equation 2.99, or" → "Equation 2.99 for the classical (or group) velocity, or".
- Page 76, line 6: "Figure 2.20" → "Figure 2.19".
- Page 88, Problem 2.63: rewrite as follows:

> **Problem 2.63** It is a fundamental result in statistical mechanics that the average energy of a system at (Kelvin) temperature T is[68]
>
> $$\bar{E} = \frac{1}{Z} \sum_{\text{states}} E_{\text{state}} \exp\left[-\frac{E_{\text{state}}}{k_B T}\right] \qquad (2.202)$$
>
> where the sum is over all the stationary states of the system, E_{state} is the energy of the particular state, k_B is **Boltzmann's constant**, and the **partition function** Z is given by
>
> $$Z = \sum_{\text{states}} \exp\left[-\frac{E_{\text{state}}}{k_B T}\right]. \qquad (2.203)$$
>
> The average in Equation 2.202 (written $\bar{E}$) is an average over all the possible states of the system; it should not be confused with the average (written $\langle E \rangle$) over all the possible outcomes of a measurement due to quantum indeterminacy. Quantum mechanics enters the problem *only* through determining the stationary states and their energies.

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[68] See, for instance, Daniel V. Schroeder, *An Introduction to Thermal Physics*, Pearson, Boston (2000), Section 6.1.

The **heat capacity** tells you how much energy (in the form of heat) a system can absorb before its temperature increases by 1° Celsius; it is given by

$$C = \frac{\partial \bar{E}}{\partial T} \,. \tag{2.204}$$

The heat capacity of a solid—which we will investigate in this problem—is due in large part to the energy stored in the vibrations of the atoms.[69]

(a) The calculation of the heat capacity is facilitated by noting that

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z \,, \tag{2.205}$$

where $\beta \equiv 1/k_B\, T$. This identity allows you to obtain $\bar{E}$ directly from Z instead of having to sum another series. Verify Equation (2.205).

(b) Consider a system consisting of a single quantum harmonic oscillator of frequency ω. In this case, the stationary states are labeled by the quantum number n, the sum over states becomes a sum over $n = 0, 1, 2, \ldots$, and the energies of the states are just the E_n from Section 2.3. Show that the partition function for this system is

$$Z = \frac{e^{-\beta\,\hbar\,\omega/2}}{1 - e^{-\beta\,\hbar\,\omega}} \,. \tag{2.206}$$

[*Hint*: The sum can be expressed as a geometric series.]

(c) For the system considered in (b), find $\bar{E}$ and the heat capacity C.

(d) A solid consisting of N atoms may be crudely modeled as a collection of N independent oscillators, each with the same frequency ω.[70] The energy and heat capacity of such a system at temperature T are $3N$ times as great as the corresponding quantities you found in part (c) for a single oscillator. The factor of 3 is because the atoms can oscillate in three dimensions.[71]

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[69] Strictly speaking, Equation 2.204 is the heat capacity at constant volume C_v, meaning that the system's volume is held fixed while it's heated. Because solids expand when they're heated, it is more typical to actually measure C_p, the heat capacity at constant pressure. That said, the two values C_v and C_p are very similar for a solid (though not for a gas) and we don't really need to worry about the distinction in this context.

[70] A less crude model would take into account the fact that the oscillators are coupled and the independent degrees of freedom are the normal modes of oscillation; see Problem 5.38.

[71] The Hamiltonian for an oscillator in three dimensions is

$$H = \frac{1}{2\,m}\,\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{1}{2}\,m\,\omega^2\,\left(x^2 + y^2 + z^2\right)$$

which is just the sum of three one-dimensional oscillator Hamiltonians, and the average energy is therefore three times as large as the one-dimensional case. The details are worked out in Problems 4.46 and 4.47.

Express your answer for the heat capacity of a solid in terms of the **Einstein temperature**[72] $\theta_E = \hbar\,\omega/k_B$ and make a plot of $C/N k_B$ *vs* T/θ_E. It should look something like the heat capacity shown in Figure 2.24.

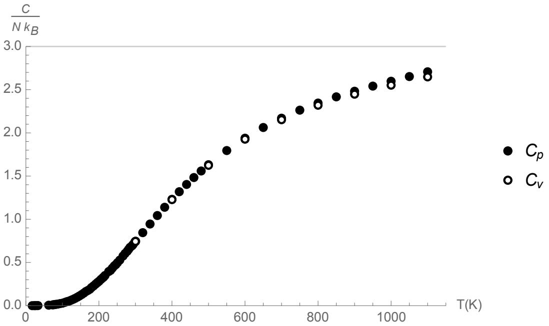

Figure 2.24: Heat capacity of diamond, based on data from W. Desorbo, *J. Chem. Phys.* **21**, 876 (1953) and A. C. Victor, *J. Chem. Phys.* **36**, 1903 (1962).

For a *classical* oscillator the internal energy at temperature T is simply $\bar{E} = k_B\,T$, in accordance with **equipartition of energy**,[73] and a solid consisting of N independent classical oscillators would have a heat capacity of $3\,N\,k_B$, independent of temperature. For materials with a large Einstein temperature, as is the case in Figure 2.24, the quantum nature of the material is evident in the significant departure of the heat capacity from this classical value.

- Page 90: Change the Equation number from (2.208) to (2.207) and the footnote number from 69 to 74.
- Page 90, Problem 2.64(b): change the ending to read "...will diverge for $x > 1$ (it also diverges at $x = 1$; for a proof, see Arfken, Weber, and Harris, footnote 33, page 9)."
- Page 131, two lines above Eq. 4.6: "$d^3\mathbf{r} = dx\,dy\,dz$" → "$d^3\mathbf{r} \equiv dx\,dy\,dz$".
- Page 157, three lines after Eq. 4.96: erase extra "the" at beginning of line.
- Page 167, Problem 4.28: rewrite as follows:

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[72] Known now as the **Einstein model**, the calculation of the heat capacity that you are exploring in this problem was originally published in A. Einstein, *Annalen der Physik* **22**, 180 (1907). An english-language translation is available at einsteinpapers.press.princeton.edu.

[73] See R. Shankar, *Principles of Quantum Mechanics, 2e*, Springer, New York (1994), Exercise 7.5.4, for an extended version of this problem that also guides you through the classical calculation.

> **Problem 4.28** Suppose the electron were a classical solid sphere, with radius
>
> $$R = \frac{3}{5}\, r_c, \quad \text{where} \quad r_c \equiv \frac{e^2}{4\pi\epsilon_0\, mc^2} \tag{4.138}$$
>
> is the so-called **classical electron radius**. (R is the radius you get by assuming the mass of the electron is attributable to the energy stored in its electric field, via the Einstein formula $E = mc^2$. For a spherical *shell* the factor would be 1/2 instead of 3/5.) Suppose also that its angular momentum is $\hbar/2$. How fast would a point on the "equator" be moving? Does this model make sense? (Actually, the radius of the electron is known experimentally to be much less than R, but that only makes matters worse.[39]

- Page 169, top line: "or course" → "of course".
- Page 213, four lines from end of first paragraph: "horizonal" → "horizontal".
- Page 222, footnote 26: "3nd" → "3rd".
- Page 249, footnote 17: add "Here (and below) a repeated index (k, in Eq. 6.33) is to be summed from 1 to 3, by the **Einstein summation convention**."
- Page 262, second line of Eq. 6.66: first subscript on first C on the right should be "$m_1 + 1$", not "$m + 1$".
- Page 267, footnote 39: insert "$i\hbar$" in front of "$\hat{U}^\dagger$".
- Page 299, footnote 13: "Yi-ding" → "Yi-Ding".
- Page 360, line above Eq. 9.25: insert space between "let" and "r".
- Page 362, Problem 9.4, 4 lines after Eq. 9.31: "relevant nuclear masses" → "nuclear (or atomic) masses".
- Page 438, Problem 11.31: replace the whole problem (but keeping the three stars) with the following:

> **Problem 11.31** In Eq. 11.38 I ignored the spatial variation of the electric field, and in constructing the Hamiltonian (11.39) I used the electro*static* formula for the energy of a charge; moreover, I neglected *magnetic* forces entirely. These approximations lead to the so-called "**allowed**" (**electric dipole**) transitions, which typically dominate. But the whole truth is more complicated, and includes "**forbidden**" transitions, which are ordinarily much weaker, but can be significant—especially when selection rules block the electric dipole route.

(a) Starting with Eq. 11.127, but keeping the next term in the Taylor expansion of $e^{i\mathbf{k}\cdot\mathbf{r}}$, show that the correction to the matrix element is

$$\Delta V_{ba} = \frac{e}{m\omega}\langle b|(\mathbf{k}\cdot\mathbf{r})(\mathbf{E}_0\cdot\mathbf{p})|a\rangle. \tag{11.128}$$

(b) Show that this can be written in the form

$$\Delta V_{ba} = \frac{ie\omega_0}{2\omega}\langle b|(\mathbf{k}\cdot\mathbf{r})(\mathbf{E}_0\cdot\mathbf{r})|a\rangle + \frac{e}{2m\omega}(\mathbf{k}\times\mathbf{E}_0)\cdot\langle b|\mathbf{L}|a\rangle. \tag{11.129}$$

The first term gives rise to **electric quadrupole** transitions, and the second to **magnetic dipole** transitions.[39] *Hint:* First prove the following (for (iii), note the hint in Prob. 11.30**c**):

(i) $[(\mathbf{k}\cdot\mathbf{p}),(\mathbf{E}_0\cdot\mathbf{r})] = 0$ (you can write them in either order),
(ii) $(\mathbf{k}\times\mathbf{E}_0)\cdot\mathbf{L} = (\mathbf{k}\cdot\mathbf{r})(\mathbf{E}_0\cdot\mathbf{p}) - (\mathbf{k}\cdot\mathbf{p})(\mathbf{E}_0\cdot\mathbf{r})$,
(iii) $\dfrac{im}{\hbar}[H^0,(\mathbf{k}\cdot\mathbf{r})(\mathbf{E}_0\cdot\mathbf{r})] = (\mathbf{k}\cdot\mathbf{r})(\mathbf{E}_0\cdot\mathbf{p}) + (\mathbf{k}\cdot\mathbf{p})(\mathbf{E}_0\cdot\mathbf{r})$.

(c) By analogy with Eq. 11.63, obtain the spontaneous emission rate for electric quadrupole transitions (don't bother averaging over polarization and propagation directions). *Answer:*

$$A = \frac{e^2\omega_0^5}{4\pi\epsilon_0\hbar c^5}|\langle b|(\hat{k}\cdot\mathbf{r})(\hat{n}\cdot\mathbf{r})|a\rangle|^2. \tag{11.130}$$

(d) Show that for a one-dimensional oscillator the electric quadrupole transitions go from level n to level $n-2$, and the transition rate (suitably averaged over $\hat{n}$ and $\hat{k}$) is

$$A = \frac{\hbar e^2\omega_0^3 n(n-1)}{60\pi\epsilon_0 m^2c^5}. \tag{11.131}$$

Find the *ratio* of this "forbidden" rate to the "allowed" rate, and comment on the terminology.

(e) Show that the $2S \to 1S$ transition in hydrogen is not possible even by these "forbidden" mechanisms. (As it turns out, this is true for all the higher multipoles as well; the dominant decay is in fact by two-photon emission, and the lifetime is about a tenth of a second.)[40]

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[39] For a systematic treatment see David Park, *Introduction to the Quantum Theory*, 3rd edn. (McGraw-Hill, New York, 1992), Chapter 11.

[40] See Masataka Mizushima, *Quantum Mechanics of Atomic Spectra and Atomic Structure* (Benjamin, New York, 1970), Section 5.6.

- Page 459, footnote 21, add (at the beginning): J. L. Park, *Found. Phys.* **1**, 23 (1970);".
- Page 475, three lines up from bottom: erase extra "the".
- Page 480, line below Eq. A.87, add the following: "(If $\mathsf{b}^{(i)} = \mathsf{V}\mathsf{a}^{(i)} = 0$, it's not an eigenvector of T, but $\mathsf{a}^{(i)}$ is still an eigenvector of V—with eigenvalue 0.)"
- Page 488, "efficitive mass → "effective mass"; add subheading for "Ehrenfest's theorem": "generalized 110"; "Fourier's trick": "102" → "103"; under "Einstein" add subentry "summation convention 249".
- Page 490, "linear transformation": "94468" → "94, 468".
- Page 493, add "summation convention 249".
- Page 494: "Uncertainty principle/angular momentum": erase "132".
- Inside back cover: move "Law of cosines" and "Exponential integrals" slightly left, for consistent alignment.