

Kopplung der Elektronen- und Kernbewegung in Molekeln und Kristallen

Von

M. Born

Vorgelegt in der Sitzung am 23. November 1951

citation: M. Born, Kopplung Der Elektronen- und Kernbewegung in Molekeln und Kristallen. Nachrichten der Akademie der Wissenschaften in Göttingen. Mathematisch-Physikalische Klasse, volume 6, pages 1–3 (1951).

Translated by D. G. Truhlar.

Coupling of electron and nuclear motion in molecules and crystals

by

M. Born

Published at the headquarters on November 23, 1951

In my work "The limits of validity of the theory of ideal crystals and overcoming them,"¹ I separated the motion of electrons by an approximation method that differs from the usual "adiabatic" way. I believed that this was the only way to achieve a calculation in which the mean nuclear positions X remained unspecified throughout the entire calculation. I have now seen that the same result can also be achieved in an adiabatic way.

The Hamiltonian of the entire system is the same as before:

$$H = \frac{1}{2} \sum_k \frac{1}{M_k} P_k^2 + \frac{1}{2} \sum_l \frac{1}{m} p_l^2 + \Phi(x, X), \quad (1)$$

where Φ is the potential (Coulombic) energy.

If the nuclei are held fixed, the Hamiltonian of the electrons is

$$H^0 = \frac{1}{2} \sum_l \frac{1}{m} p_l^2 + \Phi(x, X). \quad (2)$$

It is assumed that the electronic problem has been solved, so that the Schrödinger equation

$$(H^0 - E_n^0(X)) \varphi_n(x, X) = 0 \quad (3)$$

is satisfied for a complete set of normalized eigenfunctions $\varphi_n(x, X)$ and eigenvalues $E_n^0(X)$, which depend on arbitrarily chosen nuclear coordinates X_k as parameters.

For the Schrödinger equation of the overall system

$$(H - E) \Psi(x, X) = 0 \quad (4)$$

we postulate

$$\Psi(x, X) = \sum \psi_n(X) \varphi_n(x, X) \quad (5)$$

When this is inserted into (4), multiplying the result by $\varphi_{n'}^*(x, X)$ and integrating over the electronic coordinates gives

$$\left(\frac{1}{2} \sum_k \frac{1}{M_k} P_k^2 + E_n^0(X) - E \right) \psi_n(X) + \sum_{n'} C_{nn'}(X, P) \psi_{n'}(X), \quad (6)$$

where

$$C_{nn'} = \sum_k \frac{1}{M_k} (A_{nn'}^{(k)} P_k + B_{nn'}^{(k)}) \quad (7)$$

is a differential operator containing coefficients

$$\left. \begin{aligned} A_{nn'}^{(k)}(X) &= \int \varphi_n^*(x, X) P_k \varphi_{n'}(x, X) dx, \\ B_{nn'}^{(k)}(X) &= \int \varphi_n^*(x, X) P_k^2 \varphi_{n'}(x, X) dx, \end{aligned} \right\} \quad (8)$$

that are functions of the X_k .

The diagonal elements $A_{nn}^{(k)}$ and $B_{nn}^{(k)}$ must be considered separately. For stationary states one can choose the $\varphi_n(x, X)$ as real functions; then, with $P_k = -i\hbar \partial / \partial X_k$, it follows that

$$A_{nn}^{(k)}(X) = -\frac{1}{2} i\hbar \frac{\partial}{\partial X_k} \int [\varphi_n(x, X)]^2 dx = 0, \quad (9)$$

since the φ_n are at identical X_k and are normalized. Therefore, in C_{nn} the term with P_k is omitted and there remains only a multiplicative operator that can be combined with $E_n^0(X)$:

$$E_n^0(X) + \sum_k \frac{1}{M_k} B_{nn}^{(k)} = U_n(X). \quad (10)$$

One can now write (6) in the form

$$\left(\frac{1}{2} \sum_k \frac{1}{M_k} P_k^2 + U_n(X) - E \right) \psi_n + \sum_{n'}' C_{nn'} \psi_{n'} = 0, \quad (11)$$

where the term $n' = n$ is to be omitted in the sum. The term without a sum obviously describes the nuclear motion under the effect of the potential $U_n(X)$, which is essentially the electronic energy in state n . The sum expresses the coupling of the nuclear motions in different electron states.

When applied to crystals, a distinction must be made between conductors and non-conductors. For the conductors, the electronic spectrum is continuous and (11) becomes an integral equation. It seems to me that this method may be important for the development of Frohlich's theory of superconductivity.

For nonconductors, all higher electronic states are energetically far away from the ground state. Then you can neglect the coupling of the ground state with the higher states as a first approximation, and if you omit the sum, you have

$$H = \frac{1}{2} \sum_k \frac{1}{M_k} P_k^2 + U(X). \quad (13)$$

This is the usual Hamiltonian of nuclear motion, which provides the nuclear vibrations.

The difference between this method and the one used in the work cited is that there $U(X)$ was the potential energy averaged over the electronic motion, whereas here, apart from a small correction term, it means the total energy [of the electrons with the nuclei fixed]. All further explanations in the work cited remain unchanged if one now chooses a nuclear configuration X_k^0 arbitrarily and expands $U(X)$ in the deviations $X_k - X_k^0$.

Finally, the difference between the method given here and that of Born and Oppenheimer² should be pointed out. The latter uses an expansion in powers of $x = (m/M_0)^{1/4}$, where M_0 is an average nuclear mass, and the differences $X_k - X_k^0$ are assumed to be of order x . It turns out that the expansion is only possible if the X_k^0 are chosen so that the linear terms in the $U(X)$ power series in $X_k - X_k^0$ disappear. So the X_k^0 are fixed from the start. Furthermore, an equation of the form (13), without coupling to excited electronic states, is only valid up to terms of order 4 in x . The new procedure has no such limitations. In particular, the choice of X_k^0 can be postponed until the end of the statistical calculation, and that was the aim of my previous work.

- 1) M. Born, Festschrift Gött. d. Wiss., I: Math.-Phys. KI. 1 (1951).
- 2) M. Born and R. Oppenheimer, Ann. d. Phys., 84, p. 45 (1927).