CHAPTER II

BORN-OPPENHEIMER HAMILTONIAN

The discovery of geometrical phases in physics was not a sudden event. As we have seen previously, isolated examples of holonomy have been known in a few areas of physics for many years. In the quantum mechanics of molecules, and in the analysis of polarized light, a number of examples were analyzed using concepts equivalent to those we would now recognize as geometrical phases, well before the recent upsurge of interest. Clearly, Berry's phase could have been discovered long before it was, the relevant quantum mechanics had been in place for fifty years. The impact of Berry's paper was prepared by a decade of increasing interest in geometric and topological ideas in physics. This interest, in turn, was stimulated by the rise of fundamentally geometric gauge theories of elementary particles, and by increasing recognition of the role of broken symmetry states in physics.

The standard Born-Oppenheimer effective Hamiltonian for nuclei was incomplete in its failure to predict this behavior, and without a proper effective Hamiltonian, actual computations would be difficult. This problem was solved by Mead and Truhlar (Mead and Truhlar, 1979) , who showed that, in spite of the lack of well-defined electronic and nuclear wavefunctions, it is possible to form an effective Hamiltonian for the nuclei of polyatomic molecules if one introduces an external "gauge potential" (Sakurai, 1985). The sole effect of the extra term is to create a fictitious magnetic flux emanating from the crossing point, which produces the requisite phase change in the nuclear wave function.

The Adiabatic Approximation

The Born-Oppenheimer approximation first arose in the context of molecular physics (Gasiorowicz, 1974), but more generally applies whenever a system exhibits two widely separated energy scales. This approximation is often described as a separation of slow and fast variables. These are just the variables associated with the different energy scales. Quantum mechanically, the separation is made possible by the existence of a large energy gap.

In original applications to molecular physics, the gap involved is the spacing between the electronic energy levels. This gap is typically much larger than the separation between levels associated with vibrations and rotations the nuclear degrees of freedom that do not involve re-arrangement of electronic orbitals. Now if we want to describe the spectrum of low-energy excitations of the molecule, i.e., the excitations with energy much less than the electronic energy gap, then we should be able to form a description that involves only the nuclear degrees of freedom. Indeed, at such low energies the electrons have no independent dynamics, there are "enslaved" to the nuclear degree of freedom, because only one state is available to them. Therefore, it is possible to describe the low-energy excitations by an effective Lagrangian involving the nuclear degrees of freedom alone, with no explicit reference to the electrons. Of course the value of the numerical parameters appearing in this Lagrangian will depend implicitly upon the electrons.

We find this way of formulating the Born-Oppenheimer idea much more appropriate, and easier to generalize, than the usual formulation in terms of fast and slow variables. The connection between the two is as follows. Transitions to states separated by a large energy gap require large changes in frequency, and are therefore associated with fast variables. Rapid oscillations in time accompany such transitions, and lead to cancellations in processes whose characteristic time scale is much longer,

that is, in processes associated with motion of the slow variables. Towards the end of this article we shall discuss the relationship between these two approaches more precisely. It is appropriate to mention one conclusion from that discussion now. However, we shall find quantum variables can only be slow in a very weak sense. For example, in a path integral description the important space-time paths are not differentiable, and the typical velocity is strictly speaking infinite even for so-called slow variables. Nevertheless, not being fussy, we shall freely refer to fast and slow variables thoughout this thesis.

The Born-Oppenheimer Hamiltonian

In molecular physics, it is useful to treat the electronic and nuclear degrees of freedom as fast and slow variables, respectively. This is because the gap between electronic energy levels is typically much larger than the gap between nuclear levels, by a factor of order $(M/m)^{1/4}$. In the Born-Oppenheimer approximation, one solves for the electronic states in a fixed nuclear background. By the adiabatic theorem, one expects relatively slow motion of the nuclei. We can thus obtain an effective description for the nuclear motion, relative to a fixed electronic orbital, by integrating over electronic coordinates. We shall find that the effective nuclear Lagrangian obtained in this way involves both an ordinary potential term due to electronic energy levels and a background gauge potential which couples to the nuclear current. This gauge potential takes into account the Berry phase accumulated by the electronic wave functions when the nuclear coordinates change adiabatically (Moody, Shapere and Wilczek, 1986).

The Born-Oppenheimer approximation begins with the full Schrödinger's equation

$$(T_{nuc} + T_{el} + V)\,\psi \;=\; E\psi \tag{1}$$

where T_{el} and T_{nuc} are the electronic and nuclear kinetic energy terms, $V(r, R)$ contains the potential and interaction energies of the electrons and nucleons, and r and R are the electronic and nuclear coordinates. The wave Function $\psi(r, R)$ is separated into nuclear and electronic components Φ_n and $\emptyset_n$ as

$$\psi(r, R) = \sum_n \Phi_n(R) \, \emptyset_n(r, R) \tag{2}$$

where the subscript n labels the electronic energy eigenstates in a fixed nuclear background. That is, $\emptyset_n(r, R)$ satisfies the electronic Schrödinger equation at a fixed value of R

$$[T_{el} + V(r, R)] \, \emptyset_n(r, R) = \varepsilon_n(R) \, \emptyset_n(r, R) \tag{3}$$

In term of the electronic eigenfunctions, the full Schrödinger equation may now be rewritten as

$$\sum_n [T_{nuc} + \varepsilon_n(R)] \, \Phi_n(R) \, \emptyset_n(r, R) = E \sum_n \Phi_n(R) \, \emptyset_n(r, R) \tag{4}$$

We may now integrate out the electronic degrees of freedom to leave a system of equations for the nuclear wave function alone. Using bracket notation for the normalized electronic eigenstates, we get

$$\sum_n \langle \emptyset_m | T_{nuc} \, \Phi_n | \emptyset_n \rangle + \varepsilon_n(R) \, \Phi_m = E \, \Phi_m \tag{5}$$

The nuclear kinetic energy operator $T_{nuc} = -\hbar^2 \nabla^2 /2m$ operates on both the nuclear and electronic wave functions, $\Phi_n(\mathbf{R})$ and $|\emptyset_n(\mathbf{r}, \mathbf{R})\rangle$. Thus the kinetic energy terms in Eq.(5) are proportional to

$$\langle \emptyset_m | \nabla_{\mathbf{R}}^2 \Phi_n | \emptyset_n \rangle = \sum_k \left(\delta_{mk} \nabla_{\mathbf{R}} + \langle \emptyset_m | \nabla_{\mathbf{R}} \emptyset_k \rangle \right) \left(\delta_{kn} \nabla_{\mathbf{R}} + \langle \emptyset_k | \nabla_{\mathbf{R}} \emptyset_n \rangle \right) \tag{6}$$

The Born-Oppenheimer approximation applies when the mixing between different electronic levels is small, so that the off-diagonal matrix elements in Eq.(6) can be neglected. If, furthermore the electronic states can be chosen to be real for each $\mathbf{R}$, then $\langle \emptyset_n | \nabla_{\mathbf{R}} \emptyset_n \rangle = 0$ and Eq.(6) reduces to

$$\left(-\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 + \sum_{k \neq n} \frac{\hbar^2}{2M} \langle \emptyset_n | \nabla_{\mathbf{R}} \emptyset_k \rangle \langle \emptyset_k | \nabla_{\mathbf{R}} \emptyset_n \rangle + \varepsilon_n(\mathbf{R}) \right) \Phi_n = E \Phi_n \tag{7}$$

In this approximation, the nuclei propagate in a background potential $\tilde{\varepsilon}(\mathbf{R})$

$$\tilde{\varepsilon}(\mathbf{R}) = \varepsilon_n(\mathbf{R}) + \sum_{k \neq n} \frac{\hbar^2}{2M} \langle \emptyset_n | \nabla_{\mathbf{R}} \emptyset_k \rangle \langle \emptyset_k | \nabla_{\mathbf{R}} \emptyset_n \rangle$$

The peculiar extra term may be rewritten as follows

$$\frac{\hbar^2}{2M} \sum_{k \neq n} \left| \frac{\langle \emptyset_n | \nabla H | \emptyset_k \rangle}{\varepsilon_n - \varepsilon_k} \right|^2 \tag{8}$$

Hence, when the energy splittings between level n and the other levels are large, this term may be neglected. Berry has pointed out that it is proportional to the trace of the "natural matrix" on projective Hilbert space (Berry, 1989).

However, it is not always possible to form a basis of electronic wave functions that are everywhere real. Furthermore, corrections to adiabatic evolution will involve mixing of electronic levels. To account for both of these possibilities, we introduce the "Gauge potential" notation

$$A_{mn} = i \langle \emptyset_m | \nabla_R \emptyset_n \rangle \tag{9}$$

Putting together Eq.(4), Eq.(5) and Eq.(9), we can write a complete matrix-value Schrödinger operator for the nuclear wave functions

$$\hat{H}_{mn}^{eff} = - \frac{\hbar^2}{2M} \sum_k \left(\delta_{mk} \nabla_R - i A_{mk}(R) \right) \cdot \left(\delta_{kn} \nabla_R - i A_{kn}(R) \right) + \delta_{mn} \varepsilon_n(R)$$

$$\tag{10}$$

which acts on the vector Φ_n

$$\hat{H}_{mn}^{eff} \Phi_n = E\Phi_m \tag{11}$$

Eq.(11) shows the nuclear wave functions change from eigenstate n to m (the Schrödinger operator is, of course, associated with an effective Hamiltonian after the replacement $-i\hbar\nabla_R = p_R$).

Born-Oppenheimer Approximation

In the Born-Oppenheimer approximation, the effect of the off-diagonal matrix elements A_{mn} which mix different energy levels is ignored. Then for a

nondegenerate electronic level, the effective nuclear Schrödinger operator in the Born-Oppenheimer approximation is then simply

$$\hat{H}_n^{BO} = -\frac{\hbar^2}{2M}\left(\nabla_R - i\, A_n\,(\mathbf{R})\right)^2 + \tilde{\varepsilon}_n\,(\mathbf{R}) \tag{12}$$

where $A_n = A_{nn}$

Eq. (12) looks like the Schrödinger operator of a charged particle in the presence of a background magnetic potential. To further strengthen this analogy, the vector field A_n even transforms likes a U(1) gauge potential, as we shall now explain. The phase each of the wave functions $|\emptyset_n\,(\mathbf{R})\rangle$ is arbitrary, and our description of the dynamics of the nuclei must always respect this arbitrariness. The use of a vector potential brings out the fact that our description possesses the freedom of performing gauge transformations in analogy with electromagnetism [Appendix A]. The effect of a redefinition of phases of electronic wave functions

$$|\emptyset_n\,(\mathbf{R})\rangle \rightarrow e^{i\,\Lambda_n(\mathbf{R})}\,|\emptyset_n\,(\mathbf{R})\rangle \tag{13}$$

is to rotate the nuclear wave functions oppositely

$$|\Phi(\mathbf{R})\rangle \rightarrow e^{-i\,\Lambda_n(\mathbf{R})}\,|\Phi\,(\mathbf{R})\rangle \tag{14}$$

so that the full wave function $\psi\,(\mathbf{r}, \mathbf{R})$ is preserved. From Eq.(9), we see that the gauge potential transforms just as it should

$$A_n\,(\mathbf{R}) \rightarrow A_n\,(\mathbf{R}) + \nabla_R \Lambda_n\,(\mathbf{R}) \tag{15}$$

and it is easy to see that the overall effect of the phase redefinition is to leave the nuclear Schrödinger equation invariant (including the term (8)).

We conclude that the nuclei behave like charged particles in a magnetic field $\mathbf{B}$ ($\mathbf{B} = \nabla \times \mathbf{A}_n$, Gauss's law). Semiclassically speaking, when the nuclei go around a closed path, the wave function will accumulate a geometrical phase proportional to the enclosed magnetic flux. This phase is nothing but Berry's phase in quantum mechanical clothing. The phase that the evolving electron wave functions accumulate when their external parameters $\mathbf{R}$ are slowly varied has just been passed down to the nuclear wave functions.

In the chapter IV we will demonstate the molecular Born-Oppenheimer Approximation by a path integral technique. From the derivation of effective Lagrangians, we should expect and will find that geometrical phases occur. This is particularly clear if we think in terms of path integral.