

Fig. 8.1. Schottky anomaly in the specific heat

in § 1.4.4 for the specific heat of a paramagnetic substance placed in a fixed magnetic field.

8.4 Diatomic and Polyatomic Gases

8.4.1 The Born-Oppenheimer Approximation

In order to determine the internal partition function (8.4) and to find from it the thermal properties of the gas, we need to evaluate the eigenenergies ε_q of one molecule, for the ground state ε_0 and for those excited state which lie sufficiently close to the ground state that $\varepsilon_q - \varepsilon_0$ is *at most of the order of magnitude of kT* . To do this we shall use the so-called Born-Oppenheimer approximation (1927) which is of major interest not only in the theory of molecules, but also in the theory of solids (§ 11.1.1).

In the case of a molecule consisting of several atoms an analysis of the spectrum implies not only a study of the motion of the electrons, as in the case of a monatomic molecule, but above all a study of the relative motion of the nuclei. To carry that out we note that the atomic nuclei are several thousand times heavier than the electrons and therefore move much more slowly than the latter, if the kinetic and potential energies are of the same order of magnitude. The Born-Oppenheimer approximation now consists in solving the problem in *two stages*.

We start by studying the *motion of the electrons, neglecting that of the nuclei* which we assume to be fixed in some, arbitrary, positions. We must thus solve a Schrödinger equation describing the electrons, which interact through Coulomb forces, and are subject to a fixed external potential due to the nuclei and depending on the relative positions of the latter. For most

molecules which have rather large binding energies this equation produces electron levels with spacings of the order of 1 eV, corresponding to characteristic temperatures of the order of 10 000 K. As a result, for most gases at room temperature the electron cloud is *frozen in into its lowest state*. The electronic degrees of freedom will therefore, as in the case of monatomic gases, lead only to supplying a multiplicity factor in ζ , if several electronic wavefunctions have the same, or almost the same, energy. In Chap.11 we shall see that the situation is not quite as simple when we apply the Born-Oppenheimer method to solids, since in that case the electron cloud is thermally excited at room temperatures. For the rather tightly bound and rather small molecules considered here we can, on the other hand, restrict ourselves to the single electronic eigenstate with minimum energy, for each, assumed given, arrangement of the nuclei.

To be more precise, the Hamiltonian of one molecule, in the model of § 8.1.1, has the form

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \hat{h} = \hat{T}_n + \hat{T}_e + \hat{V}, \quad (8.38)$$

where \hat{T}_n and \hat{T}_e are the kinetic energies of the nuclei and the electrons and \hat{V} the total Coulomb interaction energy, which depends on both the electron coordinates $\hat{\mathbf{r}}_e$ and the nuclear coordinates $\hat{\mathbf{R}}_n$. The global translational kinetic energy of the molecule, $\hat{\mathbf{p}}^2/2m$ is included in \hat{T}_n , as the mass of the electrons is small compared to the nuclear masses. The first stage of the Born-Oppenheimer method consists in looking for the ground state of the Schrödinger equation

$$\left[\hat{T}_e + \hat{V}(\hat{\mathbf{r}}_e, \mathbf{R}_n) \right] |\psi_e\rangle = W(\mathbf{R}_n) |\psi_e\rangle \quad (8.39)$$

in the Hilbert space of *only the electrons*, dropping \hat{T}_n and regarding the \mathbf{R}_n not as operators, but as parameters. *The energy $W(\mathbf{R}_n)$ of the electronic ground state thus depends on the positions of the nuclei.*

In the second stage we study the *motion of the nuclei* for the lowest electron configuration which we have just determined. To do that we must reintroduce the term \hat{T}_n from (8.38) that we omitted until now, and regard the $\hat{\mathbf{R}}_n$ again as operators which do not commute with \hat{T}_n – a feature which did not occur in (8.39). The approximation made consists in assuming that the electron cloud, which is very mobile, adjusts itself instantly to the configuration of the nuclei which in this way feel the effect of the electrons indirectly. The Hamiltonian of the nuclei thus contains, on top of the kinetic energy \hat{T}_n , the energy $W(\hat{\mathbf{R}}_n)$ which comes both from the Coulomb interaction between the nuclei and from their interaction with the electrons, after the electron coordinates have been eliminated as a result of their being frozen in into the lowest energy state of (8.39). The lowest energy levels of the molecule are thus finally obtained by looking for the eigenvalues of the Schrödinger equation

$$\left[\widehat{T}_n + W(\widehat{\mathbf{R}}_n) \right] |\psi_n\rangle = \varepsilon |\psi_n\rangle \quad (8.40)$$

in the Hilbert space of *only the nuclei*.

We should note that the motion of the centre of mass of the molecule can be separated off in the Born-Oppenheimer approximation (8.40), as it could be done in the case of the exact Hamiltonian (8.1). The eigenenergies ε of (8.40) contain therefore a trivial contribution, the translational kinetic energy $p^2/2m$, which must be subtracted when we construct the required energies ε_q contributing to $\zeta(T)$.

For instance, for a *diatomic molecule* such as HCl the energy W depends only on the distance ϱ between the two nuclei. If for the moment we disregard the direct Coulomb interaction between the nuclei, the energy of the ground state of the 18 electrons is negative; it increases with ϱ from the binding energy of an atom of charge 18 – the combined charge of the Cl and H nuclei – for $\varrho = 0$, to the sum of the binding energies of the two separate, Cl and H, atoms for $\varrho = \infty$. To obtain W we must add to this function the repulsion between the H and Cl nuclei which becomes very large as $\varrho \rightarrow 0$. The result is the curve $W(\varrho)$ shown in Fig.8.2 where we dropped an additive constant. At small distances apart the direct repulsion dominates; at larger distances apart the binding energy of the electrons becomes dominant and $W(\varrho)$ shows a *pronounced minimum* near some value $\varrho = \bar{\varrho}$. The energy $W(\varrho)$ plays the rôle of an *effective interaction potential* for the nuclei in the Schrödinger equation (8.40), where the total energy of the system is equal to $W(\varrho)$ plus the kinetic energy T_n of the nuclei. The latter can be split into a sum of two terms,

$$\widehat{T}_n = \frac{\widehat{\mathbf{p}}^2}{2m} + \frac{\widehat{\boldsymbol{\pi}}^2}{2\mu}, \quad (8.41)$$

where $\widehat{\mathbf{p}}$ is the momentum of the centre of mass of the diatomic molecule, m its total mass, $\widehat{\boldsymbol{\pi}}$ the relative momentum of the two nuclei, the masses of which are μ_1 and μ_2 , and μ the reduced mass

$$\mu = \frac{\mu_1\mu_2}{\mu_1 + \mu_2}. \quad (8.42)$$

Finally, if we drop, as in (8.1), the translational kinetic energy of the molecule, there remains for us the task to solve a Schrödinger equation (8.40), where the coordinates of the electrons and of the centre of mass have been eliminated, with an *effective internal Hamiltonian*

$$\widehat{h} \simeq \frac{\widehat{\boldsymbol{\pi}}^2}{2\mu} + W(\widehat{\varrho}), \quad (8.43)$$

which is the same as that of a single particle with coordinates $\widehat{\varrho}$ in a central potential $W(\varrho)$.

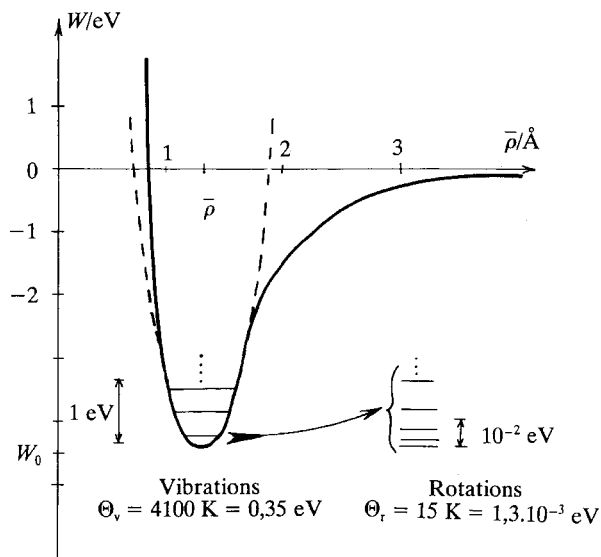


Fig. 8.2. Energy levels of the HCl molecule

The eigenvalues ε_q of (8.43) are found by *separating the angular and the radial variables* and they are characterized by the quantum numbers $q = l, m, n$ where l has a multiplicity $2l + 1$ connected with the quantum number m . Moreover, we should include the quantum numbers of the nuclear spins which may give rise to additional degeneracies – or to quasi-degeneracies, as the magnetic interactions of those spins are negligibly small. In the rest of this chapter we shall study the *rotational* motion (associated with the quantum numbers l and m) and the *vibrational* motion (associated with the radial quantum number n) and their thermodynamic consequences.

A study of the quantum harmonic oscillator shows that the vibrational frequencies $\omega/2\pi$, and thus the spacing $\hbar\omega$ of the levels, are for a given potential inversely proportional to the square root of the mass of the oscillator. As the masses of the nuclei are much larger than the electron mass, one expects that the energy levels of \hat{h} , associated with the relative motion of the nuclei, are much more closely spaced than the excited levels of the electron cloud – which we have justifiably assumed to be frozen in into its ground state. In fact, a numerical estimate of the inertia coefficients for the rotations and vibrations of diatomic molecules, defined by (8.63), shows that they are usually rather large. Hence the corresponding levels lie densely and the *characteristic rotation and vibration temperatures are much lower than the electronic characteristic temperatures*. For instance, for HCl the characteristic rotation temperature is $\Theta_r = 15 \text{ K}$, and the vibration temperature $\Theta_v = 4100 \text{ K}$, corresponding, respectively, to excitation energies of the order of 10^{-3} eV and 0.35 eV .

If the gas is at a *temperature well above these characteristic temperatures* quantization of the levels does not play any rôle as they lie densely on the scale kT ; one can therefore treat the effective Hamiltonian (8.43) as a *classical Hamiltonian* and replace the calculation of the trace in (8.4) by an integration, as we saw in §2.3.2, which leads to

$$\zeta^{\text{cl}} = \int \frac{d^3\pi d^3\boldsymbol{\rho}}{h^3} e^{-h(\pi, \boldsymbol{\rho})/kT}. \quad (8.44)$$

As a first approximation, valid at temperatures which are high as compared to Θ_r and Θ_v , we shall thus treat in § 8.4.3 the internal molecular rotational and vibrational variables by classical statistical mechanics using (8.44). Before doing this we shall prove the energy equipartition theorem which will be useful in that analysis.

Expression (8.44) must in actual cases be multiplied by a multiplicity factor g similar to the one in § 8.3.2. Moreover, if the two atoms of the molecule are *indistinguishable* we must introduce a factor $\frac{1}{2}$, which is a special case of the factor $1/S$ of (2.59), to compensate for the fact that a single configuration of the molecule is represented by two different points in phase space, $\boldsymbol{\pi}, \boldsymbol{\rho}$ and $-\boldsymbol{\pi}, -\boldsymbol{\rho}$. These constant factors do not affect the specific heats, but appear, for instance, in expression (8.14) for the entropy and in the mass action law through (8.30); they thus play an important rôle in chemical thermodynamics. Ehrenfest and Trkal recognized the importance of the symmetry factor S in this context in 1921.

8.4.2 The Energy Equipartition Theorem

One of the problems of statistical mechanics consists in determining *how the energy of a system is distributed* over its various degrees of freedom. We have seen that the general answer to this question is obtained by writing down that the temperatures associated with the independent degrees of freedom become equal. The result takes a particularly simple form for all problems *in classical statistical mechanics where the Hamiltonian is quadratic* in each of the phase space variables which occur in it. Let x_1, \dots, x_n be those variables; they can be either coordinates or momenta. The Hamiltonian is supposed to be a sum of n terms of the form

$$H = \sum_{j=1}^n h_j = \sum_{j=1}^n \frac{1}{2} \alpha_j x_j^2; \quad (8.45)$$

the α_j are arbitrary positive constants, which can be interpreted as elastic force coefficients if x_j is a position coordinate, and as inverse masses or inertia coefficients if x_j is a momentum. In thermal equilibrium the internal energy $U = \langle H \rangle$ is the sum of the average energies $\langle h_j \rangle$ associated with the n degrees of freedom.

The energy equipartition theorem states that under those conditions the *internal energy per degree of freedom* $\langle h_j \rangle$ is equal to $\frac{1}{2}kT$, whatever the value of the constants α_j :