

ELIMINATION OF THE ELECTRONIC MOTION (p. 172)

In the text (see § 14) and in Appendix VII, the laws of motion for the nuclei are obtained by a systematic expansion in powers of the parameter $\kappa = (m/M_0)^{1/2}$ (14.5), and it is shown that the adiabatic approximation, in which the electronic motion is calculated as if the nuclei were at rest, is valid up to terms of the fourth order in κ . The averaged electronic energy (eigenvalue) in a given state plays, to this approximation, the part of the potential energy of the nuclei.

It has, however, been found, in particular by studying molecular vibrations, that the adiabatic model has a wider application than predicted by this theory. There exists in fact another method which contains this practical result, with the only modification that the potential energy of the nuclei is not the energy eigenvalue of the electronic state considered, but a slightly different quantity. This method has the further advantage that it leads to a system of simultaneous equations for all electronic states which represent the coupling of electronic and nuclear motion in a rigorous way.

In the notation of IV, § 14, the total Hamiltonian is

$$H = T_E + T_N + U(x, X), \quad (\text{VIII.1})$$

and that corresponding to fixed nuclei

$$H^0 = T_E + U(x, X). \quad (\text{VIII.2})$$

It is assumed, as in IV, § 14, that the latter problem is solved; in the equation

$$(H^0 - \Phi_n(X))\phi_n(x, X) = 0 \quad (\text{VIII.3})$$

the functions $\Phi_n(X)$ and $\phi_n(x, X)$, which represent the energy and the wave function of the electrons in the state n for a fixed nuclear configuration X , are regarded as known. The actual wave equation is

$$(H - E)\Psi(x, X) = 0; \quad (\text{VIII.4})$$

we try to solve it by an expansion

$$\Psi(x, X) = \sum_n \psi_n(X)\phi_n(x, X). \quad (\text{VIII.5})$$

Substituting this in (VIII.4), multiplying the result by $\phi_n^*(x, X)$ and integrating over x we obtain, with $T_N = \frac{1}{2} \sum_k P_k^2/M_k$, (14.1):

$$(T_N + \Phi_n(X) - E)\psi_n(X) + \sum_{n'} C_{nn'}(X, P)\psi_{n'}(X) = 0, \quad (\text{VIII.6})$$

where

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

and

$$A_{nn'}^{(k)}(X) = \int \phi_n^*(x, X) P_k \phi_{n'}(x, X) dx, \quad (\text{VIII.8})$$

$$B_{nn'}^{(k)}(X) = \frac{1}{2} \int \phi_n^*(x, X) P_k^2 \phi_{n'}(x, X) dx.$$

Consider the diagonal elements of these matrices. For stationary states the $\phi_n(x, X)$ can be chosen as real functions; then

$$A_{nn}^{(k)}(X) = -\frac{i\hbar}{2} \frac{\partial}{\partial X_k} \int \phi_n^2(x, X) dx = 0, \quad (\text{VIII.9})$$

since the ϕ_n can be supposed to be normalized to the same constant value for all values of X_k . Hence C_{nn} is independent of the differential operator P ; it is a multiplication operator, a function of X .

We can now write (VIII.6) in the form

$$(T_N + U_n(X) - E)\psi_n(X) + \sum_{n'} C_{nn'}(X, P)\psi_{n'}(X) = 0, \quad (\text{VIII.10})$$

where the dash at the summation symbol indicates that the term $n' = n$ has to be omitted. Here $U_n(X)$ is defined by

$$U_n(X) = \Phi_n(X) + \sum_k \frac{1}{M_k} B_{nn}^{(k)}. \quad (\text{VIII.11})$$

It is this quantity, and not $\Phi_n(X)$, which plays the part of the potential energy of the nuclei, provided the coupling of different electronic states, represented by the sum in (VIII.10) with the coefficients $C_{nn'}$ ($n' \neq n$), can be neglected. The difference between $U_n(X)$ and $\Phi_n(X)$ as given by (VIII.11) can be determined when the electronic eigenfunctions for fixed nuclei are known.†

The equation of the nuclear motion under the assumption of negligible coupling is

$$(T_N + U_n(X) - E)\psi_n(X) = 0. \quad (\text{VIII.12})$$

The question, under what conditions the coupling parameters $C_{nn'}$ will be small, cannot be answered in general. Even if they are not very small their influence will be negligible if the electronic state n is separated from all others by a large gap, as can be seen from well-known perturbation formulae. This will be the case for the ground state of many molecules and non-conducting crystals; then the zero approximation is a non-harmonic nuclear vibration with the potential energy $U_0(X)$, and the coupling with higher electronic states can be calculated from (VIII.10) by perturbation methods. For metals, however, where the electronic states form a quasi-continuum, the sum in (VIII.10) cannot be regarded as a small perturbation; it will go over into an integral, and the equation (VIII.10) will become an integro-differential equation, which expresses the coupling of electronic and nuclear motion in a rigorous way.

† The method outlined here has been published by M. Born, *Zell. Natur. math. phys.* **Kl.** (1951), 1.