

## Transition from Quantum to "Classical" Partition Function\*

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The quantum-mechanical partition function for a system of interacting electrons and nuclei is examined in the "classical" limit, in which  $\hbar \rightarrow 0$  in the nuclear kinetic energy operator while  $\hbar$  is constant in the electronic kinetic energy operator. It is shown that in the "classical" limit, the apparent nuclear potential energy which appears in the partition function is actually the free energy of the electrons in a system of fixed nuclei, as a function of nuclear configuration and temperature. The lowest order quantum correction is obtained. The effect of the adiabatic approximation is studied; it leads to the correct "classical" limit but a formally inexact lowest order quantum correction.

### I.

THE partition function, in classical statistical mechanics, associated with the Hamiltonian

$$H = \sum_{\alpha=1}^{\nu} \frac{p_{\alpha}^2}{2m_{\alpha}} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{\nu}) \quad (1)$$

is

$$Q_c = \int \int \exp(-\beta H) d\mathbf{r}^{\nu} d\mathbf{p}^{\nu}. \quad (2)$$

(The system contains  $\nu$  particles, with positions  $\mathbf{r}_{\alpha}$ , momenta  $\mathbf{p}_{\alpha}$ , and masses  $m_{\alpha}$ ;  $\beta = 1/kT$ , where  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. The sets of all momenta and all coordinates are denoted by  $\mathbf{p}^{\nu}$  and  $\mathbf{r}^{\nu}$ .) The corresponding quantum-mechanical partition function is

$$Q = \sum_j \exp(-\beta E_j), \quad (3)$$

where  $E_j$  is the energy of the  $j$ th quantum state of the entire system, and is an eigenvalue of the Hamiltonian operator

$$\mathcal{H} = - \sum_{\alpha=1}^{\nu} \frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + U(\mathbf{r}^{\nu}). \quad (4)$$

Kirkwood<sup>1</sup> has discussed the transition from the quantum to the classical partition function for a system with a Hamiltonian of this sort. In particular, he obtained an expansion in powers of  $\hbar$ , of which the first few terms are

$$\frac{\hbar^{3\nu} Q}{Q_c} = 1 + \frac{\hbar^2 \beta}{12} \sum_{\alpha} \frac{1}{2m_{\alpha}} \langle (\nabla_{\alpha} \beta U)^2 - 2 \nabla_{\alpha}^2 \beta U \rangle + O(\hbar^4), \quad (5)$$

where the average  $\langle \rangle$  is taken over the classical Boltzmann distribution in configuration space. This result applied only in the case where the constituent particles are assumed to be distinguishable. Kirkwood also considered the case where the particles obey Bose or

Fermi statistics. He showed that the Gibbs factor  $1/\nu!$  is introduced, and that there are additional quantum corrections which vanish with  $\hbar$ .

In this article we shall extend Kirkwood's discussion to systems in which the potential  $U$  describes the interactions of electrons and nuclei. The electronic contribution to the partition function will be treated in a quantum-mechanically correct way, and the transition to a "classical" partition function will be carried out for the nuclear motions only. We place quotation marks around "classical" because we use the word in a special sense, namely to refer to the limit as  $\hbar \rightarrow 0$  in the nuclear kinetic energy operator, while  $\hbar$  is held constant in the electronic kinetic energy operator. We shall consider only the case in which all nuclei are distinguishable: the extension to Bose or Fermi statistics can be made in exactly the same way as in Kirkwood's treatment, and will lead to the factor  $1/\nu!$  and the same kind of quantum corrections. Our principal result is the following: in the "classical" limit,

$$Q \cong \frac{1}{\hbar^{3\nu}} \int \int \exp \left\{ -\beta \left[ \sum_{\alpha=1}^{\nu} \frac{p_{\alpha}^2}{2m_{\alpha}} + U(\mathbf{r}^{\nu}; \beta) \right] \right\} d\mathbf{r}^{\nu} d\mathbf{p}^{\nu}, \quad (6)$$

where the apparent nuclear potential energy  $U(\mathbf{r}^{\nu}; \beta)$  is given in terms of the electronic energy levels  $\Phi_j(\mathbf{r}^{\nu})$  of the system with nuclei fixed in the configuration  $\mathbf{r}^{\nu}$ ,

$$\exp[-\beta U(\mathbf{r}^{\nu}; \beta)] = \sum_j \exp[-\beta \Phi_j(\mathbf{r}^{\nu})]. \quad (7)$$

That is, the apparent potential energy in the "classical" nuclear Hamiltonian is actually the free energy of the electron system as a function of nuclear configuration and temperature. We shall also obtain the lowest order quantum correction to this result, and compare it with the correction one obtains when the adiabatic approximation is used to separate electronic and nuclear motions.

### II.

We consider a system of  $\nu$  nuclei and  $n$  electrons, with a potential energy of interaction  $U_e(\mathbf{r}^{\nu}, \mathbf{r}^n)$ . The total Hamiltonian  $\mathcal{H}$  of the system is a sum of the

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<sup>1</sup> J. G. Kirkwood, *Phys. Rev.* **44**, 31 (1933); **45**, 116 (1934).

nuclear kinetic energy operator

$$\mathcal{T}_\nu = - \sum_{\alpha=1}^{\nu} \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2, \quad (8)$$

the electronic kinetic energy operator

$$\mathcal{T}_e = - \sum_{j=1}^n \frac{\hbar^2}{2m_e} \nabla_j^2, \quad (9)$$

and the potential energy, so that

$$\begin{aligned} \mathcal{H} &= \mathcal{T}_\nu + \mathcal{H}_e, \\ \mathcal{H}_e &= \mathcal{T}_e + U_e. \end{aligned} \quad (10)$$

(In the following discussion, Greek indices will refer to nuclei and Roman indices will refer to electrons.) The partition function may be written in the form

$$Q = \sum_j \int \int \varphi_j^*(\mathbf{r}^n, \mathbf{r}^\nu) \exp(-\beta \mathcal{H}) \varphi_j(\mathbf{r}^n, \mathbf{r}^\nu) d\mathbf{r}^n d\mathbf{r}^\nu, \quad (11)$$

where the  $\varphi_j$  are an arbitrary complete set, orthonormal in the electronic and nuclear coordinates. Spin quantum numbers can be included implicitly by, for example, interpreting  $\int d\mathbf{r}_j$  as an integral over the space coordinate of the  $j$ th electron and a sum over its spin. We assume that the  $\varphi_j$  have been properly antisymmetrized in the electrons in accordance with the Pauli principle; as indicated before, we treat the nuclei as distinguishable.

A particularly convenient set of functions for our purpose is the one in which  $\mathcal{H}_e$  is diagonal and the nuclear states are plane waves. The eigenfunctions and eigenvalues of  $\mathcal{H}_e$  are given by

$$\mathcal{H}_e \psi_k(\mathbf{r}^n; \mathbf{r}^\nu) = \Phi_k(\mathbf{r}^\nu) \psi_k(\mathbf{r}^n; \mathbf{r}^\nu). \quad (12)$$

The  $\psi_k$  are orthonormal in the electronic coordinates for any  $\mathbf{r}^\nu$ . We therefore replace the  $\varphi_j$  by

$$k^{-3\nu/2} \exp\left(-\frac{i}{\hbar} \sum_{\alpha} \mathbf{p}_\alpha \cdot \mathbf{r}_\alpha\right) \psi_k(\mathbf{r}^n; \mathbf{r}^\nu), \quad (13)$$

and replace the sum over  $j$  in Eq. (11) by a sum over  $k$  and an integral over  $\mathbf{p}^\nu$ . The quantum corrections to the partition function can now be localized in a function  $w_k$  defined by

$$\begin{aligned} \exp(-\beta \mathcal{H}) \exp\left(-\frac{i}{\hbar} \sum_{\alpha} \mathbf{p}_\alpha \cdot \mathbf{r}_\alpha\right) \psi_k \\ = \exp\left(-\frac{i}{\hbar} \sum_{\alpha} \mathbf{p}_\alpha \cdot \mathbf{r}_\alpha\right) \psi_k \exp(-\beta H_k) w_k, \end{aligned} \quad (14)$$

where

$$H_k = \sum_{\alpha=1}^{\nu} \frac{p_\alpha^2}{2m_\alpha} + \Phi_k(\mathbf{r}^\nu). \quad (15)$$

Then the partition function becomes

$$Q = \frac{1}{h^{3\nu}} \int \int \sum_k \exp(-\beta H_k) b_k(\mathbf{r}^\nu) d\mathbf{r}^\nu d\mathbf{p}^\nu, \quad (16)$$

where

$$b_k(\mathbf{r}^\nu) = \int \psi_k^* \psi_k \langle w_k \rangle d\mathbf{r}^n, \quad (17)$$

and

$$\begin{aligned} \langle w_k \rangle = \int \exp\left(-\beta \sum_{\alpha} \frac{p_\alpha^2}{2m_\alpha}\right) w_k d\mathbf{p}^\nu / \\ \int \exp\left(-\beta \sum_{\alpha} \frac{p_\alpha^2}{2m_\alpha}\right) d\mathbf{p}^\nu \end{aligned} \quad (18)$$

is the average of  $w_k$  over the classical momentum distribution.

A differential equation for  $w_k$  may be obtained by differentiating Eq. (14) with respect to  $\beta$  and rearranging the result. This equation is

$$\begin{aligned} \frac{\partial w_k}{\partial \beta} = \sum_i \frac{\hbar_e^2}{2m_e} [\nabla_j^2 w_k + 2(\nabla_j \ln \psi_k) \cdot \nabla_j w_k] \\ + \sum_{\alpha} \frac{1}{2m_\alpha} [\hbar^2 \beta^2 (\nabla_\alpha \Phi_k)^2 w_k - \hbar^2 \beta (\nabla_\alpha^2 \Phi_k) w_k \\ + \hbar^2 (\nabla_\alpha^2 \psi_k w_k) / \psi_k - 2\hbar^2 \beta (\nabla_\alpha \Phi_k) \cdot (\nabla_\alpha \psi_k w_k) / \psi_k \\ - 2i\hbar \beta \mathbf{p}_\alpha \cdot (\nabla_\alpha \Phi_k) w_k + 2i\hbar \mathbf{p}_\alpha \cdot (\nabla_\alpha \psi_k w_k) / \psi_k]. \end{aligned} \quad (19)$$

We wish to find a solution of this equation of the form

$$w_k = w_k^{(0)} + \hbar w_k^{(1)} + \hbar^2 w_k^{(2)} + \dots, \quad (20)$$

where  $\hbar$  in this expression comes solely from the nuclear part of the Hamiltonian  $\mathcal{H}$ . For this reason, we denote by  $\hbar_e$  the Planck's constant which goes with the electronic Hamiltonian  $\mathcal{H}_e$ . This means that we do not expand  $\Phi_k$  and  $\psi_k$  in powers of  $\hbar$ , but keep them in their exact forms. The initial condition for the equation for  $w_k$  is clearly

$$\lim_{\beta \rightarrow 0} w_k = 1. \quad (21)$$

The first term in the expansion can be obtained by inspection. It is  $w_k^{(0)} = 1$ . The equation for  $w_k^{(1)}$  is

$$\frac{\partial w_k^{(1)}}{\partial \beta} = \Omega_k \cdot w_k^{(1)} + i \sum_{\alpha} \frac{\mathbf{p}_\alpha}{m_\alpha} \cdot [(\nabla_\alpha \ln \psi_k) - \beta \nabla_\alpha \Phi_k], \quad (22)$$

where

$$\Omega_k = \frac{\hbar_e^2}{2m_e} \sum_i [\nabla_j^2 + 2(\nabla_j \ln \psi_k) \cdot \nabla_j]. \quad (23)$$

A formal solution in terms of the operator  $\Omega_k$  is

$$w_k^{(1)} = -\frac{i\beta^2}{2} \sum_{\alpha} \frac{\mathbf{p}_{\alpha}}{m_{\alpha}} \cdot \nabla_{\alpha} \Phi_k + i \sum_{\alpha} \frac{\mathbf{p}_{\alpha}}{m_{\alpha}} \cdot [(\exp \beta \Omega_k) - 1] \Omega_k^{-1} \nabla_{\alpha} \ln \psi_k. \quad (24)$$

Since  $w_k^{(1)}$  is linear in the momenta, we see that  $\langle w_k^{(1)} \rangle = 0$ .

The equation for  $w_k^{(2)}$  is

$$\begin{aligned} \frac{\partial w_k^{(2)}}{\partial \beta} = & \Omega_k \cdot w_k^{(2)} + \sum_{\alpha} \frac{1}{2m_{\alpha}} \{ \beta^2 (\nabla_{\alpha} \Phi_k)^2 - \beta \nabla_{\alpha}^2 \Phi_k \\ & + (\nabla_{\alpha}^2 \psi_k) / \psi_k - 2\beta (\nabla_{\alpha} \Phi_k) \cdot \nabla_{\alpha} \ln \psi_k \\ & - 2i \mathbf{p}_{\alpha} \cdot (\nabla_{\alpha} \Phi_k) w_k^{(1)} + 2i \mathbf{p}_{\alpha} \cdot (\nabla_{\alpha} \ln \psi_k) w_k^{(1)} \\ & + 2i \mathbf{p}_{\alpha} \cdot \nabla_{\alpha} w_k^{(1)} \}. \quad (25) \end{aligned}$$

Instead of obtaining a formal closed solution of this equation, we solve for the first few terms of an expansion of  $w_k^{(2)}$  in powers of  $\beta$ . We then average these terms over momenta, thus introducing a new factor  $\beta$  from each average  $\langle p_{\alpha}^2 \rangle$ . Also, we associate a factor  $\beta$  with each  $\Phi_k$  which appears in the solution. After these changes, the series expansion may be rearranged to the following result:

$$\frac{\langle w_k^{(2)} \rangle}{\beta} = \frac{1}{12} \sum_{\alpha} \frac{1}{2m_{\alpha}} [(\nabla_{\alpha} \beta \Phi_k)^2 - 2 \nabla_{\alpha}^2 \beta \Phi_k] + \text{terms of order } \beta. \quad (26)$$

To the lowest order in which quantum effects appear,  $b_k$  is given by

$$b_k = 1 + \hbar^2 \langle w_k^{(2)} \rangle + \dots \quad (27)$$

The quantum correction for each electronic energy level, neglecting the terms of order  $\beta$  in Eq. (26), has just the same form as the one Kirkwood obtained. We thus obtained Eq. (6) in the "classical" limit.

### III.

It is interesting to compare the preceding results with what one would get by a straightforward application of the adiabatic approximation. We follow the discussion of the adiabatic approximation which has been given by Born and Huang.<sup>2</sup> First, the eigenvalues and eigenfunctions of  $\mathcal{H}_e$  are obtained. Then the exact eigenvalue equation for the total system becomes

$$(\mathcal{T}_v + \Phi_j - C_{jj} - E) \phi_j = \sum_k' C_{jk} \phi_k, \quad (28)$$

where

$$C_{jk} = \sum_{\alpha} \frac{-\hbar^2}{2m_{\alpha}} \left[ \int \psi_j^* \nabla_{\alpha}^2 \psi_k d\mathbf{r}^n + 2 \int \psi_j^* (\nabla_{\alpha} \psi_k) d\mathbf{r}^n \cdot \nabla_{\alpha} \right], \quad (29)$$

and the prime on the summation indicates that the term  $k=j$  is to be omitted. The essence of the adiabatic approximation is that the off-diagonal elements of the matrix  $C_{jk}$  are neglected, thus leading to a separation of electronic and nuclear motions. Physically, this amounts to the assumption that no transitions occur between distinct electronic states. The diagonal elements  $C_{jj}$  simplify to

$$C_{jj} = - \sum_{\alpha} \frac{\hbar^2}{2m_{\alpha}} \int \psi_j^* \nabla_{\alpha}^2 \psi_j d\mathbf{r}^n. \quad (30)$$

(Wu<sup>3</sup> and Wu and Bhatia<sup>4</sup> have estimated  $C_{jj}$  for the lowest electronic states of  $\text{H}_2$ ,  $\text{H}_2^+$ , and  $\text{He}+\text{He}$ . They conclude that for these systems it can be comparable with the Van der Waal's energies of interaction. For systems of heavier nuclei it may be negligible, however.)

When the adiabatic approximation is made, the nuclear Hamiltonian for the  $j$ th electronic state is  $\mathcal{T}_v + \Phi_j - C_{jj}$ . Now that the electronic contributions to the partition function have been split off, we may apply Kirkwood's procedure directly to each electronic energy level. The result is easily obtained, and is

$$Q^{(a)} = \frac{1}{\hbar^{3v}} \int \int \sum_k \exp(-\beta H_k) b_k^{(a)}(\mathbf{r}^v) d\mathbf{r}^v d\mathbf{p}^v, \quad (31)$$

where the superscript  $(a)$  stands for adiabatic, and  $b_k^{(a)}$  is

$$b_k^{(a)} = 1 + \frac{\hbar^2 \beta}{12} \sum_{\alpha} \frac{1}{2m_{\alpha}} \left\{ (\nabla_{\alpha} \beta \Phi_k)^2 - 2 \nabla_{\alpha}^2 \beta \Phi_k - 12 \int \psi_k^* \nabla_{\alpha}^2 \psi_k d\mathbf{r}^n \right\}, \quad (32)$$

with the neglect of higher powers of  $\hbar$ . The last term in Eq. (32) comes from  $C_{jj}$  in  $\exp[-\beta(\Phi_j - C_{jj})]$ . It is clear that when the adiabatic approximation is made, and then the expansion in powers of  $\hbar$  is formed, the resulting quantum correction is not identical with the one obtained by our earlier more direct calculation, partly because of the  $C_{jj}$  contribution to  $b_k^{(a)}$  and partly because of the terms of order  $\beta$  which appear in Eq. (26) but not in Eq. (32).

We have not investigated the convergence of the expansion in powers of  $\hbar$ , nor have we estimated the relative magnitudes of the various terms which appear in the quantum corrections. We see, however, that in a purely formal way the adiabatic approximation does not lead to an exact result as far as the lowest order quantum correction is concerned, and also that the  $C_{jj}$  terms should not be included in the nuclear Hamiltonian in the "classical" limit.

<sup>2</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

<sup>3</sup> T-Y. Wu, J. Chem. Phys. 24, 444 (1956).

<sup>4</sup> T-Y. Wu and A. B. Bhatia, J. Chem. Phys. 24, 48 (1956).