# The geometric phase in molecular systems

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The fundamental theory of the geometric phase is summarized in a way suitable for use in molecular systems treated by the Born-Oppenheimer approach. Both Abelian and non-Abelian cases are considered. Applications discussd include the Abelian geometric phase associated with an intersection of two electronic potential-energy surfaces; screening of nuclei by the electrons from an external magnetic field; non-Abelian gauge potentials in molecular systems with Kramers degeneracy; and the coupling between different electronic levels (Born-Oppenheimer breakdown) represented as a gauge potential. Experimental tests for these systems are discussed, as well as a number of experiments on spin systems.

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## I. INTRODUCTION

In recent years, the so-called geometric phase, also known as the "Berry phase" because of the very influential paper by Berry (1984), has been a topic of increasing interest and activity. Physical science contains many examples of objects whose behavior is specified up to a phase by certain parameters. Under certain circumstances, traversal of a closed path by the parameters, at the end of which they have returned to their original values, can result in a change of phase whose magnitude depends on the path. A simple example of this is a magnet precessing about a magnetic field, in which the parameters are the three components of the field. If the field is slowly rotated, finally returning to its original direction, the phase angle of the precession will be shifted from what it would be if the field had been held constant (Cina, 1986). There are other examples from classical physics (Hannay, 1985), but most of the activity has been in the quantum-mechanical area, where a typical case is that of a wave function determined up to a phase by the requirement that it be an eigenfunction of a parameter-dependent Hamiltonian. Again, when the parameters traverse a closed path and return to their initial values, there can be a change in phase in the wave function. Berry (1989) has coined the work "anholonomy" for such phase changes, although it would apparently be considered by most mathematicians to belong to the class of phenomena referred to as "holonomy" (Simon, 1983).

Although the rapid acceleration of interest in the geometric phase dates from the mid 1980s, its origins go back at least to the 1950s. Pancharatnam (1956), in his treatise on interference and relative phases between light beams of arbitrary states of elliptical polarization, succeeded in giving a consistent definition to the concept of relative phase between beams in different states of polarization and was able to show that two beams both in phase with a third beam are not necessarily in phase with each other, and that the relative phase between them is related to the area of the spherical triangle formed by the representations of the three beams on the Poincaré sphere. In a very famous and influential paper, Aharonov and Bohm (1959) showed that the wave function of a charged particle acquires a phase change when the particle is carried around a closed path enclosing a magnetic flux, even if the magnetic field itself is zero everywhere along the path.

Special cases of the effect of the geometric phase on molecular systems, the main thrust of the present article, were noticed and treated correctly by chemists some years prior to the influential work of Berry. Herzberg

and Longuet-Higgins (1963) showed that a Born-Oppenheimer electronic wave function, if required to be real and smoothly varying, undergoes a sign change when the nuclear coordinates traverse a closed path around a conical intersection of two electronic potential-energy surfaces. This effect had previously been treated correctly by Longuet-Higgins *et al.* (1958) for a model of a Jahn-Teller distorted molecule (Jahn and Teller, 1937). The phase factor experienced by a Born-Oppenheimer wave function under traversal by the nuclei of a closed path was discussed in a more general way by Mead and Truhlar (1979), who showed that the resulting multiple-valuedness of the electronic wave function can be removed, but only at the cost of introducing a vector-potential-like term into the effective Hamiltonian for the nuclear motion. They also showed that the effect was analogous to that of Aharonov and Bohm (1959). In subsequent papers (Mead, 1980a, 1980b), the name "molecular Aharonov-Bohm effect" was proposed for this phenomenon.

Another very interesting and related phenomenon originating in the field of plasma physics was discussed by Littlejohn (1984), who showed that a classical charged particle undergoing "guiding-center motion" (motion in a twisted helix about a nonuniform magnetic field) could acquire an extra phase depending on the geometry of the field.

Widespread interest in the subject, however, unquestionably dates from the paper by Berry (1984), in which he considered a quantum-mechanical state evolving adiabatically in time under a slowly varying parameter-dependent Hamiltonian. He showed that, when the parameters return to their initial values, having traversed a closed path, the wave function may acquire a "geometric" phase factor, dependent on the path, in addition to the well-known "dynamical" phase factor

$$\exp\left[-\frac{i}{\hbar}\int E(t)dt\right].$$

In a paper that actually appeared before Berry's because of different publication schedules of different journals, Simon (1983) called attention to Berry's work and emphasized its relation to the theory of holonomy in fiber bundle theory.

The first modern experimental observation of the geometric phase was made by Tomita and Chiao (1986), who observed a phase shift in the direction of polarization of a light beam when propagated through an optical fiber and showed that this was just proportional to the solid angle of rotation of the direction of propagation. The theory of this experiment had been developed by Chiao and Wu (1986). There has been some discussion of whether this is a quantum or a classical effect (Berry, 1987a; Haldane, 1987; Segert, 1987a), but it certainly is a manifestation of the geometric phase and helped to stimulate interest in the topic. Recently, using coincidence techniques, Kwiat and Chiao (1991) have observed the Pancharatnam phase in experiments involving single photons.

Since the appearance of Berry's work, a plethora of publications have dealt with the theory of the geometric phase and its application in various fields. Manifestations of the phase have been discussed in classical systems (Hannay, 1985), in the theory of the quantized Hall effect (Arovas *et al.*, 1984), in the use of collective coordinates in many-body theory (Bulgac, 1989, 1990), and in the treatment of anomalies in elementary-particle theory (M. Stone, 1986), as well as in molecular systems. Littlejohn (1988b) showed the connection between guiding-center motion of a charged particle in a nonuniform magnetic field and the phase angle of Hannay (1985). Berry (1985) also discussed the relation between the quantum situation and the classical case considered by Hannay (1985). Jordan (1988b) used the ideas of Pancharatnam (1956) to arrive at a definition of the phase change for partial cycles. The ideas of Pancharatnam (1956) were also used by Samuel and Bhandari (1988) to place the phase in a general setting in which the process was required to be neither unitary nor cyclic. Aharonov and Anandan (1987) showed that the phase change experienced by a quantum state taken around a closed path depends only on the path in Hilbert space, regardless of whether or not the traversal is carried out adiabatically. A similar result for evolving spin states was obtained independently by Jordan (1987). Bulgac (1988) has also treated a similar problem. This nonadiabatic approach was used by Littlejohn (1988a) in discussing the geometric phase in semiclassical mechanics. Garrison and Chiao (1988) discussed a class of nonlinear classical fields exhibiting an Aharonov-Anandan phase. Littlejohn and Flynn (1991a, 1991b) have discussed the role of the geometric phase in the WKB limit for propagation of multicomponent waves. Ralston (1989a) emphasized the "mapping" of quantum onto classical systems and exhibited the quantum geometric phase in a way that permitted an immediate recognition of a classical analog. Ralston (1989b) showed that the dynamical and geometric phases could be considered on an equal footing by treating time and space coordinates symmetrically. Gamliel and Freed (1989) have considered the geometric phase in a spin system undergoing a stochastic process, while Kepler and Kagan (1991) have treated the case of classical dissipative oscillatory systems.

There has also been much discussion of the "non-Abelian" case, in which the wave function being transported belongs to a degenerate energy level, and traversal of the closed path may result not only in a phase change but also in mixing of the degenerate states (Wilczek and Zee, 1984). Anandan (1988) showed that one of the restrictions of Garrison and Chiao (1988) could be relaxed and that their results could be generalized to the non-Abelian case. Anandan and Pines (1989) showed how a non-Abelian phase could be obtained by a sequence of "incomplete quantum measurements," i.e., measurements of less than a complete set of commuting observables resulting in projection onto a multidimensional space rath-

er than onto a single state. Montgomery (1990) has considered a kind of inverse problem: Given a phase change, Abelian or non-Abelian, what is the "optimal" path (according to some appropriate criterion) for achieving this change?

Earlier reviews have been published by Jackiw (1988), by Vinitskii *et al.* (1990), and by Zwanziger *et al.* (1990a), and a very useful book containing reprints and some original articles has also appeared (Shapere and Wilczek, 1989). The proceedings of a Society conference on the geometric phase have also been published (Markovski and Vinitsky, 1989). A general survey, including historical and other observations, has been given by Berry (1989). Berry (1988, 1990b) has also contributed two accounts, partly historical in nature, for nonspecialists. This list, of course, is only intended to be representative, certainly not exhaustive. More references will be given as the article proceeds.

The present article emphasizes the manifestations of the geometric phase in molecular systems and will thus be confined to the quantum-mechanical case, in which the quantity whose phase is being studied is a quantum-mechanical state vector (ket) that depends in some way on parameters. Broadly speaking, there are two types of situation in the molecular realm in which a ket can be considered as determined by parameters. We call the two situations cases A and B. In case A, the parameters determining the ket are themselves dynamical variables of the system being studied and are subject to quantization, but are considered to be "slow" compared to the degrees of freedom to which the ket refers, so that a separate treatment is appropriate (Jackiw, 1988). This case is exemplified by the Born-Oppenheimer treatment of molecules, in which the electronic ket depends parametrically on the nuclear coordinates, but in which these coordinates are not controlled by the experimenter but are part of the system being studied and must be quantized. Most of this article will be concerned with this case and with the general theory applicable to it. In case B, the evolution of the ket depends on external classical parameters that are actually under the control of the experimenter. An example of this is a spin (or an atomic system whose angular momentum is singled out for study) in an external field. The Hamiltonian governing the time development of the state of the spin is determined by the field, and this in turn can be controlled by the experimenter. Our treatment of case B will be less detailed, but it is very important because of theoretical simplicity and experimental accessibility. To a considerable degree, the theory of the two cases can be treated in a unified way, but in any particular application the nature of the physical situation being studied must be kept clearly in mind.

Before summarizing the contents of the paper, and in order to motivate the more detailed and abstract treatment that will follow, we now present a brief demonstration of how the geometric phase can appear in the Born-Oppenheimer treatment of molecular systems, including the actual form of the phase in what is probably the simplest case, that considered by Herzberg and Longuet-Higgins (1963).

The degrees of freedom of a molecular system can be thought of as consisting of the nuclear coordinates, represented collectively by $\mathbf{R}$, and the electronic degrees of freedom. It is evident that any state of such a system can be represented as a ket in the Hilbert space of the electronic degrees of freedom which depends on $\mathbf{R}$, so that operators involving nuclear degrees of freedom can be applied to it. Thus we are using the position representation for the nuclear degrees of freedom (since we need to consider explicitly the dependence of the state ket on the nuclear coordinates), while describing the electronic state by a more abstract ket vector. We denote such a state ket by $|\Psi(\mathbf{R})\rangle$. In Born-Oppenheimer approximation, an energy eigenstate is approximated by

$$|\Psi(\mathbf{R})\rangle \approx |\chi(\mathbf{R})\rangle \psi(\mathbf{R}) , \tag{1.1}$$

where $\psi(\mathbf{R})$ is interpreted as the wave function for nuclear motion, and $|\chi(\mathbf{R})\rangle$, the electronic eigenstate, is an eigenket of the $\mathbf{R}$-dependent electronic Hamiltonian $\hat{H}(\mathbf{R})$:

$$\hat{H}(\mathbf{R})|\chi(\mathbf{R})\rangle = |\chi(\mathbf{R})\rangle U(\mathbf{R}) , \tag{1.2}$$

where the eigenvalue $U(\mathbf{R})$ is the electronic energy. Evidently, the eigenvalue equation (1.2), together with normalization, only determines $|\chi(\mathbf{R})\rangle$ up to an $\mathbf{R}$-dependent phase factor. We can always make the transformation

$$|\chi(\mathbf{R})\rangle \rightarrow |\chi(\mathbf{R})\rangle e^{if(\mathbf{R})} . \tag{1.3}$$

In the Born-Oppenheimer treatment, we use Eqs. (1.1) and (1.2) together with the full Hamiltonian of the molecule to obtain an effective Schrödinger equation for $\psi(\mathbf{R})$. To do this, we need to express the nuclear momentum operator $\hat{\mathbf{P}}$, operating on $|\Psi(\mathbf{R})\rangle$, as an effective operator $\hat{\boldsymbol{\Pi}}$ operating only on $\psi(\mathbf{R})$. This is done as follows (in units where $\hbar = 1$):

$$\hat{\boldsymbol{\Pi}}\psi(\mathbf{R}) = \langle \chi(\mathbf{R})|\hat{\mathbf{P}}|\Psi(\mathbf{R})\rangle = \left\langle \chi(\mathbf{R}) \left| \frac{1}{i}\nabla|\Psi(\mathbf{R})\right.\right\rangle$$

$$= \frac{1}{i}\nabla\psi(\mathbf{R}) + \mathbf{A}(\mathbf{R})\psi(\mathbf{R}) , \tag{1.4}$$

where $\nabla$ is with respect to the nuclear coordinates $\mathbf{R}$ and the vector-potential-like term $\mathbf{A}(\mathbf{R})$ is given by

$$\mathbf{A}(\mathbf{R}) = \frac{1}{i}\langle \chi(\mathbf{R})|\nabla\chi(\mathbf{R})\rangle . \tag{1.5}$$

It is easy to see that the transformation (1.3) induces a gauge transformation on $\mathbf{A}(\mathbf{R})$:

$$\mathbf{A}(\mathbf{R}) \rightarrow \mathbf{A}(\mathbf{R}) + \nabla f(\mathbf{R}) . \tag{1.6}$$

In familiar textbook treatments of the Born-Oppenheimer method, the vector potential $\mathbf{A}(\mathbf{R})$ is rarely mentioned; it is tacitly assumed to be zero. As is well known from vector calculus, the gauge transformation (1.6) can cause the transformed $\mathbf{A}(\mathbf{R})$ to vanish if and

only if the curl of $\mathbf{A}(\mathbf{R})$ is zero. In a sense, though, one can make $\mathbf{A}(\mathbf{R})$ vanish along a path in nuclear configuration space. Referring to Eq. (1.5), we see that the vanishing of $\mathbf{A}(\mathbf{R})$ would mean that the infinitesimal change in $|\chi(\mathbf{R})\rangle$ under a small change in $\mathbf{R}$ is orthogonal to $|\chi(\mathbf{R})\rangle$ itself:

$$\langle\chi(\mathbf{R})|\delta\chi(\mathbf{R})\rangle=\langle\chi(\mathbf{R})|\nabla\chi(\mathbf{R})\rangle\cdot\delta\mathbf{R}=0\ . \tag{1.7}$$

For any infinitesimal change in $\mathbf{R}$, one can manipulate the phase factor in Eq. (1.3) in such a way that Eq. (1.7) is satisfied, and one can continue this along a path in $\mathbf{R}$-space. However, when the path is a closed one, returning to its starting point, there is in general no assurance that $|\chi(\mathbf{R})\rangle$ will have returned to its original value. The electronic Hamiltonian $\hat{H}(\mathbf{R})$ will be the same as before, so $|\chi(\mathbf{R})\rangle$ can change at most by a phase factor, but this "geometric phase," which in general will depend on the path, will not always be unity. When this happens, the electronic eigenket satisfying Eq. (1.7) is not single valued as a function of $\mathbf{R}$, so that $\psi(\mathbf{R})$ must be required to satisfy multiple-valued boundary conditions if $|\Psi(\mathbf{R})\rangle$ is to be single valued.

To see how a nontrivial phase factor can arise in a simple case, consider the problem treated by Herzberg and Longuet-Higgins (1963). Two electronic states are degenerate at a point in $\mathbf{R}$-space, and in the neighborhood of that point the Hamiltonian $\hat{H}$ can be truncated as a matrix acting only on the near-degenerate states. Apart from an additive multiple of the unit matrix, and in terms of appropriately chosen coordinates $x$ and $y$, the Hamiltonian is

$$\hat{H}(\mathbf{R})=\begin{bmatrix}x & y\\ y & -x\end{bmatrix}=r\begin{bmatrix}\cos\varphi & \sin\varphi\\ \sin\varphi & -\cos\varphi\end{bmatrix}\ . \tag{1.8}$$

The eigenvalues are $\pm r$, with eigenvectors

$$|\chi_+\rangle=\begin{bmatrix}\cos\frac{\varphi}{2}\\ \sin\frac{\varphi}{2}\end{bmatrix}\ ;\quad |\chi_-\rangle=\begin{bmatrix}-\sin\frac{\varphi}{2}\\ \cos\frac{\varphi}{2}\end{bmatrix}\ . \tag{1.9}$$

It is easy to see that

$$|\delta\chi_+\rangle=\tfrac{1}{2}|\chi_-\rangle\delta\varphi;\quad |\delta\chi_-\rangle=-\tfrac{1}{2}|\chi_+\rangle\delta\varphi\ , \tag{1.10}$$

so Eq. (1.7) is satisfied. The eigenkets are not single valued, however, undergoing a change of sign when $\varphi$ makes a full circuit from 0 to $2\pi$. In this case, it is easy to find a phase factor that will make the kets single values. For $|\chi_-\rangle$, for example, define

$$|X_-\rangle=|\chi_-\rangle e^{i\varphi/2}\ . \tag{1.11}$$

The transformation (1.11) obviously restores the single-valuedness, but now there is a nonzero vector potential:

$$A_\varphi=\frac{1}{i}\left\langle X_-\left|\frac{d}{d\varphi}X_-\right.\right\rangle=\frac{1}{2}\ . \tag{1.12}$$

This is an example of the situation that frequently arises in the theory of the geometric phase in molecular systems: One has to choose between vanishing vector potential and single-valuedness of the electronic eigenstate; it is not in general possible to have both.

If one takes the curl of the vector potential (1.12) to find the corresponding (pseudo) magnetic field, one finds a $\delta$ function at the origin. According to classical notions, this would mean that the vector potential should have no physical effect if the motion of the nuclei avoids the origin. As shown by Aharonov and Bohm (1959), however, quantum-mechanical interference effects can arise when the motion is able to circle the flux region, even if the flux region is not penetrated, and the effects on the molecular system turn out to be in precise analogy to the situation considered by them. For this reason the name "molecular Aharonov-Bohm effect" has been suggested for this phenomenon (Mead, 1980a).

The vector potential (1.12) is not a mere mathematical curiosity, but has experimental consequences that have already been observed. As pointed out by Longuet-Higgins *et al.* (1958) and by Mead (1980a), it leads to half-odd integral quantum numbers for pseudorotation degrees of freedom of certain molecules, of which the simplest are metallic trimers $X_3$. These effects have been observed, for example, in the spectrum of $Cu_3$ by Morse *et al.* (1983) and in that of $Na_3$ by Delacrétaz *et al.* (1986).

We now give a brief summary of the sections to follow.

Sections II–III take up the general formalism for the continuous transport of parameter-dependent kets, or sets of kets, around closed paths in parameter space. The treatment will be general, but one will lose nothing essential if one thinks of the kets being transported as Born-Oppenheimer electronic states, and of the parameters as nuclear coordinates. Section II is devoted to the "Abelian" case of transport of a single ket (single electronic state, usual Born-Oppenheimer situation), while Sec. III takes up the "non-Abelian" case in which two or more kets are transported, the molecular example being that of two or more electronic states which are either degenerate or close enough in energy that the coupling between them cannot be neglected.

In Sec. IV, we obtain the general Born-Oppenheimer eigenvalue equation, applicable to Abelian and non-Abelian cases, and including vector-potential terms. In Secs. V–VIII, the application of this to various molecular and spin problems is discussed, along with the experimental tests. There is some discussion in Sec. IX.

We have tried to make the theoretical treatment rigorous (as that word is understood by the chemical physicist) and thorough, but still accessible to the chemical physicist. In particular, while certainly not wishing to denigrate its value, we have avoided explicit use of fiber bundle theory in this paper. The approach using fiber bundle theory is discussed by Simon (1983), by Zwanziger *et al.* (1990a), and by Bohm, Boya, and Kendrick (1991). We have tried to give a reasonably complete set of references, not for all aspects of the geometric

phase, but for those aspects most relevant to the molecular realm. The author apologizes, and takes full responsibility, for any significant omissions. The main goal, however, is not so much a review of who has done what as a clear and useful exposition of the subject. There is some new material in terms of formulation in Secs. II and III, and some new results of substance in Secs. V, VI, and VII. Naturally, the author's own prejudices have influenced the choice of topics and the nature of the formulation.

## II. CLOSED PATH IN PROJECTIVE (RAY) SPACE, ABELIAN CASE

### A. General relations

In this section, we consider a one-dimensional projection operator $\hat{P}(\mathbf{R})=|\chi(\mathbf{R})\rangle\langle\chi(\mathbf{R})|$ in a Hilbert space, depending continuously on parameters $x_\mu$ which are collectively denoted by $\mathbf{R}$. The manifold spanned by $\mathbf{R}$ will be denoted by $\mathcal{R}$. The parameters $x_\mu$ may represent nuclear coordinates or otherwise determine an operator of which $|\chi(\mathbf{R})\rangle$ is an eigenket, but this is not necessary; all that is essential is that the $x_\mu$ uniquely determine the projection $\hat{P}(\mathbf{R})$. We consider the case in which the parameters traverse a closed path, so that $\hat{P}(\mathbf{R})$ also undergoes a continuous evolution, eventually returning to its original form. In much of the discussion that follows, it will be convenient to discuss evolution of $\hat{P}(\mathbf{R})$ and/or $|\chi(\mathbf{R})\rangle$ without reference to the parameters ($\mathbf{R}$), and in such cases the parameters will not appear explicitly in the equations.

As already noted, such a projection may always be written in terms of a normalized ket as

$$\hat{P}(\mathbf{R})=|\chi(\mathbf{R})\rangle\langle\chi(\mathbf{R})| \ . \tag{2.1}$$

The ket $|\chi(\mathbf{R})\rangle$, however, is determined by $\hat{P}(\mathbf{R})$ only up to a phase factor, and the phase factor may depend not only on $\mathbf{R}$ but also on other factors, such as the path by which $\mathbf{R}$ was reached. Thus, when $\hat{P}(\mathbf{R})$ traverses its closed trajectory, the trajectory of $|\chi(\mathbf{R})\rangle$ is determined only in the projective or ray space, i.e., the space in which no distinction is made between kets that differ only by a phase factor (more generally, only by a multiplicative constant). Of course, all physical properties, such as expectation values, associated with $|\chi(\mathbf{R})\rangle$ alone [and not involving interference between $|\chi(\mathbf{R})\rangle$ and some other ket], are determined by the corresponding point in ray space, i.e., by the projection operator independently of the phase factor. There are a number of situations in which we might wish to study the development of a ket along a path in ray space, and in different situations there may be different convenient or appropriate choices of the phase factor. The situations of importance to us, corresponding to cases A and B as defined in Sec. I, are the following:

*Case A:* We might want to generate a complete set of kets $|\chi_j(\mathbf{R})\rangle$ for each $\mathbf{R}$ (for example, electronic eigenstates) by continuously varying parameters that determine a ket (e.g., parameters in an eigenvalue problem that it must satisfy), eventually obtaining in this way a set of kets for every point $\mathbf{R}$. In this case, as discussed briefly in Sec. I, single-valuedness of each $|\chi(\mathbf{R})\rangle$ as a function of $\mathbf{R}$ is important.

*Case B:* We might be interested in the evolution of $|\chi\rangle$ under the time-dependent Schrödinger equation with a time-dependent Hamiltonian, determined by parameters controlled by the experimenter and chosen in such a way that $|\chi\rangle$ eventually returns to its starting point in ray space. In this case, the phase along the path is determined completely by the initial conditions and the Hamiltonian, and there is no reason why the ket at a later time must have the same phase that it possessed previously.

If we wish, we may impose some phase convention that singles out a particular ket $|X\rangle$ for each projection operator, thus guaranteeing that $|X\rangle$, at least, is single valued, returning to its original form after a closed path is traversed. In terms of the $|X\rangle$, an arbitrary ket can be written

$$|\chi\rangle=|X\rangle e^{i\lambda} \ . \tag{2.2}$$

One way of defining single-valued kets $|X\rangle$ is the method of Pancharatnam (1956), who defined two light beams in different states of elliptical polarization as being in phase if the intensity of their sum is maximal, i.e., if the interference between them is maximally constructive. He showed that the amount by which two beams both in phase with a third beam are out of phase with each other is related to the area of the spherical triangle whose vertices are the representations of the three beams on the Poincaré sphere (Born and Wolf, 1959). The quantum-mechanical analog (Berry, 1987c) is to defined two kets $|X\rangle$ and $|0\rangle$ as being in phase (or parallel) if $\langle 0|X\rangle$ is real and positive, which also corresponds to maximum constructive interference, i.e., to the maximum of $(\langle X|+\langle 0|)(|X\rangle+|0\rangle)$. Thus, having selected some arbitrary ket $|0\rangle$, we can define a unique ket $|X\rangle$ for each projection that does not annihilate $|0\rangle$ by

$$|X\rangle=|0\rangle\cos\tau+|\phi\rangle\sin\tau\equiv|0\rangle\cos\tau+|\Phi\rangle \ , \tag{2.3}$$

where $0\le\tau\le\pi/2$ and $|\phi\rangle$ is some normalized ket orthogonal to $|0\rangle$. The ket $|\Phi\rangle$ thus has the norm $\sin^2\tau$. Equation (2.3) defines a unique ket for every projection that does not annihilate $|0\rangle$. For those that annihilate $|0\rangle$ but not some other ket $|1\rangle$, we can define kets in phase with $|1\rangle$, and in principle continue this process so as to reach every projection encountered in any particular problem. In practice, for any particular path, Eq. (2.3) alone will nearly always suffice, except perhaps for isolated points on the path.

In terms of Eq. (2.2), we can write for the infinitesimal change in the ket $|\chi\rangle$

$$|d\chi\rangle=|dX\rangle e^{i\lambda}+|\chi\rangle i d\lambda \ , \tag{2.4}$$

so that

$$\langle\chi|d\chi\rangle=\langle X|dX\rangle+id\lambda\ , \tag{2.5}$$

which can be rearranged to

$$d\lambda=\frac{1}{i}\{\langle\chi|d\chi\rangle-\langle X|dX\rangle\}$$
$$=\frac{1}{2i}[(\langle\chi|d\chi\rangle-\langle d\chi|\chi\rangle)-(\langle X|dX\rangle-\langle dX|X\rangle)]\ , \tag{2.6}$$

with the second equality being a consequence of normalization:

$$\langle\chi|d\chi\rangle+\langle d\chi|\chi\rangle=\langle X|dX\rangle+\langle dX|X\rangle=0\ . \tag{2.7}$$

Integrating Eq. (2.6) around the closed path $C$ gives the phase change experienced by $|\chi\rangle$ after traversing the path, i.e., the amount by which the final $|\chi\rangle$ is out of phase with the initial one:

$$\Delta\lambda(C)=f(C)-\mathcal{F}(C)\ , \tag{2.8}$$

where $f(C)$ and $\mathcal{F}(C)$ are fluxes given by

$$f(C)=\frac{1}{i}\oint_c\langle\chi|d\chi\rangle=\frac{1}{2i}\oint_c(\langle\chi|d\chi\rangle-\langle d\chi|\chi\rangle)\ , \tag{2.9}$$

$$\mathcal{F}(C)=\frac{1}{i}\oint_c\langle X|dX\rangle=\frac{1}{2i}\oint_c(\langle X|dX\rangle-\langle dX|X\rangle)\ . \tag{2.10}$$

The case of a one-dimensional projection operator is called the Abelian case, essentially because the integrands in Eqs. (2.9) and (2.10) are simply numbers, so that integrands at different points along the curve commute with one another.

The flux $\mathcal{F}(C)$ depends only on the single-valued kets $|X\rangle$, and it is easy to see that $\mathcal{F}(C)$ (mod $2\pi$) depends only on the path $C$ traversed by the projection operator. For, suppose we define new single-valued kets by a revised phase convention,

$$|\tilde{X}\rangle=|X\rangle e^{i\kappa}\ , \tag{2.11}$$

where of course the phase factor $e^{i\kappa}$ must return to its original value when $C$ is traversed, i.e., $\Delta\kappa(C)$ must be a whole multiple of $2\pi$. On the other hand, it is clear from the definition (2.10) that the new flux is given by

$$\tilde{\mathcal{F}}(C)=\mathcal{F}(C)+\Delta\kappa(C)\ , \tag{2.12}$$

so that $\mathcal{F}(C)(\mathrm{mod}2\pi)$ is unchanged, which is what was asserted. The invariant flux $\mathcal{F}(C)(\mathrm{mod}2\pi)$ is *the* geometric phase associated with the path $C$.

Further insight into the meaning of the flux $\mathcal{F}(C)$ can be obtained by imagining $|X\rangle$ expanded in some complete set,

$$|X\rangle=\sum_j|j\rangle\rho_j e^{i\phi_j}\ , \tag{2.13}$$

where the kets $|j\rangle$ are fixed and the variation of $|X\rangle$ is determined by that of the coefficients $\rho_j e^{i\phi_j}$. We easily find

$$\frac{1}{2i}(\langle X|dX\rangle-\langle dX|X\rangle)=\sum_j\rho_j^2 d\phi_j=\sum_{j\neq0}\rho_j^2 d\phi_j\ , \tag{2.14}$$

where the last equality holds if the single-valued kets are defined by Eq. (2.3), since the phase angle associated with the ket $|0\rangle$ does not change. When Eq. (2.14) is integrated around $C$, it is clear that each term in the sum just contributes twice the area $\mathcal{A}_j(C)$ swept out in the counterclockwise sense by the coefficient of $|j\rangle$ in the complex plane as $C$ is traversed:

$$\mathcal{F}(C)=2\sum_j\mathcal{A}_j(C)=2\sum_{j\neq0}\mathcal{A}_j(C)\ , \tag{2.15}$$

where again the second equality applies to kets defined by Eq. (2.3). A rephasing of the single-valued kets by the transformation (2.11) will affect the differential expression (2.14) at a given point, but not the integral result (2.15), except perhaps by a multiple of $2\pi$. For, Eq. (2.11) simply causes $\kappa$ to be added to all the phases $\phi_j$:$\phi_j\rightarrow\phi_j+\kappa$, and the change in $\mathcal{F}$ brought about by this is

$$\Delta\mathcal{F}(C)=\oint_c\sum_j\rho_j^2 d\kappa=\oint_c d\kappa=\Delta\kappa(C)\ , \tag{2.16}$$

which is just a multiple of $2\pi$, as noted before.

It is also evident after a little thought that the second equality (2.15) is independent of the choice of reference ket $|0\rangle$ for given choice of phase for $|X\rangle$. For, the left side of Eq. (2.14) is clearly invariant, independent of the representation in which $|X\rangle$ is to be expanded; a choice of reference ket just means that, in some representation, one of the $\phi_j$ is constant, so that one term can be omitted from the sum after the first equal sign in (2.14). If there is more than one representation for which one of the $\phi_j$ is constant, and/or more than one term with constant $\phi_j$ in a given representation, any such representation can be chosen and any such term can be omitted from the sum without affecting the result.

As a simple example of the area formula (2.15), we consider the two-dimensional problem also used as an example by Berry (1984). Let $\theta$ and $\phi$ be colatitude and longitude angles, respectively, and let the single-valued ket $|\chi\rangle$ be given by

$$|X\rangle=\begin{bmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}e^{i\phi}\end{bmatrix}\ , \tag{2.17}$$

which is an eigenket of the operator

$$\hat{H}=\begin{bmatrix}\cos\theta & \sin\theta e^{-i\phi}\\ \sin\theta e^{i\phi} & -\cos\theta\end{bmatrix} \tag{2.18}$$

with eigenvalue unity. Here we have $\tau=\theta/2$ in Eq. (2.3) and the second sum in (2.15) has only one term. According to Eqs. (2.15) and (2.17), we would have

$$\mathcal{F}(C)=2\mathcal{A}=\oint_C\sin^2\frac{\theta}{2}d\phi=\tfrac{1}{2}\oint_C(1-\cos\theta)\,d\phi$$
$$=\tfrac{1}{2}\int\int_C\sin\theta\,d\theta\,d\phi\ , \tag{2.19}$$

where the last (double) integral goes over the area on the sphere enclosed by $C$ and is just the solid angle subtended by the path $C$. This relation between geometric phase and solid angle is one of the best-known results obtained in the article by Berry (1984).

It may happen that the ket $|0\rangle$ will be annihilated by the projection $\hat{P}$ at certain points along the path. Except in pathological cases, this will happen only at isolated points where the coefficient of $|0\rangle$ passes through zero. If $\xi$ is such a point, then Eq. (2.3) can be maintained on both sides of $\xi$ only by having $\cos\tau$ remain positive while the coefficients of the other kets $|j\rangle$ in Eq. (2.13) all change sign, i.e., they all experience a phase change of $\pi$. Since the norm of $|\Phi\rangle$ at $\xi$ is unity, we see from Eq. (2.14) that there is a discontinuous contribution to the flux $\mathcal{F}$ at such a point of just $\pi$:

$$\Delta_{\xi}\mathcal{F}=\pi \ . \tag{2.20}$$

The invariant flux $\mathcal{F}(C)$ can also be expressed directly in terms of the projection operator. From Eqs. (2.1), (2.3), and (2.13), we have

$$\langle 0|\hat{P}|j\rangle=\rho_0\rho_j e^{-i\phi_j} \ , \quad \langle j|\hat{P}|0\rangle=\rho_0\rho_j e^{i\phi_j} \ , \tag{2.21}$$

from which it is easy to see that

$$i\langle 0|[\hat{P}, d\hat{P}]|0\rangle=-2\rho_0^2\sum_{j\neq 0}\rho_j^2 d\phi_j \ , \tag{2.22}$$

which in combination with Eq. (2.14) gives

$$\mathcal{F}(C)=-\frac{i}{2}\oint_C\frac{\langle 0|[\hat{P}, d\hat{P}]|0\rangle}{\langle 0|\hat{P}|0\rangle} \ . \tag{2.23}$$

Equation (2.23) shows that $\mathcal{F}(C)$ can be calculated from $\hat{P}$ without specifying the phase convention for $|\chi(\mathbf{R})\rangle$. It is valid whenever the evolution of each coefficient is continuous in the complex plane; when there is an abrupt change of sign, leading to a discontinuous contribution (2.20) to $\mathcal{F}$, Eq. (2.23) can still represent the flux via a limiting process. This is discussed briefly in Appendix A.

In terms of the parameters $\mathbf{R}$, we can define "vector potentials" associated with $|\chi\rangle$ and $|X\rangle$ as follows:

$$\mathbf{a}(\mathbf{R})=\frac{1}{i}\langle\chi(\mathbf{R})|\tilde{\nabla}\chi(\mathbf{R})\rangle$$

$$=\frac{1}{2i}[\langle\chi(\mathbf{R})|\tilde{\nabla}\chi(\mathbf{R})\rangle-\langle\tilde{\nabla}\chi(\mathbf{R})|\chi(\mathbf{R})\rangle] \ , \tag{2.24}$$

$$\mathbf{A}(\mathbf{R})=\frac{1}{i}\langle X(\mathbf{R})|\nabla X(\mathbf{R})\rangle$$

$$=\frac{1}{2i}[\langle X(\mathbf{R})|\nabla X(\mathbf{R})\rangle-\langle\nabla X(\mathbf{R})|X(\mathbf{R})\rangle] \ . \tag{2.25}$$

In Eq. (2.24), the tilde ($\sim$) over the $\nabla$ operator reminds us of the fact that $|\chi(\mathbf{R})\rangle$, unlike $|X(\mathbf{R})\rangle$, is not a single-valued function of $(\mathbf{R})$, so that the derivatives are to be taken locally along the path. In terms of these vector potentials, one sees from the definitions (2.9), (2.10), (2.24), and (2.25) that the fluxes are given by

$$f(C)=\oint_C\mathbf{a}\cdot d\mathbf{R} \ , \tag{2.26}$$

$$\mathcal{F}(C)=\oint_C\mathbf{A}\cdot d\mathbf{R} \ . \tag{2.27}$$

Because the vector potentials $\mathbf{A}(\mathbf{R})$ and $\mathbf{a}(\mathbf{R})$ are numbers, not operators, so that all components at all points in $\mathbf{R}$-space commute with each other, $[A_\mu(\mathbf{R}), A_\nu(\mathbf{R}')]=0$, etc., the case of a one-dimensional projection is called the Abelian case, as already remarked in the discussion following Eq. (2.10).

### B. Gauge and phase-gauge transformations

Equation (2.8) can be rewritten as

$$f(C)-\Delta\lambda(C)=\mathcal{F}(C) \ , \tag{2.28}$$

emphasizing that the invariant flux $\mathcal{F}(C)$ can be thought of as being made up of two contributions, each depending not only on the path in ray space but on the way in which the phase of $|\chi\rangle$ is defined along that path. We can redefine the phase of $|\chi\rangle$, for example, by the "phase-gauge transformation"

$$|\chi(\mathbf{R})\rangle\rightarrow|\chi(\mathbf{R})\rangle\exp\left[i\int_{(C)}^{\mathbf{R}}\mathbf{k}(\mathbf{R}')\cdot d\mathbf{R}'\right] \ . \tag{2.29}$$

This does not affect the single-valued kets $|X\rangle$, and so does not affect $\mathcal{F}(C)$, but from Eqs. (2.9) and (2.24) we see that it does induce the transformations

$$\mathbf{a}(\mathbf{R})\rightarrow\mathbf{a}(\mathbf{R})+\mathbf{k}(\mathbf{R}) \ , \tag{2.30}$$

$$f(C)\rightarrow f(C)+\oint_C\mathbf{k}(\mathbf{R})\cdot d\mathbf{R} \ , \tag{2.31}$$

$$\Delta\lambda(C)\rightarrow\Delta\lambda(C)+\oint_C\mathbf{k}(\mathbf{R})\cdot d\mathbf{R} \ . \tag{2.32}$$

Thus the transformation (2.29) does not affect $\mathcal{F}(C)$, but does alter $f(C)$ and $\Delta\lambda(C)$ by the same amount and adds a vector to the potential $\mathbf{a}(\mathbf{R})$. In particular, by choosing $\mathbf{k}(\mathbf{R})=-\mathbf{a}(\mathbf{R})$, one can cause the transformed $\mathbf{a}(\mathbf{R})$ to vanish, and with it $f(C)$, but not the difference $f(C)-\Delta\lambda(C)=\mathcal{F}(C)$.

Another transformation is the "gauge transformation" applied to the single-valued kets $|X(\mathbf{R})\rangle$, similar to Eq. (2.11):

$$|X(\mathbf{R})\rangle\rightarrow|X(\mathbf{R})\rangle e^{iq(\mathbf{R})} \ , \tag{2.33}$$

where now $q(\mathbf{R})$ is single valued. The transformation (2.33) induces in the vector potential $A(\mathbf{R})$ the gauge transformation

$$\mathbf{A}(\mathbf{R})\rightarrow\mathbf{A}(\mathbf{R})+\nabla q(\mathbf{R}) \ . \tag{2.34}$$

If the phase of $|\chi(\mathbf{R})\rangle$ relative to $|X(\mathbf{R})\rangle$ is unchanged, the vector potential $\mathbf{a}(\mathbf{R})$ also undergoes the gauge transformation (2.34). In this case, the fluxes $\mathcal{F}(C)$ and $f(C)$ are unaffected, as is $\Delta\lambda(C)$.

We see that Eq. (2.33) is just an ordinary gauge transformation, while Eq. (2.29) is something a bit more general, affecting not only the vector potential $\mathbf{a}(\mathbf{R})$ but also the flux $f(C)$ and the phase change $\Delta\lambda(C)$, but not their difference $\mathcal{F}(C)$.

We now consider some special cases of traversal of a closed path in ray space, in each of which the physical or mathematical situation determines the appropriate phasing for the ket $|\chi\rangle$ along the path. To do this in a unified way, it is convenient to introduce the idea of "connection."

### C. Connections

For our purposes, a "connection" is just a rule whereby the phasing of the ket $|\chi\rangle$ is determined for each infinitesimal increment along the path. In other words, given $\hat{P}(\mathbf{R}), \hat{P}(\mathbf{R}+\delta\mathbf{R})$, and $|\chi(\mathbf{R})\rangle$, the connection completes the determination of $|\chi(\mathbf{R}+\delta\mathbf{R})\rangle$. For a more rigorous treatment see, for example, Nash and Sen (1983). The ket $|\chi\rangle$ is thus completely determined along the path if one specifies the connection, the path in ray space, and the ket at some point on the path. When the trajectory along the path has some physical interpretation, the connection is likely to be determined, at least partly, by the physical meaning. We now consider some important examples.

#### 1. Time dependence: Hamiltonian connection

A well-known example of a ket undergoing continuous change is that of time development via a time-dependent Schrödinger equation. In this case we have

$$|d\chi(t)\rangle = -i\hat{H}(t)|\chi(t)\rangle dt \ , \tag{2.35}$$

where $\hat{H}(t)$ is the Hamiltonian operator, in general time dependent. We shall call Eq. (2.35) the "Hamiltonian connection." For this to be an example of a closed-path evolution, $\hat{H}(t)$ must be chosen so that, after a time $T$ has elapsed, the projection $|\chi\rangle\langle\chi|$ has returned to its original form. In the case of evolution according to Eq. (2.35), we have

$$\frac{1}{i}\langle\chi(t)|d\chi(t)\rangle = -\langle\chi(t)|\hat{H}(t)|\chi(t)\rangle dt \ , \tag{2.36}$$

so that, according to Eq. (2.9) that flux $f$ is evidently given by

$$f(C) = -\int_0^T \langle\chi(t)|\hat{H}(t)|\chi(t)\rangle dt \ , \tag{2.37}$$

in other words, $f(C)$ is just minus the average energy integrated over time. The contribution of $f(C)$ to the final change in phase $\Delta\lambda(C)$ is thus just the so-called "dynamical phase," $\int_0^T \langle E\rangle(t)\,dt$. According to Eq. (2.8), however, this is not the only contribution to $\Delta\lambda(C)$. There is an additional term $\mathcal{F}(C)$, which depends only on the path in projective space and is termed the "geometric phase."

In the original paper by Berry (1984), the existence of the geometric phase was established for adiabatic time-dependent processes in which $\hat{H}(t)$ varies so slowly along a closed path that $|\chi(t)\rangle$ is always an eigenket of $\hat{H}(t)$. It was later shown by Aharonov and Anandan (1987) that the geometric phase can be defined also for nonadiabatic evolution, and that it depends only on the path in projective space. This result is seen to appear naturally in our formulation. Berry (1987b) has also considered the case in which $\hat{H}(t)$ traverses a closed path, but not infinitesimally slowly, so that $|\chi\rangle\langle\chi|$ does not necessarily return to its original form, and he has obtained an asymptotic expansion for the geometric correction to the phase.

#### 2. Parallel connection

A natural and appealing connection is to require that $|\chi\rangle$ keep its phase unchanged to the extent possible for infinitesimal changes, in other words, that $\{|\chi\rangle+|d\chi\rangle\}$ be in phase with ("parallel to") $|\chi\rangle$. This means that

$$\langle\chi|\{|\chi\rangle+|d\chi\rangle\}$$

is required to be real and positive, which in turn requires

$$\langle\chi|d\chi\rangle = 0 \ , \tag{2.38}$$

since $\langle\chi|\chi\rangle=1$ and $\langle\chi|d\chi\rangle$ is necessarily pure imaginary because of normalization. Equation (2.38) defines what we shall call the "parallel connection." With this connection, evidently $f(C)=0$ for every closed path, and therefore $\Delta\lambda(C) = -\mathcal{F}(C)$.

The parallel connection is closely related to the Hamiltonian connection. Suppose we take a ket $|\chi(t)\rangle$ defined with the Hamiltonian connection and factor out the dynamical phase by defining the related ket

$$|\tilde{\chi}(t)\rangle = |\chi(t)\rangle \exp\left[i\int_0^t \langle\chi(t')|\hat{H}(t')|\chi(t')\rangle dt'\right] . \tag{2.39}$$

It is seen immediately from Eqs. (2.35) and (2.39) that

$$\langle\tilde{\chi}(t)|d\tilde{\chi}(t)\rangle = 0 \ , \tag{2.40}$$

i.e., that $|\tilde{\chi}(t)\rangle$ is phased with the parallel connections. In the work of Berry (1984), which dealt with adiabatic time evolution, the Hamiltonian connection was used. Because of the relation (2.40) between Hamiltonian and parallel connection, and because the Hamiltonian connection was used in the work of Berry, the parallel connection is sometimes called the "Berry connection."

#### 3. Single-valued connection

In this connection, one requires that $|\chi\rangle$ be single valued, returning to its original form, including phase, after traversing a closed path. In other words, for some appropriate choice of the single-valued kets $|X\rangle$, we have $\lambda=0, \Delta\lambda(C)=0$. For example, choosing a reference ket $|0\rangle$, one can enforce constant phase of $\langle 0|\chi\rangle$ by requiring

$$\langle 0|d\chi\rangle - \langle d\chi|0\rangle = 0 \ . \tag{2.41}$$

If condition (2.41) is enforced, $|\chi\rangle$ will differ at most by a constant phase factor from $|X\rangle$ as given by Eq. (2.3).

The single-valued connection is appropriate, for example, if $|\chi\rangle$ represents an electronic state, and the purpose of developing it along a trajectory is to map out well-defined $|\chi(\mathbf{R})\rangle$, which depend only on $\mathbf{R}$, and not on the trajectory by which $\mathbf{R}$ is reached. Since in this connection $|\chi\rangle=|X\rangle$, we have $\mathbf{a}(\mathbf{R})=\mathbf{A}(\mathbf{R})$, and for every closed path $\Delta\lambda(C)=0, f(C)=\mathcal{F}(C)$.

In terms of Eq. (2.28), the single-valued connection and the parallel connection are in a sense opposites, in that the former assures $\Delta\lambda(C)=0$ at the cost of having a nonvanishing vector potential and flux $f(C)$, while the latter eliminates $f(C)$ and thus also $\mathbf{a}(\mathbf{R})$ with an additional gauge transformation, but at the cost of a nonzero $\Delta\lambda(C)$.

### D. Effect of time-reversal invariance

It may happen that we wish to restrict the allowable kets $|\chi(\mathbf{R})\rangle$ along a path by some condition that all must satisfy. For example, if we are considering adiabatic time evolution under a Hamiltonian $\hat{H}(t)$ that possesses certain symmetry properties for all $t$, or mapping out a set of kets $|\chi(\mathbf{R})\rangle$ that are eigenkets of a Hamiltonian $\hat{H}(\mathbf{R})$ which posseesses certain symmetry properties for all $\mathbf{R}$, we need only consider kets $|\chi(\mathbf{R})\rangle$ that are compatible with that symmetry. In practice, the symmetry of most interest in molecular systems is time reversal, which is normally the only symmetry that obtains for all $\mathbf{R}$.[1] Accordingly, we consider that case in this subsection; the treatment of other symmetries would be similar.

The properties of the antiunitary time-reversal operator $\hat{T}$ have been discussed extensively in the literature (Wigner, 1959; Gottfried, 1966; Truhlar *et al.*, 1975). As an antiunitary operator, $\hat{T}$ satisfies the relations

$$\hat{T}(|\psi\rangle\gamma)=(\hat{T}|\psi\rangle)\gamma^* \tag{2.42}$$

and

$$\langle\hat{T}\psi|\hat{T}\varphi\rangle=\langle\psi|\varphi\rangle^* , \tag{2.43}$$

where $|\psi\rangle$ and $|\varphi\rangle$ are any two kets and $\gamma$ any complex number. Moreover, $\hat{T}$ is "involutional," meaning that $\hat{T}^2$ reproduces the same physical state, i.e., the same ket up to a phase factor. Indeed, it can be shown that always $\hat{T}^2=\pm 1$. If the total spin is integer (even number of electrons), or if it is permitted to ignore spin, we have

$$\hat{T}^2=1 . \tag{2.44}$$

(The case $\hat{T}^2=-1$ leads to the non-Abelian case, to be considered in Sec. III.) If $|\chi(\mathbf{R})\rangle$ is an eigenket of an operator $\hat{H}(\mathbf{R})$ which is invariant under $\hat{T}$, and if Eq. (2.44) is satisfied, then one can require that the $|\chi(\mathbf{R})\rangle$ be eigenkets of $\hat{T}$ as well:

$$\hat{T}|\chi(\mathbf{R})\rangle=|\chi(\mathbf{R})\rangle e^{i\lambda(\mathbf{R})} . \tag{2.45}$$

From kets satisfying Eq. (2.45), we can construct kets $|\tilde{\chi}(\mathbf{R})\rangle$ that are simply unchanged by time reversal by means of the transformation

$$|\tilde{\chi}(\mathbf{R})\rangle=|\chi(\mathbf{R})\rangle e^{i\lambda(\mathbf{R})/2} . \tag{2.46}$$

From Eqs. (2.42) and (2.46), it is easy to see that the kets $|\tilde{\chi}(\mathbf{R})\rangle$ satisfy

$$\hat{T}|\tilde{\chi}(\mathbf{R})\rangle=|\tilde{\chi}(\mathbf{R})\rangle . \tag{2.47}$$

Moreover, Eq. (2.47) determines the phasing of the kets completely.

Choosing a set of constant kets $|j\rangle$, all satisfying Eq. (2.47), and expanding $|\tilde{\chi}(\mathbf{R})\rangle$ in terms of them,

$$|\tilde{\chi}(\mathbf{R})\rangle=\sum_j |j\rangle a_j(\mathbf{R}) , \tag{2.48}$$

we see immediately that the $a_j$ must all be real. It is also clear that continuous variation of the $a_j$ will cause $|\tilde{\chi}(\mathbf{R})\rangle$ to vary in accordance with the parallel connection. Accordingly, the only possible nonzero invariant flux $\mathcal{F}(C)$ is that associated with a coefficient passing through zero, given by Eq. (2.20): $\mathcal{F}(C)$ can only be a multiple of $\pi$, the phase change on traversing a closed path with parallel connection being either no change at all or just a change of sign.

If a path $C$ is continuously distorted, as illustrated in Fig. 1, the only change that can occur in $\mathcal{F}(C)$ is an abrupt change of $\pi$. There must therefore be infinitesimally small paths that bring a sign change. As the above analysis shows, a sign change requires that the coefficient of one basis ket, say $|0\rangle$, pass through zero at *one* point (or an odd number of points) along the path. If it passes through zero at an even number of points, the

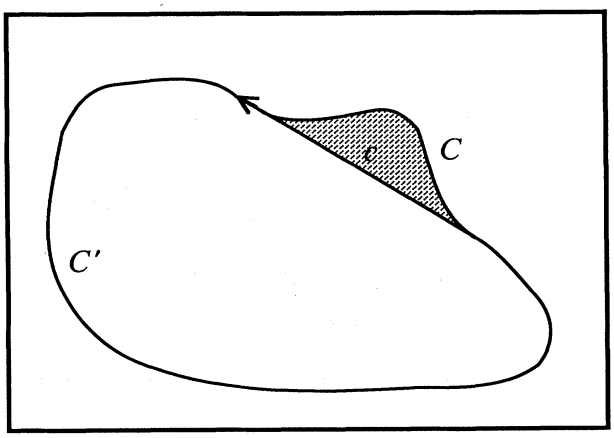


FIG. 1. Abrupt change in parity of closed path for nondegenerate time-reversal-invariant case, $\hat{T}^2=+1$. If the outer curve $C$ produces a sign change and the inner curve $C'$, slightly deformed from $C$, does not, the infinitesimally small curve $c$ (around the shaded area) must involve a sign change.

[1]The only exceptions are diatomic molecules with $C_{\infty v}$ or $D_{\infty h}$ symmetry always obtaining, and triatomic systems with $C_s$ symmetry, whose properties are taken up in Sec. V.

sign changes will cancel out. The points $\mathbf{R}$ at which a given coefficient is zero are those for which the corresponding ket is annihilated by $\hat{P}(\mathbf{R})$:

$$\hat{P}(\mathbf{R})|0\rangle=0 \ . \tag{2.49}$$

Since Eq. (2.49) represents one requirement on $\mathbf{R}$, the manifold $\mathcal{M}$ of points where it is satisfied is of codimension 1 [dimension $(n-1)$ if $n$ is the dimension of $\mathcal{R}$]. Its boundary $\mathcal{B}$ (if $\mathcal{M}$ has a boundary) is thus of codimension 2. As illustrated in Fig. 2, closed paths that encircle $\mathcal{B}$, and only these, will pass through $\mathcal{M}$ once and bring about a sign change. The infinitesimally small paths that bring about sign changes, therefore, are the ones encircling the codimension-2 manifold $\mathcal{B}$.

It is evident also that the boundary manifold $\mathcal{B}$ must be a singular point for $\hat{P}(\mathbf{R})$. To see this, we note that the existence or nonexistence of a sign change is independent of the choice of reference ket $|0\rangle$: If another reference ket $|\tilde{0}\rangle$ is chosen, then $\mathcal{B}$ must also form the boundary of the manifold $\tilde{\mathcal{M}}$ for which, instead of Eq. (2.49),

$$\hat{P}(\mathbf{R})|\tilde{0}\rangle=0 \ , \tag{2.50}$$

and this must be true regardless of the choice of $|\tilde{0}\rangle$. Since there cannot be a manifold on which $\hat{P}(\mathbf{R})$ annihilates every ket, it must be that, as $R$ approaches $\mathcal{B}$ from different directions, $\hat{P}(\mathbf{R})$ approaches different limits.

The situation is simply illustrated by an example in which the space of the kets and the configuration space $\mathcal{R}$ are both two dimensional. In polar coordinates, let $\hat{P}(\mathbf{R})$ be given by

$$\hat{P}(\mathbf{R})=\frac{1}{2}\begin{bmatrix}1+\cos\theta & \sin\theta \\ \sin\theta & 1-\cos\theta\end{bmatrix} . \tag{2.51}$$

Any ket in the real two-dimensional ket space is acceptable as reference ket. Let an arbitrary reference ket $|0_\phi\rangle$ be denoted by

$$|0_\phi\rangle=\begin{bmatrix}\cos\frac{\phi}{2} \\ \sin\frac{\phi}{2}\end{bmatrix} , \tag{2.52}$$

with $-\pi\le\phi\le\pi$. All possible reference kets are of the form of Eq. (2.52). It is easy to see that the manifold $\mathcal{M}_\phi$ in $\mathcal{R}$ in which $\hat{P}(\mathbf{R})$ annihilates $|0_\phi\rangle$ is that for which

$$\theta=\phi\pm\pi \ , \tag{2.53}$$

i.e., it is a region of constant $\theta$. Each such domain has the origin as boundary, but $\hat{P}(\mathbf{R})$ does not possess a well-defined limit at the origin: As the origin is approached on a manifold with constant $\theta$, the limit of $\hat{P}(\mathbf{R})$ will depend on $\theta$.

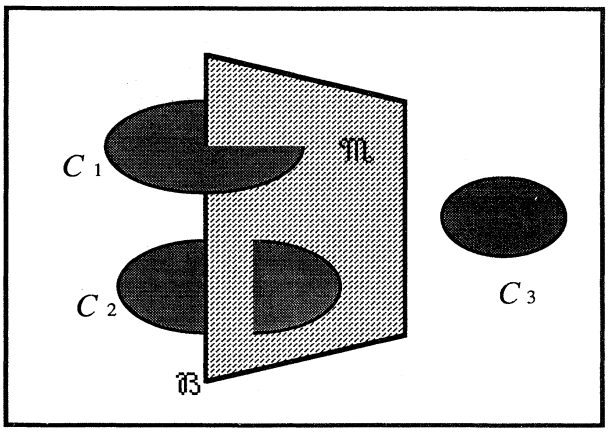


FIG. 2. Requirement that a closed path can lead to a sign change in $\hat{T}$-invariant, $\hat{T}^2=+1$ case if the path encloses the boundary $\mathcal{B}$ of manifold $\mathcal{M}$ in which $\hat{P}(\mathbf{R})|0\rangle=0$. The path $C_1$ encircles $\mathcal{B}$ and thus intersects $\mathcal{M}$ just once, bringing about a sign change. $C_2$, which penetrates $\mathcal{M}$ and thus intersects it twice, and $C_3$, which lies entirely outside $\mathcal{M}$, are not associated with sign changes.

## III. DIFFERENTIAL FORMULATION: ABELIAN AND NON-ABELIAN CASES

We now consider the case in which more than one ket must be transported. In the molecular context, this means that more than one electronic state must be considered. For this "non-Abelian" case, it is more useful to work with a differential formulation involving infinitesimal closed paths than with the finite closed paths used in Sec. II. For the special case in which only one ket is being transported, the formulas of this section are also applicable to the Abelian case. To avoid undue burdening of the notation, we shall frequently omit the argument $\mathbf{R}\Longleftrightarrow x_\mu$, it being understood that projections, kets, sets of kets, and other defined quantities related to them are in general functions of $\mathbf{R}$.

### A. Preliminaries for *n*-dimensional case

#### 1. Developments in notation

In this section, we are again concerned with projection operators $\hat{P}(\mathbf{R})$ (or simply $\hat{P}$), which are single-valued functions of continuously varying parameters, but now the projections are of arbitrary dimensionality. If the dimension of the subspace onto which $\hat{P}(\mathbf{R})$ projects is $n$, the expression analogous to (2.1) is

$$\hat{P}(\mathbf{R})=\sum_{j=1}^{n}|\chi_j(\mathbf{R})\rangle\langle\chi_j(\mathbf{R})| \ . \tag{3.1}$$

As in the one-dimensional case, the kets $|\chi_j(\mathbf{R})\rangle$ are only partially determined by the projection, since there are an infinite number of ways of choosing a complete orthonormal basis for an $n$-dimensional subspace. In the special case $n=1$, the choice of basis reduces just to a choice of phase.

The generalization of a rephasing in one dimension, therefore, is a change of basis in $n$ dimensions, and the entity that will be transported continuously as a function

of parameters $x_\mu \Longleftrightarrow \mathbf{R}$ is a set of $n$ orthonormal kets $|\chi_j(\mathbf{R})\rangle$ spanning the space of $\hat{P}(\mathbf{R})$. It is therefore convenient to have a notation for the entire set of basis kets. We accomplish this by using $\{|$ to denote a row vector of length $n$, so that $\{|\chi\rangle|$, a "ket row," denotes a row whose elements are the basis vectors $|\chi_j\rangle$:

$$\{|\chi\rangle| = (|\chi_1\rangle \;\; |\chi_2\rangle \;\; \cdots |\chi_n\rangle) \; . \tag{3.2}$$

Using $|\}$ to denote a column of length $n$, we define the "bra column" conjugate to $\{|\chi\rangle|$ in the obvious way:

$$|\langle\chi|\} = \begin{pmatrix} \langle\chi_1| \\ \langle\chi_2| \\ \vdots \\ \langle\chi_n| \end{pmatrix} \; . \tag{3.3}$$

We shall also use $\{|$ and $|\}$ to denote $n$-dimensional rows and columns of ordinary numbers, or functions. When combining ket rows and bra columns with each other and with rows and columns of numbers or functions, we use symbolically the rules of matrix multiplication, with "multiplication" of bras and kets defined according to the usual rules for combining these. Thus, for example, if $\{|\chi\rangle|$ and $\{|\chi'\rangle|$ are two ket rows, then the "inner product" $|\langle\chi|\}\{|\chi'\rangle|$ is defined as

$$\begin{aligned} |\langle\chi|\}\{|\chi'\rangle| &= \begin{pmatrix} \langle\chi_1| \\ \langle\chi_2| \\ \vdots \\ \langle\chi_n| \end{pmatrix} (|\chi_1'\rangle \;\; |\chi_2'\rangle \;\; \cdots \;\; |\chi_n'\rangle) \\ &= \begin{pmatrix} \langle\chi_1|\chi_1'\rangle & \langle\chi_1|\chi_2'\rangle & \cdots & \langle\chi_1|\chi_n'\rangle \\ \langle\chi_2|\chi_1'\rangle & \langle\chi_2|\chi_2'\rangle & \cdots & \langle\chi_2|\chi_n'\rangle \\ \cdots & \cdots & \cdots & \cdots \\ \langle\chi_n|\chi_1'\rangle & \langle\chi_n|\chi_2'\rangle & \cdots & \langle\chi_n|\chi_n'\rangle \end{pmatrix} \equiv \mathsf{s} \; , \end{aligned} \tag{3.4}$$

where $\mathsf{s}$ is seen to be just the overlap matrix. We shall always use sans-serif letters to denote $n \times n$ matrices.

Combining $\{|\chi\rangle|$ with its own bra column in the opposite direction, we obtain

$$\begin{aligned} \{|\chi\rangle|\langle\chi|\} &= (|\chi_1\rangle \;\; |\chi_2\rangle \;\; \cdots \;\; |\chi_n\rangle) \begin{pmatrix} \langle\chi_1| \\ \langle\chi_2| \\ \vdots \\ \langle\chi_n| \end{pmatrix} \\ &= \sum_{j=1}^{n} |\chi_j\rangle\langle\chi_j| = \hat{P} \; . \end{aligned} \tag{3.5}$$

## 2. Differential evolution of projections

We need to consider $n$-dimensional projection operators $\hat{P}(\mathbf{R})$, evolving continuously as the parameters $x_\mu \Longleftrightarrow \mathbf{R}$ evolve. $\hat{P}(\mathbf{R})$ is considered to be a single-valued function of the parameters, so when the parameters $\mathbf{R}$ return to their original values, $\hat{P}(\mathbf{R})$ also resumes its original form. We shall also need the projection onto the reciprocal space, $\hat{P}' = 1 - \hat{P}$, with $\hat{P}\hat{P}' = \hat{P}'\hat{P} = 0$. For an infinitesimal change in $\hat{P}$, we have

$$\delta\hat{P} = (\delta x_\mu)\partial_\mu \hat{P} \; , \tag{3.6}$$

where we sum over repeated indices and $\partial_\mu = \partial/\partial x_\mu$. $\hat{P}$ is a projection operator, satisfying the relation $\hat{P}^2 = \hat{P}$, and this must also be true of $(\hat{P} + \delta\hat{P})$, which to lowest order in infinitesimals gives

$$\begin{aligned} &(\hat{P} + \delta\hat{P})^2 = \hat{P} + \hat{P}(\delta\hat{P}) + (\delta\hat{P})\hat{P} = \hat{P} + \delta\hat{P} \; , \\ &\hat{P}(\delta\hat{P}) + (\delta\hat{P})\hat{P} = \delta\hat{P} \; . \end{aligned} \tag{3.7}$$

Multiplying Eq. (3.7) by $\hat{P}$ from both left and right, and then repeating the process with $\hat{P}'$, we obtain

$$\hat{P}(\delta\hat{P})\hat{P} = \hat{P}'(\delta\hat{P})\hat{P}' = 0 \; . \tag{3.8}$$

The meaning of Eq. (3.8), of course, is that the block-diagonal part of $\delta\hat{P}$ is zero: Applied to a ket lying in the subspace of $\hat{P}$, it produces a ket orthogonal to that subspace, and vice versa. We shall sometimes refer to operators having this property as "off-block" operators.

We can obtain a Hermitian operator $\delta\hat{G}$ by defining

$$i\delta\hat{G} = [\delta\hat{P}, \hat{P}] \; . \tag{3.9}$$

Using Eqs. (3.7), (3.8), and (3.9), it is easy to obtain

$$i[\delta\hat{G}, \; \hat{P}] = \delta\hat{P} \tag{3.10}$$

and

$$\hat{P}(\delta\hat{G})\hat{P} = \hat{P}'(\delta\hat{G})\hat{P}' = 0 \; . \tag{3.11}$$

Using Eq. (3.6) and the definition

$$\delta\hat{G} = \hat{g}_\mu \delta x_\mu \; , \tag{3.12}$$

one obtains, in analogy with Eqs. (3.7)–(3.11),

$$\hat{P}(\partial_\mu\hat{P}) + (\partial_\mu\hat{P})\hat{P} = \partial_\mu\hat{P} \; , \tag{3.13}$$

$$\hat{P}(\partial_\mu\hat{P})\hat{P} = 0 \; , \tag{3.14}$$

$$i\hat{g}_\mu = [\partial_\mu\hat{P}, \hat{P}] \; , \tag{3.15}$$

$$i[\hat{g}_\mu, \hat{P}] = \partial_\mu\hat{P} \; , \tag{3.16}$$

$$\hat{P}\hat{g}_\mu\hat{P} = \hat{P}'\hat{g}_\mu\hat{P}' = 0 \; . \tag{3.17}$$

Since $\hat{P}$ is a single-valued function of the parameters, so is $\hat{g}_\mu$, according to Eq. (3.15). Moreover, from Eqs. (3.11) and (3.17), we see that $\delta\hat{G}$ and $\hat{g}_\mu$ are off-block operators.

We shall also need the expression for the "curl" of the vector $\hat{\mathbf{g}} \Longleftrightarrow \hat{g}_\mu$. Using Eqs. (3.15) and (3.16), we find

$$\begin{aligned} i\partial_\mu\hat{g}_\nu &= [\partial_\mu\partial_\nu\hat{P}, \hat{P}] + [\partial_\nu\hat{P}, \partial_\mu\hat{P}] \\ &= [\partial_\mu\partial_\nu\hat{P}, \hat{P}] - [[\hat{g}_\nu, \hat{P}], [\hat{g}_\mu, \hat{P}]] \\ &= [\partial_\mu\partial_\nu\hat{P}, \hat{P}] - [\hat{g}_\mu, \hat{g}_\nu] \; , \end{aligned} \tag{3.18}$$

where we have also used the off-block character of the $\hat{g}_\mu$ in obtaining the last equality. Interchanging $\mu$ and $\nu$ in Eq. (3.18) and subtracting, remembering that $\hat{P}$ is single valued so that $\partial_\mu\partial_\nu\hat{P}=\partial_\nu\partial_\mu\hat{P}$, we find

$$i(\partial_\mu\hat{g}_\nu-\partial_\nu\hat{g}_\mu)=-2[\hat{g}_\mu,\ \hat{g}_\nu]\ . \tag{3.19}$$

We note that the right-hand side of Eq. (3.19) is evidently a block-diagonal operator, commuting with $\hat{P}$.

### 3. Change of basis; definition of parallelism

In the situations in which we are interested, $\hat{P}$ is a single-valued operator function of $\mathbf{R}$. The ket row $\{|\chi\rangle|$ must of course satisfy

$$\hat{P}\{|\chi\rangle|=\{\hat{P}|\chi\rangle|=\{|\chi\rangle| \tag{3.20}$$

[which is equivalent to Eq. (3.5)], but is otherwise arbitrary. The first equality in Eq. (3.20) gives a rather obvious definition of what is meant by having $\hat{P}$, or any other operator, operate on a ket row: It gives a ket row whose elements are obtained by applying $\hat{P}$ to each of the elements of $\{|\chi\rangle|$. If Eqs. (3.5) and (3.20) are satisfied by a ket row $\{|\chi^{(0)}\rangle|$, they will evidently also be satisfied by $\{|\chi\rangle|$, with elements

$$|\chi_j\rangle=\sum_{k=1}^{n}|\chi_k^{(0)}\rangle u_{kj}\ , \tag{3.21}$$

where the $u_{kj}$ are the elements of a unitary $n\times n$ matrix u. Our shorthand for this change of basis is

$$\{|\chi\rangle|=\{|\chi^{(0)}\rangle|\mathsf{u}\ . \tag{3.22}$$

In the one-dimensional case considered in Sec. II, we considered two kets $|\chi_a\rangle$ and $|\chi_b\rangle$ to be parallel or in phase if

$$s=\langle\chi_a|\chi_b\rangle=(\text{real, positive})\ . \tag{3.23}$$

In the present case, $s$ is replaced by the overlap matrix s, Eq. (3.4), so a natural generalization of Eq. (3.23) is to say that the ket rows $\{|\chi_a\rangle|$ and $\{|\chi_b\rangle|$ are in phase or parallel if

$$\mathsf{s}=|\langle\chi_a|\}\{|\chi_b\rangle|=(\text{Hermitian, positive definite})\ . \tag{3.24}$$

If Eq. (3.24) is satisfied, then for any column $|\alpha\}$ with complex number elements $\alpha_1,\alpha_2,\ldots,\alpha_n$, the two kets

$$|\psi_a\rangle=\sum_{j=1}^{n}|\chi_{aj}\rangle\alpha_j=\{|\chi_a\rangle|\alpha\}\ ,\quad |\psi_b\rangle=\{|\chi_b\rangle|\alpha\} \tag{3.25}$$

are parallel according to Eq. (3.23).

To see how Eq. (3.24) can be satisfied, we consider two projections $\hat{P}_a$ and $\hat{P}_b$, with a fixed basis $\{|\chi_a\rangle|$ for the first and a tentative one $\{|\chi_b^{(0)}\rangle|$ for the other, with overlap matrix

$$\mathsf{s}^{(0)}=|\langle\chi_a|\}\{|\chi_b^{(0)}\rangle|\ , \tag{3.26}$$

and try to find a new basis for $\hat{P}_b$ such that Eq. (3.24) will be satisfied. The new basis must be generated from the old by a transformation of the type (3.22),

$$\{|\chi_b\rangle|=\{\chi_b^{(0)}\rangle|\mathsf{u}\ , \tag{3.27}$$

and one sees easily from Eqs. (3.26) and (3.27) that the new overlap matrix is

$$\mathsf{s}=|\langle\chi_a|\}\{|\chi_b\rangle|=\mathsf{s}^{(0)}\mathsf{u}\ . \tag{3.28}$$

If $\mathsf{s}^{(0)}$ is nonsingular, one sees by inspection that s in Eq. (3.28) will be Hermitian and positive definite if u is given by

$$\mathsf{u}=(\mathsf{s}^{(0)\dagger}\mathsf{s}^{(0)})^{-1/2}\mathsf{s}^{(0)\dagger}\ . \tag{3.29}$$

If $\mathsf{s}^{(0)}$ is singular, there is no solution, just as there is no solution of Eq. (3.23) if $s=0$. The meaning of $\mathsf{s}^{(0)}$ being nonsingular is that there is no ket lying in the space of $\hat{P}_a$ that is annihilated by $\hat{P}_b$, and vice versa. This will be satisfied in all situations that we have to consider.

One sees easily that the solution (3.29) is unique. For, if it were not, it would be possible to apply another transformation of the form (3.28) and still have a Hermitian positive-definite overlap matrix. In other words, for a Hermitian positive-definite s, there would have to be a unitary $\mathsf{v}=e^{i\mathsf{q}}$, with q Hermitian, such that $\mathsf{s}'=\mathsf{sv}$ is also Hermitian and positive definite. For s′ to be merely Hermitian, we must have

$$(\mathsf{s}e^{i\mathsf{q}})^\dagger=e^{-i\mathsf{q}}\mathsf{s}=\mathsf{s}e^{i\mathsf{q}}\ , \tag{3.30}$$

which can only be satisfied if

$$\mathsf{sq}=-\mathsf{qs}\ . \tag{3.31}$$

It is easy to see, however, that there is no nonzero Hermitian matrix that anticommutes with a positive-definite Hermitian matrix, so there is no solution to Eq. (3.30) and no other solution to Eq. (3.24).

As has also been discussed elsewhere (Mead, 1991), the transformation (3.29) is the same as the one obtained in the context of a molecular problem by Cederbaum *et al.* (1989) and called by them "block diagonalization." It has been shown (Pacher *et al.*, 1988; Pacher *et al.*, 1989) that this transformation can be useful in finding electronic basis states that are "quasiadiabatic," i.e., that in a certain sense have as small a derivative coupling as possible between different electronic states. This matter will be discussed further in Sec. VIII.

### B. Transport of basis around infinitesimal closed path

As we shall see, transport of a ket row along a closed path is more complicated than transport of a single ket as in Sec. II, because of the non-Abelian property of the vector potential. Transport around an infinitesimal closed path, however, can be analyzed fairly simply and also gives us most of the results that we shall need.

We consider an infinitesimal change $\delta x_\mu$ in the parameters $x_\mu$, causing a change in $\hat{P}(\mathbf{R})$, and a concomitant

change in the ket row $\{|\chi\rangle|$. While $\hat{P}$ is single valued, $\{|\chi\rangle|$ need not be, since it is only required to satisfy Eqs. (3.5) and (3.20). We represent the infinitesimal change in $\{|\chi\rangle|$ by

$$\delta\{|\chi\rangle|=\delta x_\mu \tilde{\partial}_\mu\{|\chi\rangle| \ , \tag{3.32}$$

where the tilde over the partial derivative symbol reminds us that, since $\{|\chi\rangle|$ is not necessarily single valued, partial derivatives of it are taken along the path. The ket row must change in such a way that it continues to satisfy Eq. (3.20). Using Eqs. (3.16) and (3.32), we see that this requirement takes the form

$$\begin{aligned}(\hat{P}+\delta\hat{P})(\{|\chi\rangle\}|+\delta\{|\chi\rangle|)&=(\hat{P}+i\delta x_\mu[\hat{g}_\mu,\ \hat{P}])\\ &\quad\times\{|\chi\rangle|+\delta x_\mu\tilde{\partial}_\mu\{|\chi\rangle|)\\ &=\{|\chi\rangle|+\delta x_\mu\tilde{\partial}_\mu\{|\chi\rangle| \ .\end{aligned} \tag{3.33}$$

Carrying this out to first order in infinitesimals, separating the coefficient of $\delta x_\mu$, and rearranging, we find

$$(1-\hat{P})\tilde{\partial}_\mu\{|\chi\rangle|=i[\hat{g}_\mu,\ \hat{P}]\{|\chi\rangle=i\hat{g}_\mu\{|\chi\rangle| \ , \tag{3.34}$$

where the last equality follows from Eq. (3.20) and the off-block property of $\hat{g}_\mu$. Equation (3.34) determines only a part of $\tilde{\partial}_\mu\{|\chi\rangle|$, leaving $\hat{P}\tilde{\partial}_\mu\{|\chi\rangle|$ open. This simply corresponds to the fact that $\{|\chi\rangle|$ can always be subjected to a transformation of the type (3.22), in our case an infinitesimal one, without violating Eq. (3.20). Using Eq. (3.5), we can write $\hat{P}\hat{\partial}_\mu\{|\chi\rangle|$ as

$$\hat{P}\hat{\partial}_\mu\{|\chi\rangle|=\{|\chi\rangle|\langle\chi|\}\hat{\partial}_\mu\{|\chi\rangle|=i\{|\chi\rangle|\mathsf{a}_\mu \ , \tag{3.35}$$

where

$$\mathsf{a}_\mu=\frac{1}{i}|\langle\chi|\}\tilde{\partial}_\mu\{|\chi\rangle| \ . \tag{3.36}$$

The matrix $\mathsf{a}_\mu$ plays a role analogous to that of the vector-potential component $a_\mu$ in Sec. II and is generally called a gauge potential. The gauge potential will depend on the connection; apart from being Hermitian, it is not determined by Eqs. (3.20) or (3.5). Combining Eqs. (3.34), (3.35), and (3.36), we have for the change in the ket row

$$\tilde{\partial}_\mu\{|\chi\rangle|=i\hat{g}_\mu\{|\chi\rangle|+i\{|\chi\rangle|\mathsf{a}_\mu \ . \tag{3.37}$$

The change in $\{|\chi\rangle|$ on traversing an infinitesimal closed path is determined by the difference between path partial derivatives taken in different orders. Taking the path derivative of Eq. (3.37) with respect to $x_\nu$, we find

$$\begin{aligned}\tilde{\partial}_\nu\tilde{\partial}_\mu\{|\chi\rangle|&=i(\partial_\nu\hat{g}_\mu)\{|\chi\rangle|+i\{|\chi\rangle|(\tilde{\partial}_\nu\mathsf{a}_\mu)\\ &\quad-\hat{g}_\mu(\hat{g}_\nu\{|\chi\rangle|+\{|\chi\rangle|\mathsf{a}_\nu)\\ &\quad-(\hat{g}_\nu\{|\chi\rangle|+\{|\chi\rangle|\mathsf{a}_\nu)\mathsf{a}_\mu \ .\end{aligned} \tag{3.38}$$

Reversing the roles of $\mu$ and $\nu$ in Eq. (3.38) and subtracting, we find

$$\begin{aligned}(\tilde{\partial}_\mu\tilde{\partial}_\nu-\tilde{\partial}_\nu\tilde{\partial}_\nu)\{|\chi\rangle|&=i(\partial_\mu\hat{g}_\nu-\partial_\nu\hat{g}_\mu)\{|\chi\rangle|\\ &\quad+i\{|\chi\rangle|(\tilde{\partial}_\mu\mathsf{a}_\nu-\tilde{\partial}_\nu\mathsf{a}_\mu)\\ &\quad+[\hat{g}_\mu,\hat{g}_\nu]\{|\chi\rangle|-\{|\chi\rangle|[\mathsf{a}_\mu,\ \mathsf{a}_\nu] \ ,\end{aligned} \tag{3.39}$$

which with the aid of Eq. (3.19) is transformed into

$$\begin{aligned}(\tilde{\partial}_\mu\tilde{\partial}_\nu-\tilde{\partial}_\nu\tilde{\partial}_\mu)\{|\chi\rangle|&=-[\hat{g}_\mu,\ \hat{g}_\nu]\{|\chi\rangle|\\ &\quad+i\{|\chi\rangle|(\tilde{\partial}_\mu\mathsf{a}_\nu-\tilde{\partial}_\nu\mathsf{a}_\mu+i[\mathsf{a}_\mu,\ \mathsf{a}_\nu]) \ .\end{aligned} \tag{3.40}$$

Since we know that $[\hat{g}_\mu,\ \hat{g}_\nu]$ is block diagonal, we can apply $\hat{P}$ to the first term on the right-hand side without affecting it. Doing this and using Eq. (3.5), we obtain

$$[\hat{g}_\mu,\ \hat{g}_\nu]\{|\chi\rangle|=\hat{P}[\hat{g}_\mu,\ \hat{g}_\nu]\{|\chi\rangle|=i\{|\chi\rangle|\mathsf{Z}_{\mu\nu} \ , \tag{3.41}$$

where the Hermitian matrix $\mathsf{Z}_{\mu\nu}$ is given by

$$\mathsf{Z}_{\mu\nu}=\frac{1}{i}|\langle\chi|\}[\hat{g}_\mu,\ \hat{g}_\nu]\{|\chi\rangle| \ . \tag{3.42}$$

Combining Eqs. (3.41) and (3.42) with (3.40), we finally obtain

$$(\tilde{\partial}_\mu\tilde{\partial}_\nu-\tilde{\partial}_\nu\tilde{\partial}_\mu)\{|\chi\rangle|=i\{|\chi\rangle(\tilde{\partial}_\mu\mathsf{a}_\nu-\tilde{\partial}_\nu\mathsf{a}_\mu+i[\mathsf{a}_\mu,\ \mathsf{a}_\nu]-\mathsf{Z}_{\mu\nu}) \ . \tag{3.43}$$

If $\{|\chi\rangle|$ is carried around an infinitesimal rectangle in the $\mu\nu$ plane with sides $\delta x_\mu\delta x_\nu$, the infinitesimal change in $\{|\chi\rangle|$ is given by $\delta x_\mu\delta x_\nu$ times the right-hand side of Eq. (3.43). It is evident from the definitions that $\mathsf{Z}_{\mu\nu}$ is a "covariant quantity," being determined up to a unitary transformation by the path (cf. Sec. III.D below).

When $\{|\chi\rangle|$ is carried around a closed path, the result is now in general not just a phase change but a unitary transformation of type (3.22). The infinitesimal version of this is represented on the left-hand side of Eq. (3.43). Analogously to Eq. (2.8), the right-hand side breaks this up into two contributions: an invariant part represented by $\mathsf{Z}_{\mu\nu}$, analogous to $\mathcal{F}$ in Eq. (2.8), and the additional term dependent on the choice of gauge potential analogous to $f$ in Eq. (2.8).

A single-valued ket row $\{|X\rangle|$ is by definition one that does not change on traversal of a closed path. In analogy with Sec. II, we use a capital letter to denote the gauge-potential matrix for such a ket row:

$$\mathsf{A}_\mu=\frac{1}{i}|\langle X|\}\partial_\mu\{|X\rangle| \ . \tag{3.44}$$

According to Eq. (3.42), single-valuedness of $\{|X\rangle|$ requires that $\mathsf{A}_\mu$ satisfy

$$\partial_\mu\mathsf{A}_\nu-\partial_\nu\mathsf{A}_\mu+i[\mathsf{A}_\mu,\ \mathsf{A}_\nu]=\mathsf{Z}_{\mu\nu} \ . \tag{3.45}$$

Apart from the commutator, which would vanish if the $\mathsf{A}_\mu$ were ordinary numbers instead of matrices, Eq. (3.45) looks just like the expression for a magnetic-field strength as the curl of a vector potential. Accordingly, $\mathsf{Z}_{\mu\nu}$ is re-

ferred to as the field strength and the commutator term represents the generalization to the non-Abelian case in which the $A_\mu$ do not commute. In most of the applications to molecular systems, we shall be concerned with single-valued bases, and Eq. (3.45) for the vector potential will play a role.

If we wish, in analogy to the treatment of Sec. II, we can express an arbitrary ket row in terms of a single-valued one via

$$\{|\chi\rangle|=\{|X\rangle|\mathsf{u}\ , \tag{3.46}$$

where the unitary matrix u is not necessarily single valued, but changes along a path. We denote the change in u along the path by

$$\tilde{\partial}_\mu \mathsf{u}=i\mathsf{u}\mathsf{f}_\mu\ . \tag{3.47}$$

Starting with $\mathsf{u}=1$ and allowing u to evolve according to Eq. (3.47) along a closed path $C$, we find that the result when the $x_\mu$ have returned to their original values, $\mathsf{u}(C)$, gives the change in $\{|\chi\rangle|$ for the path. Because the $\mathsf{f}_\mu$ for different points along the path do not commute, however, $\mathsf{u}(C)$ is not given by a simple loop integral, but by a path-ordered integral:

$$\mathsf{u}(C)=\mathcal{P}\exp\oint_C i\mathsf{f}_\mu dx_\mu\ , \tag{3.48}$$

where $\mathcal{P}$ is the path-ordering operator: in the series expansion of Eq. (3.48), $\mathsf{f}_\mu$ for different points on the path are always arranged in order of position along the path, with those nearest the beginning on the left. In the one-dimensional Abelian case considered in Sec. II, path ordering in expressions analogous to (3.48) is unnecessary because the integrands are ordinary numbers which commute with one another.

### C. Gauge and phase-gauge transformations

Starting with a ket row $\{|\chi\rangle|$, not necessarily single valued, we can generate a phase-gauge transformation analogous to Eq. (2.29) by making the replacement

$$\{|\chi'\rangle|=\{|\chi\rangle|\mathsf{v}\ , \tag{3.49}$$

where v also need not be single valued. For the derivative of the new ket row along a path we have

$$\tilde{\partial}_\mu\{|\chi'\rangle|=(\tilde{\partial}_\mu\{|\chi\rangle|)\mathsf{v}+\{|\chi\rangle|\tilde{\partial}_\mu\mathsf{v}\ , \tag{3.50}$$

leading to the transformed gauge potential,

$$\mathsf{a}'_\mu=\frac{1}{i}|\langle\chi'|\}\tilde{\partial}_\mu\{|\chi'\rangle|=\mathsf{v}^\dagger\mathsf{a}_\mu\mathsf{v}+\frac{1}{i}\mathsf{v}^\dagger\tilde{\partial}_\mu\mathsf{v}\ . \tag{3.51}$$

We shall mainly be interested in "ordinary" gauge transformations applied to single-valued ket rows, of the form

$$\{|X'\rangle|=\{|X\rangle|\mathsf{u}\ , \tag{3.52}$$

where now u is required to be single valued. The transformed gauge potential in this case is given by

$$\mathsf{A}'_\mu=\mathsf{u}^\dagger\mathsf{A}_\mu\mathsf{u}+\frac{1}{i}\mathsf{u}^\dagger\partial_\mu\mathsf{u}\ . \tag{3.53}$$

Equation (3.53) looks much like (3.51), but the difference is important: Because u is now single valued, there is no tilde over the partial derivative sign.

Because u must remain unitary as the $x_\mu$ are varied, it evidently satisfies

$$(\partial_\mu\mathsf{u}^\dagger)\mathsf{u}+\mathsf{u}^\dagger\partial_\mu\mathsf{u}=0\ , \tag{3.54}$$

while single-valuedness requires that

$$(\partial_\mu\partial_\nu-\partial_\nu\partial_\mu)\mathsf{u}=0\ . \tag{3.55}$$

Using Eqs. (3.53), (3.54), and (3.55), it is straightforward to obtain the result

$$\partial_\mu\mathsf{A}'_\nu-\partial_\nu\mathsf{A}'_\mu+i[\mathsf{A}'_\mu,\ \mathsf{A}'_\nu]=\mathsf{u}^\dagger(\partial_\mu\mathsf{A}_\nu-\partial_\nu\mathsf{A}_\mu+i[\mathsf{A}_\mu,\ \mathsf{A}_\nu])\mathsf{u}\ . \tag{3.56}$$

Comparing this result with Eq. (3.45), we see that (3.56) just gives a separate verification of the fact that the field strength undergoes a unitary transformation when the gauge potential experiences a gauge transformation. An important consequence is that, if the field strength is different from zero in any gauge, it is nonzero in all gauges, so that there is no gauge transformation that will cause the gauge potential to vanish. A matrix transforming under gauge transformations like the field strength, that is, a matrix just undergoing a unitary transformation, is called a "covariant" quantity.

We shall also need the infinitesimal form of the gauge transformation (3.53). Consider the case

$$\mathsf{u}=1+i\mathsf{e}\ , \tag{3.57}$$

where e is considered infinitesimally small. To first order in e, the gauge-transformed potential (3.53) is given by

$$\mathsf{A}'_\mu=\mathsf{A}_\mu+i[\mathsf{A}_\mu,\ \mathsf{e}]+\partial_\mu\mathsf{e}\ . \tag{3.58}$$

### D. Covariant differentiation

Let Q be a covariant quantity, transforming under a gauge transformation according to

$$\mathsf{Q}'=\mathsf{u}^\dagger\mathsf{Q}\mathsf{u}\ . \tag{3.59}$$

The transformation properties of a partial derivative of Q, however, are less simple. We find

$$\partial_\mu\mathsf{Q}'=(\partial_\mu\mathsf{u}^\dagger)\mathsf{Q}\mathsf{u}+\mathsf{u}^\dagger\mathsf{Q}(\partial_\mu\mathsf{u})+\mathsf{u}^\dagger(\partial_\mu\mathsf{Q})\mathsf{u}\ . \tag{3.60}$$

Using Eqs. (3.53), (3.54), (3.59), and (3.60), however, we easily find that

$$\partial_\mu\mathsf{Q}'+i[\mathsf{A}'_\mu,\ \mathsf{Q}']=\mathsf{u}^\dagger(\partial_\mu\mathsf{Q}+i[\mathsf{A}_\mu,\ \mathsf{Q}])\mathsf{u}\ . \tag{3.61}$$

The "covariant derivative" of a covariant quantity, defined as

$$\bar{\partial}_\mu\mathsf{Q}=\partial_\mu\mathsf{Q}+i[\mathsf{A}_\mu,\ \mathsf{Q}]\ , \tag{3.62}$$

is thus a covariant quantity. In particular, the first and higher covariant derivatives of the field strengths are covariant quantities.

### E. Connections

Analogously to the one-dimensional case, a connection determines the evolution of a ket row for each infinitesimal increment along the path. This means that the connection determines the gauge potential $\mathsf{a}_\mu$, since this is the only property of the evolution not determined uniquely by the path. Generalizations of the Hamiltonian and single-valued connections discussed in Sec. II.C are fairly obvious: In the one case, each ket in the row obeys the same time-dependent Schrödinger equation, while in the other the gauge potential is required to satisfy Eq. (3.45) to assure single-valuedness.

The multidimensional version of the parallel connection is obtained from the infinitesimal version of Eq. (3.24). If the two ket rows differ only infinitesimally from one another, we can write

$$\{|\chi_a\rangle|=\{|\chi\rangle| \ , \ \{|\chi_b\rangle|=\{|\chi\rangle|+\delta x_\mu \tilde{\partial}_\mu \{|\chi\rangle| \ . \tag{3.63}$$

Inserting Eq. (3.63) into (3.24) and using (3.4) (for the case $\{|\chi'\rangle|=\{|\chi\rangle|$ so that $\mathsf{s}=1$) and (3.36), we find

$$1+i\delta x_\mu \mathsf{a}_\mu = (\text{Hermitian, positive definite}) \ . \tag{3.64}$$

Since the second term in Eq. (3.64) is evidently anti-Hermitian, it must be zero, so in this case as in the one-dimensional case the parallel connection is defined by

$$\mathsf{a}_\mu = 0 \ . \tag{3.65}$$

Equation (3.65) is the connection determining infinitesimal parallel transport of a ket row. It is also easy to see that the Hamiltonian connection for a ket row spanning an $n$-fold degenerate level obeys this connection if the dynamical phase for each ket in the row is subtracted off as in Eq. (2.39).

### F. Time-reversal invariance

An important special case of non-Abelian gauge potentials is that in which the kets in a ket row are eigenkets of a Hamiltonian possessing time-reversal invariance, as in Sec. II.C, but, instead of Eq. (2.44) being obeyed, we have

$$\hat{T}^2 = -1 \ . \tag{3.66}$$

This case will occur if the total spin is half-odd integer (Wigner, 1959; Gottfried, 1966; Truhlar *et al.*, 1975). When Eq. (3.66) holds, eigenkets are degenerate in pairs related to one another by time reversal. This degeneracy is known as Kramers degeneracy, and such a pair of kets is called a Kramers doublet. Since the two kets of a Kramers doublet are always degenerate, one can never separate them or ignore the coupling between them; accordingly, in a Born-Oppenheimer-type treatment of a molecule with an odd number of electrons and with inclusion of electronic spin, we must consider the electronic part of the wave function to involve both kets of the doublet. In other words, it must be a ket row with two components, not a single ket.

We denote the two kets, both of course functions of the parameters $x_\mu$, by $|\alpha\rangle$ and $|\beta\rangle$. They are related to each other by time reversal, so we must have

$$\hat{T}|\alpha\rangle = |\beta\rangle e^{iq} \ , \tag{3.67}$$

where $q$ is a real number that can be determined by convention. The most convenient choice is usually $q=0$, but sometimes another choice is useful. Because of Eqs. (2.42) and (3.66), we have

$$\hat{T}^2|\alpha\rangle = -|\alpha\rangle = \hat{T}(|\beta\rangle e^{iq}) = (\hat{T}|\beta\rangle)e^{-iq} \ , \tag{3.68}$$

from which it follows that

$$\hat{T}|\beta\rangle = -|\alpha\rangle e^{iq} \ . \tag{3.69}$$

We shall be concerned only with single-valued kets here, which requires that $q$ also be single valued. The ket row that we are concerned with here and its projection are given by

$$\{|X\rangle| = (|\alpha\rangle \ \ |\beta\rangle) \ , \ \ \hat{P} = |\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta| \ . \tag{3.70}$$

$\{|X\rangle|$ and $\hat{P}$, of course, are functions of $\mathbf{R}$, while $\hat{T}$ remains the same operator.

Evidently, $\hat{P}$ commutes with time reversal:

$$\hat{T}\hat{P} = \hat{P}\hat{T} \ . \tag{3.71}$$

Because Eq. (3.71) must remain true as $\hat{P}$ changes, and because $\hat{T}$, according to Eq. (2.42), must anticommute with $i$, it is clear from Eq. (3.15) that $\hat{g}_\mu$ anticommutes with $\hat{T}$:

$$\hat{T}\hat{g}_\mu = -\hat{g}_\mu \hat{T} \ . \tag{3.72}$$

Applying $\hat{T}$ to the ket row $\{|X\rangle|$ and using Eqs. (3.67) and (3.69), we obtain

$$\hat{T}\{|X\rangle| = (|\beta\rangle e^{iq} \ \ -|\alpha\rangle e^{iq}) = -ie^{iq}\{|X\rangle|\sigma_y \ , \tag{3.73}$$

where $\sigma_y$ is the usual Pauli matrix.

To see how $\hat{T}$ combines with other block-diagonal operators, consider a block-diagonal operator $\hat{Q}$ applied to the ket row

$$\hat{Q}\{|X\rangle| = \{|X\rangle|\mathsf{Q} \ , \tag{3.74}$$

where

$$\mathsf{Q} = |\langle X|\}\hat{Q}\{|X\rangle| \ . \tag{3.75}$$

Using the rules (3.67), (3.69), (3.73), and (3.75), we find

$$\hat{T}\hat{Q}\{|X\rangle| = \hat{T}(\hat{Q}\{|X\rangle|) = -ie^{iq}\{|X\rangle|\sigma_y \mathsf{Q}^* \ , \tag{3.76}$$

$$\hat{Q}\hat{T}\{|X\rangle| = \hat{Q}(\hat{T}\{|X\rangle|) = -ie^{iq}\{|X\rangle|\mathsf{Q}\sigma_y \ . \tag{3.77}$$

Thus the matrices for block-diagonal operators that are left invariant or change sign under time reversal satisfy

$$\mathsf{Q}\sigma_y = \pm\sigma_y \mathsf{Q}^* \ , \tag{3.78}$$

with the plus sign applying to operators that commute with $\hat{T}$ and are thus left unchanged by it, the minus sign to those that anticommute with $\hat{T}$ and are reversed by it.

In our two-dimensional case, the only Hermitian matrices are real linear combinations of the unit matrix and the three Pauli matrices. Of these, only the unit matrix satisfies Eq. (3.78) with the plus sign, while all three Pauli matrices satisfy it with the minus sign.

To see the relation between vector potential and the phase factor $q$, we apply $\hat{T}$ to a partial derivative of $\{|X\rangle|$ in two different ways. First, differentiating Eq. (3.73) and using (3.37), we find

$$\begin{aligned}\hat{T}\partial_\mu\{|X\rangle|&=\partial_\mu\hat{T}\{|X\rangle|=e^{iq}(\partial_\mu q)\{|X\rangle|\sigma_y\\&\quad-ie^{iq}(\partial_\mu\{|X\rangle|)\sigma_y\\&=e^{iq}(\partial_\mu q)\{|X\rangle|\sigma_y\\&\quad+e^{iq}(\hat{g}_\mu\{|X\rangle|+\{|X\rangle|\mathsf{A}_\mu)\sigma_y\ .\end{aligned}\tag{3.79}$$

On the other hand, applying $\hat{T}$ directly to Eq. (3.37) and using Eqs. (3.72), (3.73), and the anticommutation of $\hat{T}$ with $i$, we obtain

$$\hat{T}\partial_\mu\{|X\rangle|=e^{iq}(\hat{g}_\mu\{|X\rangle|\sigma_y-\{|X\rangle|\sigma_y\mathsf{A}_\mu^*)\ .\tag{3.80}$$

Equating (3.79) with (3.80), we find

$$(\partial_\mu q)\sigma_y=-(\mathsf{A}_\mu\sigma_y+\sigma_y\mathsf{A}_\mu^*)\ .\tag{3.81}$$

The gauge potential $\mathsf{A}_\mu$, as a Hermitian two-by-two matrix, must be a real linear combination of the unit matrix and Pauli matrices:

$$\mathsf{A}_\mu=A_\mu+\mathbf{b}_\mu\cdot\sigma\ .\tag{3.82}$$

Comparing Eq. (3.82) with (3.81) and using the properties of the Pauli matrices, we see immediately that

$$A_\mu=-\tfrac{1}{2}\partial_\mu q\ .\tag{3.83}$$

The unit matrix part of the gauge potential is thus related only to the phase factor. In particular, the unit matrix part is zero if we use a phase convention in which $q$ is constant.

Under a gauge transformation, Eq. (3.73) must continue to hold, though perhaps with an altered value of $q$. Let $\mathsf{u}$ be a two-by-two unitary matrix, and consider the gauge transformation

$$\{|X'\rangle|=\{|X\rangle|\mathsf{u}=\{|X\rangle|e^{i\kappa}[\cos\tau+i\sin\tau(\mathbf{e}\cdot\sigma)]\ ,\tag{3.84}$$

where the unitary matrix $\mathsf{u}$ is defined by the real parameters $\kappa$ and $\tau$ and the real unit vector $\mathbf{e}$. According to Eq. (3.73), we must have

$$\hat{T}\{|X'\rangle|=-ie^{iq'}\{|X'\rangle|\sigma_y=-ie^{iq'}\{|X\rangle|\mathsf{u}\sigma_y\ .\tag{3.85}$$

Applying $\hat{T}$ directly to Eq. (3.84) and using (3.76), we find

$$\hat{T}\{|X'\rangle|=-ie^{iq}\{|X\rangle|\sigma_y\mathsf{u}^*\ .\tag{3.86}$$

Equating Eqs. (3.85) and (3.86), we find

$$\sigma_y\mathsf{u}^*=\mathsf{u}\sigma_y e^{i(q'-q)}\ ,\tag{3.87}$$

and comparing this with the expression for $\mathsf{u}$ in terms of $\kappa$, $\tau$, and $\mathbf{e}$, we obtain

$$q'-q=-2\kappa\ .\tag{3.88}$$

In particular, if $\kappa=0$, corresponding to unitary matrices belonging to the group SU(2) (unitary matrices with unit determinant), the phase $q$ will be unchanged. Thus, if we want to adhere to the phase convention $q=0$, we must restrict our gauge transformations to unitary matrices belonging to SU(2).

## IV. BORN-OPPENHEIMER TREATMENT OF MOLECULAR SYSTEMS

The Born-Oppenheimer approach to the quantum-mechanical treatment of molecular systems (Born and Oppenheimer, 1927; Born and Huang, 1954) is fundamental to nearly all of molecular quantum mechanics. Its basic ideas are well known to chemical physicists; the reader desiring more detailed knowledge is referred to the reviews by Ballhausen and Hansen (1972) and by Mead (1988). A Lagrangian-Hamiltonian formulation, suitable for considering geometric phase effects and the analogy with elementary-particle theory, has been presented by Moody *et al.* (1989). Another discussion, with emphasis on geometric phase effects, is that of Bohm, Kendrick, and Loewe (1992), which has been further developed by Bohm, Kendrick, Loewe, and Boya (1992). Some mathematical aspects of the Born-Oppenheimer approach, particularly in the neighborhood of electronic degeneracies, have been discussed by Hagedorn (1986, 1987, 1988a, 1988b, 1989, 1990, 1991a, 1991b).

As mentioned in Sec. I, a state of a molecular system described by nuclear coordinates $\mathbf{R}=\{x_\mu\}$ in addition to electronic degrees of freedom can be described quantum mechanically by a ket in the electronic Hilbert space which is a function of $\mathbf{R}$, $|\Psi(\mathbf{R})\rangle$. In atomic units,[2] the Hamiltonian operator can be written as

$$\hat{\mathcal{H}}=-\frac{1}{2M}\nabla_R^2+\hat{H}(\mathbf{R})=-\frac{1}{2M}\partial_\mu\partial_\mu+\hat{H}(\mathbf{R})\ ,\tag{4.1}$$

where $M$ is a nuclear mass (in units of the electronic mass) and $\hat{H}(\mathbf{R})$ is the electronic Hamiltonian, consisting of everything except the nuclear kinetic energy. The first term, representing the nuclear kinetic energy, is written symbolically, standing for a sum over nuclei.

In the usual Born-Oppenheimer treatment, as already pointed out in Sec. I, one approximates the state ket by

$$|\Psi(\mathbf{R})\rangle\approx|X(\mathbf{R})\rangle\psi(\mathbf{R})\ ,\tag{4.2}$$

where $|X(\mathbf{R})\rangle$ is an eigenket of $\hat{H}(\mathbf{R})$. Equation (4.2) is the same as (1.1).

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[2]The unit of length is the first Bohr radius, $a=\hbar^2/me^2$, where $m$ = electronic mass and $e$ = electronic charge in cgs units; the unit of energy is twice the binding energy of the H atom in its ground state, $me^4/\hbar^2$; and the unit of time is $\hbar^3/me^4$, which is $(1/2\pi)$ times the period of the first Bohr orbit.

In some cases, however, Eq. (4.2) is not a good approximation, and one must include two or more electronic states. In particular, this will occur if there are two or more states that are either strictly degenerate (for instance, a Kramers doublet) or sufficiently close in energy so that it is not a good approximation to neglect the coupling between them. We obtain a more general treatment by using $n$ electronic states and replacing Eq. (4.2) with

$$|\Psi(\mathbf{R})\rangle \approx \sum_{j=1}^{n} |X_j(\mathbf{R})\rangle \psi_j(\mathbf{R}) = \{|X(\mathbf{R})\rangle |\psi(\mathbf{R})\} \ , \tag{4.3}$$

where the second equality merely expresses the first in ket row notation. A special case, of course, is $n=1$, in which case Eq. (4.3) is the same as (4.2).

Differentiating Eq. (4.3) and using (3.37), we find

$$\frac{1}{i}\partial_\mu |\Psi\rangle \approx \{|X\rangle |\frac{1}{i}\partial_\mu |\psi\} + (\hat{g}_\mu \{|X\rangle + \{|X\rangle \mathsf{A}_\mu)|\psi\} \ . \tag{4.4}$$

Differentiating again, we find

$$-\partial_\mu \partial_\mu |\Psi\rangle \approx -\{|X\rangle |\partial_\mu \partial_\mu |\psi\} + \frac{2}{i}(\hat{g}_\mu \{|X\rangle | + \{|X\rangle |\mathsf{A}_\mu)\partial_\mu |\psi\} + \frac{1}{i}(\partial_\mu \hat{g}_\mu)\{|X\rangle |\psi\} + \frac{1}{i}\{|X\rangle |(\partial_\mu \mathsf{A}_\mu)|\psi\} + \hat{g}_\mu \hat{g}_\mu \{|X\rangle |\psi\} + 2\hat{g}_\mu \{|X\rangle |\mathsf{A}_\mu |\psi\} + \{|X\rangle |\mathsf{A}_\mu \mathsf{A}_\mu |\psi\} \ . \tag{4.5}$$

We now bring up the bra column $|\langle X|\}$ from the left and use the off-block property of $\hat{g}_\mu$, obtaining the result

$$|\langle X|\}(-\partial_\mu \partial_\mu |\Psi\rangle) \approx \left[\frac{1}{i}\partial_\mu + \mathsf{A}_\mu\right]\left[\frac{1}{i}\partial_\mu + \mathsf{A}_\mu\right]|\psi\} + \mathsf{G}|\psi\} \ , \tag{4.6}$$

where

$$\mathsf{G} = |\langle X|\}\hat{g}_\mu \hat{g}_\mu \{|X\rangle | \ . \tag{4.7}$$

We note that the contribution of $\partial_\mu \hat{g}_\mu$ vanishes: Because $\hat{g}_\mu$ is off-block, we have, using Eq. (3.37),

$$\frac{1}{i}\partial_\mu |\langle X|\}\hat{g}_\mu \{|X\rangle | = 0 = -\mathsf{A}_\mu |\langle X|\}\hat{g}_\mu \{|X\rangle | + |\langle X|\}\hat{g}_\mu \{|X\rangle |\mathsf{A}_\mu - |\langle X|\}\hat{g}_\mu \hat{g}_\mu \{|X\rangle | + |\langle X|\}\hat{g}_\mu \hat{g}_\mu \{|X\rangle | + \frac{1}{i}|\langle X|\}(\partial_\mu \hat{g}_\mu)\{|X\rangle | \ . \tag{4.8}$$

On the right side of Eq. (4.8), the first two terms are zero because $\hat{g}_\mu$ is off-block, and the next two terms cancel, leaving only the last term, which must therefore vanish, as asserted.

Also bringing up the bra column to the remaining terms in the eigenvalue equation $\hat{\mathcal{H}}|\Psi\rangle = E|\Psi\rangle$, we find the general form of the eigenvalue equation for the nuclear wave-function column $|\psi\}$:

$$\frac{1}{2M}\left[\frac{1}{i}\partial_\mu + \mathsf{A}_\mu\right]\left[\frac{1}{i}\partial_\mu + \mathsf{A}_\mu\right]|\psi\} + \frac{1}{2M}\mathsf{G}|\psi\} + \mathsf{U}|\psi\} = E|\psi\} \ , \tag{4.9}$$

where

$$\mathsf{U} = |\langle X|\}\hat{H}\{|X\rangle | \ . \tag{4.10}$$

In all cases that we shall consider, the kets making up the row $\{|X\rangle |$ are those belonging to a single eigenvalue of $\hat{H}$ or to two or more levels too close together to neglect the coupling between them. If $n=1$, corresponding to a single nondegenerate level, Eq. (4.9), apart from the vector-potential terms, is just the familiar Born-Oppenheimer version of the Schrödinger eigenvalue equation, with U, in this case just a number, being the electronic energy. In the limit $n \to \infty$, in which the kets making up $\{|X\rangle |$ form a complete set, Eq. (4.9) becomes exact.

In all molecular cases, the coordinates $x_\mu$ have the interpretation of nuclear coordinates, e.g., $x_\mu = x_{\gamma\kappa}$, the $\kappa$ coordinate of nucleus $\gamma$. Moreover, the space spanned by $\hat{P}$ will always be that of a single energy level of $\hat{H}$ or of two or more adjacent levels. In either case, we shall always have

$$[\hat{H}, \hat{P}] = [\hat{H}, \hat{P}'] = 0 \ . \tag{4.11}$$

Since Eq. (4.11) must continue to hold as the coordinates are varied, we obtain with the aid of Eq. (3.16)

$$[(\hat{H} + \delta x_\mu \partial_\mu \hat{H}) \ , \ (\hat{P} + i\delta x_\mu [\hat{g}_\mu, \hat{P}])] = 0 \ , \tag{4.12}$$

which to first order in infinitesimals gives

$$i[[\hat{g}_\mu, \hat{P}], \hat{H}] = [\partial_\mu \hat{H}, \hat{P}] \ , \tag{4.13}$$

which written out in full is

$$i(\hat{g}_\mu \hat{P}\hat{H} - \hat{P}\hat{g}_\mu \hat{H} - \hat{H}\hat{g}_\mu \hat{P} + \hat{H}\hat{P}\hat{g}_\mu) = (\partial_\mu \hat{H})\hat{P} - \hat{P}(\partial_\mu \hat{H}) \ . \tag{4.14}$$

We now multiply Eq. (4.14) by $\hat{P}'$, first from the left, then from the right, making use of Eq. (4.11) and the off-block nature of $\hat{g}_\mu$ to obtain

$$i[(\hat{P}'\hat{g}_\mu \hat{P}), \hat{H}] = \hat{P}'(\partial_\mu \hat{H})\hat{P} \ , \tag{4.15}$$

$$i[(\hat{P}\hat{g}_\mu \hat{P}'), \hat{H}] = \hat{P}(\partial_\mu \hat{H})\hat{P}' \ , \tag{4.16}$$

or

$$i[\hat{g}_\mu, \hat{H}] = (\partial_\mu \hat{H})_{\mathrm{ob}} \ , \tag{4.17}$$

where ob represents the off-block part of the operator.

Because of the general relation

$$i\hat{g}_\mu=[\hat{g}_\mu,\hat{H}]\ , \tag{4.18}$$

Eq. (4.17) can also be written as

$$-\hat{g}_\mu=(\partial_\mu\hat{H})_{\rm ob}\equiv(\hat{F}_\mu)_{\rm ob}\ . \tag{4.19}$$

To avoid possible confusion, we now make a few remarks about the interpretation of Eq. (4.19). The commutators appearing in Eqs. (4.17) and (4.18) are with respect to the fixed-nuclei electronic Hamiltonian. Therefore the time derivatives are also to be understood as operators in the *electronic* Hilbert space for fixed nuclei. The utility of Eq. (4.19), as we shall see, is that sometimes the right side is readily recognizable as a time derivative of another operator, essentially because force is minus the time derivative of momentum. $\partial_\mu\hat{H}$, the partial derivative of the electronic Hamiltonian with respect to $x_\mu$, is just minus the force exerted by all the electrons on nucleus $\gamma$ in the $\kappa$ direction (with the understanding mentioned above that $x_\mu=x_{\gamma\kappa}$); it is therefore also *plus* the force exerted on all the electrons by nucleus $\gamma$ in the $\kappa$ direction, and we call the operator for this force component $\hat{F}_\mu$. (The force exerted by the nuclei on each other is not only block diagonal with respect to the electronic ket space, it is an **R**-dependent multiple of the unit operator; it thus plays no role and can be ignored in what follows.) If we know the time derivative of $\hat{g}_\mu$, it will sometimes be easy to see what $\hat{g}_\mu$ itself is. In any case, we can *define* an operator $\hat{K}_\mu$ as the operator whose time derivative is $\hat{F}_\mu$ and let $\hat{k}_\mu$ be its block-diagonal part. We now have

$$\hat{g}_\mu=-(\hat{K}_\mu-\hat{k}_\mu)\ , \tag{4.20}$$

and with the aid of Eq. (3.42) we find

$$Z_{\mu\nu}=\frac{1}{i}|\langle X|\}([\hat{K}_\mu,\hat{K}_\nu]+[\hat{k}_\mu,\hat{k}_\nu])\{|X\rangle|\ . \tag{4.21}$$

The operator $\hat{k}_\mu$, which is block diagonal and therefore commutes with $\hat{H}(\mathbf{R})$ and is conserved in time, can be thought of as an integration constant in obtaining $\hat{g}_\mu$ from $\hat{F}_\mu$.

In some of the following applications, we shall find use for the relations (4.19)–(4.21). In some cases of interest, $\hat{k}_\mu$, or its contribution to the commutator, turns out to be zero, leading to a simpler form of Eq. (4.21).

In a more pedestrian way, of course, we can obtain any desired matrix element of $\hat{g}_\mu$ directly from Eq. (4.17). If $|j\rangle,|k\rangle$ are two eigenkets of $\hat{H}$, one belonging to the space of $\hat{P}$ and the other one not, with eigenvalues $U_j, U_k$, we obtain directly

$$\langle j|\hat{g}_\mu|k\rangle=\frac{\langle j|\partial_\mu\hat{H}|k\rangle}{i(U_k-U_j)}\ . \tag{4.22}$$

In the following sections, we shall apply the general results of this and the previous two sections to the most common cases that arise in molecular and spin systems and discuss examples and remaining problems.

Section V considers the simplest case: a nondegenerate parametric Hamiltonian with time-reversal invariance, so that the only type of phase change possible is just a change of sign, according to Eq. (2.20).

In Sec. VI, we again consider a nondegenerate parametric Hamiltonian, but this time in the presence of an external magnetic field, so that the time-reversal invariance is removed and there is a geometric vector potential depending on the external field.

The case of parametric Hamiltonians that are degenerate for all **R** is considered in Sec. VII. In practice, there are just two such cases that can arise in molecules, both twofold degenerate: diatomic molecules in other than $^1\Sigma$ states and molecules with an odd number of electrons, leading to Kramers degeneracy. This situation can also arise for spin systems with time-reversal invariance, e.g., in an electric field. In this case, U is no longer a single number, but is a multiple of the unit matrix.

Finally, Sec. VIII considers the case of two or more levels that are not degenerate, at least not for all **R**, but between which the coupling is nevertheless too important to be neglected. Now U is no longer just a multiple of the unit matrix.

## V. TIME-REVERSAL-INVARIANT NONDEGENERATE PARAMETRIC HAMILTONIAN

### A. General

In this section we examine in more detail the case taken up in Sec. II.D, in which the Hamiltonian for all **R** is invariant under time reversal and where $\hat{T}^2=1$. In molecular systems, which are the only ones considered in this section, this means either that the total electronic spin is an integer or that it is permissible to ignore spin. In this case there is no degeneracy that holds for all **R**, so we have the Abelian situation.

If we choose our electronic eigenkets so as to satisfy Eq. (2.47), it is a simple matter to show (Wigner, 1959; Gottfried, 1966; Truhlar, Mead, and Brandt, 1975; Mead, 1979) that all matrix elements of $\hat{H}$, and hence also $\partial_\mu\hat{H}$, taken between the eigenkets will be real. The matrix $Z_{\mu\nu}$ defined by Eq. (3.42) now has just a single element $Z_{\mu\nu}$. We label the eigenket with respect to which we are taking a diagonal element as $|\chi_0\rangle$, or $|0\rangle$ for short [not to be confused with the reference ket $|0\rangle$ in Eq. (2.3)]. With the help of Eq. (4.22), $Z_{\mu\nu}$ can now be expressed as

$$Z_{\mu\nu}=\frac{1}{i}\langle 0|[\hat{g}_\mu,\hat{g}_\nu]|0\rangle=\frac{1}{i}\sum_k\frac{\langle 0|\partial_\mu\hat{H}|k\rangle\langle k|\partial_\nu\hat{H}|0\rangle-\langle 0|\partial_\nu\hat{H}|k\rangle\langle k|\partial_\mu\hat{H}|0\rangle}{(U_0-U_k)^2}\ , \tag{5.1}$$

which is easily seen to vanish because of the real nature of the matrix elements and the Hermitian character of the Hamiltonian, *except perhaps at a point of degeneracy, where there could be a singularity.* In Sec. II.D, we saw that the geometric phase in this case can be at most a sign change, and in Sec. I it was shown that such a sign change occurs for paths around an intersection of two electronic levels. We now see that the sign change can occur *only* for paths around intersections, because without an intersection the vanishing of $Z_{\mu\nu}$ guarantees that there will be no phase change. Nevertheless, there is considerable variety and complexity in the problems that can be encountered, as we hope to show in the following subsections.

### B. Triatomic molecule $X_3$

If there is time-reversal invariance with $\hat{T}^2=1$, two conditions must always be satisfied by the nuclear coordinates in order for an intersection to occur (von Neumann and Wigner, 1929; Mead, 1979); moreover, the electronic energy depends only on the internal coordinates of the nuclei, apart from translation and rotation. With two nuclei, there is only one internal coordinate (the internuclear distance), so in general the two conditions cannot be satisfied. With three nuclei, there are three such coordinates (e.g., the three internuclear distances), so there can be an intersection on a curve in the three-dimensional space of these coordinates. This is thus the simplest case for which an intersection can occur and has therefore been the subject of considerable study. Although an intersection has recently been found in the ozone molecule which is not symmetry determined (Xantheas, Elbert, and Ruedenberg, 1990), most of the study has concentrated on symmetry-determined intersections. The alkali and other metal trimers $X_3$ with neglect of spin) form an example of this, which also exhibits interesting problems involving permutation symmetry of identical nuclei and is of experimental interest as well (Morse *et al.*, 1983; Delacrétaz *et al.*, 1986). Here we present a fairly detailed discussion of the fundamentals of the treatment of this system, including rotation as well as internal motions. Because we are interested in the geometric phase, rather than Born-Oppenheimer breakdown, we consider only one electronic level, an approximation that will be valid if the nuclear motion does not come too close to the intersection. Coupling between different levels is considered in Sec. VIII. We concentrate on symmetry and other general properties, rather than on numerical results.

#### 1. Coordinate system

We first take up the problem of construction of an appropriate coordinate system for the description of three identical nuclei, each with mass $M$ (in atomic units, that is, in units of the electronic mass). We label the nuclei $A$, $B$, $C$, with position vectors $\mathbf{R}_A,\mathbf{R}_B,\mathbf{R}_C$, and eliminate the center-of-mass motion. Because we are interested in discussing the permutation of identical nuclei, it is desirable to define a coordinate system that treats the three nuclei in a symmetric way. It is also obviously desirable to have three of the six relative coordinates be purely internal, with the other three describing orientation in space. For three nuclei, there are three internuclear distances, and these, or appropriate functions of them, are available to use as internal coordinates. To set up our coordinate system for the relative motion, we begin with the scaled Jacobi coordinates

$$\mathbf{U}=\sqrt{\tfrac{3}{2}}(\mathbf{R}_A-\mathbf{R}_B)\equiv\sqrt{\tfrac{3}{2}}\mathbf{R}_{AB}\ ; \tag{5.2}$$

$$\mathbf{V}=\frac{1}{\sqrt{2}}(2\mathbf{R}_C-\mathbf{R}_A-\mathbf{R}_B)=\frac{1}{\sqrt{2}}(\mathbf{R}_{CA}-\mathbf{R}_{BC})\ , \tag{5.3}$$

in terms of which the relative kinetic energy is given by

$$T=\frac{M}{6}(\dot{U}^2+\dot{V}^2)\ . \tag{5.4}$$

The three internal coordinates that we shall use (Mead and Truhlar, 1979; Mead, 1980a) are $Q$ $(0\le Q\le\infty)$; $s=\sin\sigma$ $(0\le s\le 1;0\le\sigma\le\pi/2)$; and $\theta$ $(0\le\theta\le 2\pi)$, along with auxiliary quantities $u$ and $v$, defined as follows:

$$Q=U^2+V^2=R_{AB}^2+R_{BC}^2+R_{CA}^2\ ; \tag{5.5}$$

$$\begin{aligned}u&=Qs\cos\theta=Q\sin\sigma\cos\theta\\&=U^2-V^2=2R_{AB}^2-R_{BC}^2-R_{CA}^2\ ;\end{aligned} \tag{5.6}$$

$$\begin{aligned}v&=Qs\sin\theta=Q\sin\sigma\sin\theta\\&=2\mathbf{U}\cdot\mathbf{V}=\sqrt{3}(R_{BC}^2-R_{CA}^2)\ .\end{aligned} \tag{5.7}$$

It is straightforward to verify that $s=\sigma=0$ corresponds to the $D_{3h}$ configuration, while $s=1$ $(\sigma=\pi/2)$ denotes a linear molecule.

If we put the center of mass at the origin, it is easy to verify from Eqs. (5.2) and (5.3) that the coordinates of the three nuclei are expressible in terms of $\mathbf{U}$ and $\mathbf{V}$ as

$$\begin{aligned}\mathbf{R}_C&=\frac{\sqrt{2}}{3}\mathbf{V}\ ;\\ \mathbf{R}_A&=\frac{\sqrt{2}}{3}\left[-\frac{1}{2}\mathbf{V}+\frac{\sqrt{3}}{2}\mathbf{U}\right]\ ;\\ \mathbf{R}_B&=\frac{\sqrt{2}}{3}\left[-\frac{1}{2}\mathbf{V}-\frac{\sqrt{3}}{2}\mathbf{U}\right]\ .\end{aligned} \tag{5.8}$$

To describe the orientation of the molecule in space, we must define molecule-fixed axes. Since we want to discuss the permutations of the nuclei, it is desirable that these be defined in such a way that the three nuclei are treated in a symmetrical way. One axis, with unit vector $\boldsymbol{\zeta}$, is obviously taken as perpendicular to the plane of the molecule. The choice of the other two requires some thought; we have chosen to define unit vectors $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$, making an angle of $\theta/2$ with the inertial principal axes. In terms of $\mathbf{U}$ and $\mathbf{V}$, as can be shown with a bit of calculation, these are

$$\xi=\sqrt{2/Q}\,\frac{\left[\cos\frac{\sigma}{2}-\sin\frac{\sigma}{2}\cos\theta\right]\mathbf{U}-\sin\frac{\sigma}{2}\sin\theta\mathbf{V}}{\cos\sigma}\ , \tag{5.9}$$

$$\eta=\sqrt{2/Q}\,\frac{\left[-\sin\frac{\sigma}{2}\sin\theta\right]\mathbf{U}+\left[\cos\frac{\sigma}{2}+\sin\frac{\sigma}{2}\cos\theta\right]\mathbf{V}}{\cos\sigma}\ . \tag{5.10}$$

In terms of these unit vectors, **U**, **V**, and the coordinates of the three nuclei (relative to the center of mass) are given by

$$\mathbf{U}=\sqrt{Q/2}\left[\cos\frac{\sigma}{2}\xi+\sin\frac{\sigma}{2}(\xi\cos\theta+\eta\sin\theta)\right]\ ; \tag{5.11}$$

$$\mathbf{V}=\sqrt{Q/2}\left[\cos\frac{\sigma}{2}\eta-\sin\frac{\sigma}{2}(\eta\cos\theta-\xi\sin\theta)\right]\ ; \tag{5.12}$$

$$\mathbf{R}_C=\frac{\sqrt{Q}}{3}\left[\cos\frac{\sigma}{2}\eta-\sin\frac{\sigma}{2}(\eta\cos\theta-\xi\sin\theta)\right]\ ; \tag{5.13}$$

$$\mathbf{R}_A=\frac{\sqrt{Q}}{3}\left\{\cos\frac{\sigma}{2}\left[-\frac{1}{2}\eta+\frac{\sqrt{3}}{2}\xi\right]-\sin\frac{\sigma}{2}\left[\eta\cos\left[\theta+\frac{2\pi}{3}\right]-\xi\sin\left[\theta+\frac{2\pi}{3}\right]\right]\right\}\ ; \tag{5.14}$$

$$\mathbf{R}_B=\frac{\sqrt{Q}}{3}\left\{\cos\frac{\sigma}{2}\left[-\frac{1}{2}\eta-\frac{\sqrt{3}}{2}\xi\right]-\sin\frac{\sigma}{2}\left[\eta\cos\left[\theta-\frac{2\pi}{3}\right]-\xi\sin\left[\frac{\theta-2\pi}{3}\right]\right]\right\}\ . \tag{5.15}$$

Although the definition (5.9) and (5.10) of the two molecule-fixed axes may have seemed arbitrary, their utility is evident from Eqs. (5.13)–(5.15). Relative to these axes, the locations of the three nuclei are single-valued functions of the internal coordinates. (Had we chosen the inertial principal axes as molecule-fixed axes, a change of $2\pi$ in the angle $\theta$ would have resulted in rotation of the molecule through $\pi$.) Moreover, it is easy to see how permutations of the nuclei are reflected in the coordinates: From inspection of Eqs. (5.13)–(5.15), one sees that an exchange of nuclei $A$ and $B$ (represented by the operator $\hat{P}_{AB}$) is obtained by reversing the sign of $\theta$ and also reversing the direction of $\xi$, i.e., rotating through $\pi$ about the $\eta$ axis:

$$\hat{P}_{AB}\colon\ \theta\to-\theta\ ,\ \ \xi\to-\xi\ \ (\text{rot through }\pi\text{ about }\eta)\ . \tag{5.16}$$

It is also easy to see from Eqs. (5.13)–(5.15) that the cyclic permutation $\hat{P}_{ABC}$ is obtained by subtracting $2\pi/3$ from both $\theta$ and $\gamma$, the Euler angle representing counterclockwise rotation about $\zeta$:

$$\hat{P}_{ABC}\colon\ \theta\to\theta-\frac{2\pi}{3}\ ,\ \ \gamma\to\gamma-\frac{2\pi}{3}\ . \tag{5.17}$$

The rest of the permutation group is generated from these two.

We see that the coordinate $Q$, Eq. (5.5), is totally symmetric under the permutation group (representation $A_1$), while $u$ and $v$, defined by Eqs. (5.6) and (5.7), transform together according to the two-dimensional representation $E$.

### 2. Electronic eigenket

The ground states of the triatomic molecules $H_3$, $Li_3$, $Na_3$, etc., all experience a symmetry-determined twofold degeneracy at the $D_{3h}$ configuration, represented in our coordinate system by $u=v=0$ or $s=\sigma=0$. The two conditions on the nuclear coordinates for a degeneracy are thus $u=v=0$, and a closed path around the intersection is just a closed path in the $uv$ plane enclosing the origin, or, equivalently, a change of $\pm2\pi$ in the angle $\theta$. Since the number of conditions for $D_{3h}$ symmetry is the same as the number for degeneracy, both being two, it follows that the degeneracy manifold (submanifold of nuclear configuration space for which the two lowest electronic levels are degenerate) just coincides with the $D_{3h}$ symmetry manifold (submanifold with $D_{3h}$ symmetry).

We are principally interested in studying the symmetry properties of the electronic eigenkets, and for this purpose a very simple model Hamiltonian will suffice, as long as it embodies these properties. Accordingly, we imagine two $p$-wave functions $|\xi\rangle$ and $|\eta\rangle$, oriented along the $\xi$ and $\eta$ axes, respectively. Using $\xi_J,\eta_J$ ($J=A,B,C$) to denote the coordinates of nucleus $J$ in the $\xi$ and $\eta$ directions, we define for each nucleus $J$ a ket $|J\rangle$ in the direction of its displacement from the origin and of length equal to that displacement, and another ket $|J'\rangle$ of the same magnitude and orthogonal to $|J\rangle$:

$$\begin{aligned}|J\rangle&=|\xi\rangle\xi_J+|\eta\rangle\eta_J\ ,\\ |J'\rangle&=-|\xi\rangle\eta_J+|\eta\rangle\xi_J\ .\end{aligned} \tag{5.18}$$

As model Hamiltonian, valid for small deviations from $D_{3h}$ symmetry, we choose

$$\begin{aligned}\hat{H}&=\Lambda\mathsf{I}+\Gamma\sum_J(|J\rangle\langle J|-|J'\rangle\langle J'|)\\ &=\Lambda\mathsf{I}+\Gamma\sum_j(\xi_J^2-\eta_J^2)(|\xi\rangle\langle\xi|-|\eta\rangle\langle\eta|)\\ &\qquad+2\xi_J\eta_J(|\xi\rangle\langle\eta|+|\eta\rangle\langle\xi|)\ ,\end{aligned} \tag{5.19}$$

where $\mathsf{I}$ is the two-dimensional unit matrix in the space of $|\xi\rangle$ and $|\eta\rangle$, $\Lambda$ is some totally symmetric function of the displacement coordinates, and $\Gamma$ is a constant. Inserting Eqs. (5.13)–(5.15) into (5.19) and carrying out the sums, we find, apart from the unimportant multiple of the unit matrix,

$$\hat{H}=\Gamma\frac{Q}{3}\sin\sigma[(|\xi\rangle\langle\xi|-|\eta\rangle\langle\eta|)\cos\theta + (|\xi\rangle\langle\eta|+|\eta\rangle\langle\xi|)\sin\theta] = \Gamma\frac{Q}{3}\sin\sigma\begin{bmatrix}\cos\theta & \sin\theta\\ \sin\theta & -\cos\theta\end{bmatrix}, \tag{5.20}$$

where the second expression is, of course, just the matrix representation of the first. The eigenvalues are $\pm\Gamma(Q/3)\sin\sigma$, and the real, smoothly varying eigenkets are, respectively,

$$|\chi_a\rangle=|\xi\rangle\cos\frac{\theta}{2}+|\eta\rangle\sin\frac{\theta}{2}=\begin{bmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\end{bmatrix} \tag{5.21}$$

and

$$|\chi_b\rangle=-|\xi\rangle\sin\frac{\theta}{2}+|\eta\rangle\cos\frac{\theta}{2}=\begin{bmatrix}-\sin\frac{\theta}{2}\\ \cos\frac{\theta}{2}\end{bmatrix}. \tag{5.22}$$

It is evident that, as expected, both eigenkets experience a change of sign when $\theta$ makes a full circuit. With the aid of Eqs. (5.16) and (5.17), one can also determine the behavior of the eigenkets under interchange of two nuclei: When $A$ and $B$ are interchanged, according to Eq. (5.16), $\theta$ changes sign and also the basis ket $|\xi\rangle$ is reversed. Applying this to Eqs. (5.21) and (5.22), one sees that $|\chi_a\rangle$ changes sign, while $|\chi_b\rangle$ is unchanged. Under the cyclic permutation $(ABC)$, according to Eq. (5.17), the changes are

$$\theta\to\theta-\frac{2\pi}{3}, \quad |\xi\rangle\to-\tfrac{1}{2}|\xi\rangle-\frac{\sqrt{3}}{2}|\eta\rangle, \quad |\eta\rangle\to-\tfrac{1}{2}|\eta\rangle+\frac{\sqrt{3}}{2}|\xi\rangle. \tag{5.23}$$

Inserting Eq. (5.23) into (5.21) and (5.22), one sees that both eigenkets change sign under the cyclic permutation.

For use in the Born-Oppenheimer procedure, we prefer electronic kets that are single valued as functions of the nuclear coordinates. We can achieve this, and also make the kets invariant under cyclic permutations, if we make the replacements

$$|X_a\rangle=|\chi_a\rangle e^{3i\theta/2}; \quad |X_b\rangle=|\chi_b\rangle e^{3i\theta/2}. \tag{5.24}$$

Although we have used a simple model Hamiltonian to obtain these kets, their symmetry properties will hold exactly: For larger displacements from the $D_{3h}$ configuration, the exact eigenkets will no longer take the simple form of Eqs. (5.21) and (5.22); by continuity, however, they must still experience a sign change when $\theta$ changes by $2\pi$, or by $2\pi/3$, and this sign change is still compensated by the rephasing (phase-gauge transformation) Eq. (5.24).

These kets defined by Eq. (5.24) are invariant under cyclic permutations such as $(ABC)$, but they are not left invariant by the $(AB)$ interchange: According to Eq. (5.16), they are multiplied, respectively, by $\pm e^{-3i\theta}$. In the next portion of this subsection, we concentrate on the ket $|X_b\rangle$, assumed to represent the lower energy level, and consider the effect of the geometric phase on the nuclear motion.

### 3. Quantum numbers, energy levels, and permutation symmetry

Using the definitions (5.5)–(5.7), the relations (5.11) and (5.12), and the classical kinetic energy (5.4), it is a straightforward, though somewhat tedious, matter to work out the operator for the kinetic energy of relative motion. The result is

$$\hat{T}=-\frac{6}{M}\left[\frac{1}{Q^2}\frac{\partial}{\partial Q}\left[Q^3\frac{\partial}{\partial Q}\right]+\frac{1}{Q\sin2\sigma}\frac{\partial}{\partial\sigma}\left[\sin2\sigma\frac{\partial}{\partial\sigma}\right]\right]+\frac{3}{MQ}\left[\left[\frac{1}{1-\cos\sigma}\right]\hat{L}_\theta^2+\left[\frac{1}{1+\cos\sigma}\right](\hat{L}_\theta-\hat{L}_\xi)^2\right] + \frac{3}{MQ\cos^2\sigma}\left[\hat{L}_\xi^2+\hat{L}_\eta^2+\frac{\sin\sigma}{2}[e^{i\theta}(\hat{L}_\xi-i\hat{L}_\eta)^2+e^{-i\theta}(\hat{L}_\xi+i\hat{L}_\eta)^2]\right], \tag{5.25}$$

where $\hat{L}_\xi,\hat{L}_\xi,\hat{L}_\eta$ are the angular momentum operators around the molecule-fixed axes and $\hat{L}_\theta=(1/i)(\partial/\partial\theta)$ is the pseudoangular momentum associated with the internal angle $\theta$.

In our Born-Oppenheimer treatment, we approximate the molecular state vector by

$$|\Psi(\mathbf{R})\rangle=|X_b\rangle\psi(\mathbf{R}). \tag{5.26}$$

By now it should be clear that the single-valued ket $|X_b\rangle$ induces a vector-potential-type term in the nuclear Hamiltonian. Comparing with Eq. (1.12), or using (2.25) or the one-dimensional version of (3.44) along with (4.9), we see that the effect of the vector potential is expressed through the transformation

$$\hat{L}_\theta\to\hat{L}_\theta+\tfrac{3}{2}. \tag{5.27}$$

We use a basis of states that are eigenstates of $\hat{L}^2,\hat{L}_\theta$, and $\hat{L}_\xi$, with eigenvalues $K(K+1)$, $m$, and $\mu$, respectively ($K,m,\mu$ all integer, $K$ non-negative). A fourth quantum number, for a component of total angular momentum relative to the laboratory, will not be written down. Using Eqs. (5.27), and (5.25), and now also including the potential energy $\Phi(Q,\sigma,\theta)$, we find that the effective nuclear Hamiltonian can be expressed as a sum of a diagonal part $\hat{H}_{\rm diag}$ and an off-diagonal part $\hat{H}_{\rm od}$, given by

$$\hat{H}_{\rm diag}=-\frac{6}{M}\left[\frac{1}{Q^2}\frac{\partial}{\partial Q}\left[Q^3\frac{\partial}{\partial Q}\right]+\frac{1}{Q\sin 2\sigma}\frac{\partial}{\partial\sigma}\left[\sin 2\sigma\frac{\partial}{\partial\sigma}\right]\right]$$
$$+\frac{3}{MQ}\left[\left[\frac{1}{1-\cos\sigma}\right](m+\tfrac{3}{2})^2+\left[\frac{1}{1+\cos\sigma}\right](m+\tfrac{3}{2}-\mu)^2\right]+\frac{3}{MQ\cos^2\sigma}[K(K+1)-\mu^2]+\Phi_{\rm diag}(Q,\sigma)\ ; \quad (5.28)$$

$$\hat{H}_{\rm od}=\Phi_{\rm od}(Q,\sigma,\theta)+\frac{3\sin\sigma}{2MQ\cos^2\sigma}[e^{i\theta}(\hat{L}_\xi-i\hat{L}_\eta)^2+e^{-i\theta}(\hat{L}_\xi+i\hat{L}_\eta)^2]\ . \quad (5.29)$$

In Eqs. (5.28) and (5.29), we have divided $\Phi(Q,\sigma,\theta)$ into a diagonal part $\Phi_{\rm diag}$ which cannot depend on $\theta$ and an off-diagonal part $\Phi_{\rm od}$.

We must now examine the effect of permutations of the nuclei on the basis functions. From Eq. (5.24), we see that $\hat{P}_{AB}$ multiplies the electronic eigenket by $e^{-3i\theta}$. But it can equally well be considered as leaving the electronic part unchanged and multiplying the nuclear part by $e^{-3i\theta}$. In addition, of course, $\hat{P}_{AB}$ acts on the nuclear wave function according to Eq. (5.16). The cyclic permutation $\hat{P}_{ABC}$ leaves the electronic ket unaffected and operates on the nuclear wave function according to Eq. (5.17). Denoting the orientation angles collectively by $\Omega$, we find for the actions of the two generating permutations on arbitrary nuclear wave functions and on our basis functions

$$\hat{P}_{AB}\psi(Q,\sigma,\theta,\Omega)=e^{-3i\theta}e^{-i\pi\hat{L}_\eta}\psi(Q,\sigma,-\theta,\Omega)\ ; \quad (5.30)$$

$$\hat{P}_{ABC}\psi(Q,\sigma,\theta,\Omega)=e^{-(2\pi i/3)\hat{L}_\xi}\psi\left[Q,\sigma,\left[\theta-\frac{2\pi}{3}\right],\Omega\right]\ ; \quad (5.31)$$

$$\hat{P}_{AB}\psi_{Km\mu}=\psi_{K,(-m-3),-\mu}\ , \quad (5.32)$$

$$\hat{P}_{ABC}\psi_{Km\mu}=e^{-2\pi i(m+\mu)/3}\psi_{Km\mu}\ . \quad (5.33)$$

We note that Eq. (5.33) leaves the quantum numbers unaffected, while (5.32) reverses both $(m+\frac{3}{2})$ and $\mu$, leaving the diagonal energy unaffected. If $(m+\mu)$ is a multiple of 3, $\psi_{Km\mu}$ is unaffected by $\hat{P}_{ABC}$, while $\hat{P}_{AB}$ just interchanges the wave functions with quantum numbers $(K,m,\mu)$ and $(K,-m-3,-\mu)$. The symmetric and antisymmetric combinations

$$\psi_\pm=\frac{1}{\sqrt{2}}(\psi_{Km\mu}\pm\psi_{K,-m-3,-\mu}) \quad (5.34)$$

thus belong to the totally symmetric (+) and the totally antisymmetric (−) representations of the permutation group. If $(m+\mu)$ is not a multiple of 3, the states $\psi_{Km\mu}$ and $\psi_{K,-m-3,-\mu}$ transform together according to the two-dimensional irreducible representation $E$. They are evidently degenerate as far as the diagonal energy is concerned.

We now consider the effect of the coupling terms in Eq. (5.29). The potential energy $\Phi$ must be real and totally symmetric under permutations, so it follows that its Fourier transform in functions $\sin n\theta$, $\cos n\theta$ will contain only cosine terms, and these only for $n$ a multiple of three. Its matrix elements $\langle m'|\Phi|m\rangle$ are thus all real, depend only on $|m'-m|$, and are zero unless $|m'-m|$ is a multiple of three. As for the angular momentum coupling in Eq. (5.29), we note first that the molecule-fixed angular momentum operators satisfy commutation relations with opposite sign to those of the lab-fixed components (Levine, 1975), so that $(\hat{L}_\xi+i\hat{L}_\eta)$ is a lowering operator for $\mu$, while $(\hat{L}_\xi-i\hat{L}_\eta)$ is a raising operator. Of the two coupling terms, therefore, one of them raises $m$ by one and $\mu$ by two, while the other lowers $m$ by one and $\mu$ by two. The sum $(m+\mu)$ is either raised or lowered by three. All the coupling terms, of course, leave $K$ invariant. Two basis states will thus be coupled to one another, directly or indirectly, if and only if they have the same values of the following three quantum numbers:

$$K\ ,$$
$$\tilde{m}\equiv(m+\mu)(\mathrm{mod}3)=0,1,2\ , \quad (5.35)$$
$$\tilde{\mu}\equiv\mu(\mathrm{mod}2)=0,1\ .$$

It is an immediate consequence of Eq. (5.32) that the interchange $\hat{P}_{AB}$, while leaving $\tilde{\mu}$ unchanged, interchanges $\tilde{m}$ values of 1 and 2, while leaving $\tilde{m}=0$ unchanged. It follows that, for each $\tilde{\mu}$, each state with $\tilde{m}=1$ is degenerate with a state with $\tilde{m}=2$, the pair transforming under permutations according to the $E$ representation. The states with $\tilde{m}=0$ are nondegenerate, belonging to the $A_1$ and $A_2$ representations.

We have thus arrived at a classification of rovibronic states of the $X_3$ system in which permutation symmetry is unambiguously related to the quantum numbers.

## 4. Consequences; comparison with experiment

The most obvious consequence of the treatment given here, also anticipated by Longuet-Higgins *et al.* (1958), is the half-odd integer values of the quantum numbers associated with the internal angle $\theta$. This effect has been observed experimentally in $Na_3$ by Delacrétaz *et al.* (1986) and in an excited state of $Li_3$ by Wolf *et al.* (1989). The half-odd integer quantum numbers, which are characteristic of Jahn-Teller systems in general, have also been utilized in fitting spectra of the Jahn-Teller molecules *sym*-triazine (Whetten and Gran, 1984; Whetten *et al.*, 1986) and benzene (Whetten and Grant, 1986). Studies of the fundamental properties of the potential-energy function $\Phi$, as well as the coupling to the surface corresponding to $|X_a\rangle$, have been carried out by Mead (1983) and

Thompson and Mead (1985), and the results used successfully (Thompson, Truhlar, and Mead, 1985) to account for the experimental results on the excited state of $Cu_3$ of Morse *et al.* (1983). Truhlar *et al.* (1986) have also successfully fit the experimental results of DiLella *et al.* (1983) and Rohlfing and Valentini (1986) on the ground state of $Cu_3$.

The general results for the potential energy and coupling have also been used to generate analytic surfaces for $H_3$ (Varandas *et al.*, 1987) and for the alkali trimers (Thompson, Izmirlian, Lemon, Truhlar, and Mead, 1985). They have also been helpful in assessing the effect of the off-diagonal coupling on collision-induced dissociation in the $H_3$ system (Blais *et al.*, 1988).

If there were no vector potential and also no coupling between states of different $K,m,\mu$, the ground state of the $X_3$ system would be that with $K=m=\mu=0$, which would be nondegenerate and of permutation symmetry $A_1$. The allowed nuclear-spin states compatible with this ground state would thus be $A_1$ or $A_2$, depending on whether the nuclei were bosons or fermions. If the vector potential (5.27) is included, the ground state becomes doubly degenerate, of $E$ symmetry, with quantum numbers $K=\mu=0$, $m=-1,-2$, and one would predict that the compatible nuclear-spin state would have to be of $E$ symmetry. In a model calculation, Mead (1980a) obtained this same inversion of the two lowest energy levels with a simple model function for $\Phi$. More recently, it has been shown (Ham, 1987; Hancock *et al.*, 1989) that this inversion of the two lowest energy levels is not an artifact of any approximation, but is a rigorous consequence of the symmetry of the Hamiltonian. Thus the relation between allowed nuclear spin and rovibraonic states for this system (analogous to the ortho-para $H_2$ problem) is decisively changed by the vector potential. As of this writing, there has been no direct experimental observation of this effect.

The time development of wave packets in a model of Jahn-Teller systems such as this one has been studied by Romero-Rochin and Cina (1989). These studies were continued by Cina and Romero-Rochin (1990), who discussed the interference of wave packets in a Jahn-Teller excited state excited at different times with definite phase relationship from a nondegenerate ground state. Cina (1991) has shown explicitly how the interference between such controlled excitations can be used to demonstrate the geometric sign change. Thus we may expect that the near future will see a number of further experimental tests of the geometric phase in Jahn-Teller systems.

The vector potential also has consequences in scattering in the $X_3$ system (Mead, 1980c). Because of the sign change of the electronic eigenket under a cyclic permutation, the superposition of direct and exchange amplitudes for the reaction $X+X_2\rightarrow X_2+X$ will be performed with the wrong relative sign if the geometric vector potential is not included. Thus inclusion of the geometric vector potential is essential for a correct calculation of the interference between these two amplitudes.

### C. Polyatomic molecule $X_n$

The $X_3$ system has three properties that simplify the analysis, namely: (i) The number of internuclear distances is equal to the number of internal degrees of freedom, so the distances, or simple combinations of them, are available as internal coordinates that treat the three nuclei symmetrically; (ii) The number of conditions on the nuclear coordinates for $D_{3h}$ symmetry is the same as the number for an intersection (both two), so for symmetry-determined intersections, the degeneracy manifold coincides with the symmetry manifold; (iii) The quantities $u(\mathbf{R})$ and $v(\mathbf{R})$ whose simultaneous vanishing defined the degeneracy manifold, with a closed path around the origin in the $uv$ plane leading to a sign change in the real electronic eigenket, transform together under permutations according to the two-dimensional $E$ representation, thus facilitating the analysis of sign changes produced by permutations.

For condition (i) to be satisfied in an $X_n$ system, the number of internal degrees of freedom, $(3n-6)$, must equal the number of internuclear distances, $n(n-1)/2$, a property that is easily seen to hold only for $n=3$ and $n=4$.

Condition (ii) is satisfied only for $n=3$. For $n=4$, for example, the number of conditions for $C_{3v}$ or $D_{2d}$ symmetry is easily seen to be four, while the number for a degeneracy always remains two. Thus, even for degeneracies that can be classified as symmetry determined, in that the degenerate states belong to multidimensional representations of the symmetry point group for symmetrical configurations, the degeneracy manifolds are of higher dimension than the symmetry manifolds, with the latter forming only a subspace.

Condition (iii) certainly can be satisfied only if the permutation group $S_n$ possesses a two-dimensional irreducible representation, and this is true only for $n=3$ and $n=4$.

For values of $n$ greater than three, therefore, the most favorable case for analysis is $n=4$ for which condition (*i*) is definitely satisfied and for which at least the hope exists that condition (iii) may be satisfied as well. Although the analysis for this case is considerably more complicated than for $n=3$, it has been carried out by Keating and Mead (1985), who showed that condition (iii) indeed can be satisfied, that rovibronic states in the presence of conical intersections can be classified according to permutation symmetry, and that corrections to the interference between direct and exchange scattering amplitudes exist which are similar to those for $X_3$.

Because condition (iii) can never be satisfied for $n>4$, there is at present no general method for analyzing the relation between permutations of identical nuclei in $X_{n>4}$ systems and sign changes due to conical intersections. Keating and Mead (1987) have discussed the general problem and treated a few special cases, but at the present time a general treatment capable, for instance, of determining the relation between nuclear spin and rovib-

ronic states for such systems does not exist.

It is interesting to note the analogy between the situation considered here and that arising in the study of fractional statistics (Wilczek and Zee, 1983; Arovas *et al.*, 1984, 1985; Wu, 1984; Arovas, 1989). Particles obeying fractional statistics (so-called "anyons") can be imagined as two-dimensional particles that are not allowed (e.g., because of repulsive forces) to occupy the same point in space. A path in which two such particles circle each other and return to their original positions cannot be continuously deformed into a point, so it is argued that the operator transporting a wave function around such a path need not be the unit operator, but may contain a phase factor. This phase factor can be changed or eliminated, however, by introducing a vector potential. For a system of $n$ anyons, the configuration space has dimension $d=2n$, and there is an inaccessible submanifold of dimension $(d-2)$ in which two or more particles coincide. A closed path around the submanifold brings about a phase change, which can be altered by a phase-gauge transformation, generating a vector potential. In our case, with $n$ nuclei, we have an effective space of dimension $d=3n-6$, again with a submanifold of dimension $(d-2)$, this time the degeneracy manifold, such that a path around it induces a phase factor that can be altered by a phase-gauge transformation.

## VI. NONDEGENERATE PARAMETRIC HAMILTONIAN, NO TIME-REVERSAL INVARIANCE

In the presence of an external magnetic field, there is no time-reversal invariance, and for nondegenerate states the possibility arises of Abelian geometric phases that are not restricted to sign changes. In this section, we consider both molecular systems (case A) and spin systems (case B).

### A. Molecular system in magnetic field (case A)

In the presence of an external magnetic field, the electronic Hamiltonian $\hat{H}$ is no longer invariant under time reversal, so the conclusions of Sec. II.D no longer hold. Even for an electronic level that is everywhere nondegenerate (which will be assumed throughout this section), there can be a geometrically determined vector-potential term in the effective nuclear Schrödinger equation, in addition to the vector potential of the external field. Moreover, this geometrical vector potential will be a function of the external field, representing an influence of the electronic degrees of freedom on the response of the nuclei to the external field.

Various aspects of the behavior of molecular systems in magnetic fields have been considered by Schmelcher and Cederbaum (1988, 1989, 1990). Of particular interest for us, however, is the work of Schmelcher *et al.* (1988a, 1988b). They noticed that the Born-Oppenheimer approach, carried out in the usual way, leads to an effective Hamiltonian for the nuclei in which the interaction with the external field is just that of the "naked" nuclei: All screening due to the electrons is omitted. By rephasing the electronic wave functions so that, at least in the limit of infinite separation of the nuclei, a consistent gauge was achieved, they obtained an additional contribution to the vector potential which (again in the limit of infinite separation) accounted exactly for the screening by the electrons. They called this formulation the "screened Born-Oppenheimer approximation" and attributed the additional vector potential to the "diagonal part" of the nonadiabatic correction. From our point of view, this additional vector potential is just the geometric vector potential. That the geometric vector potential affects the interaction of nuclei with external fields was also recognized by Cottingham and Hassan (1990), who made an explicit approximate calculation for the $H_2^+$ molecular ion.

In this section, it is convenient to be less abstract and general than in Secs. II–IV and to use three-dimensional vector notation, taking explicit note of the fact that the parameters $x_\mu$ are nuclear coordinates, with a vector $\mathbf{r}_\gamma$ associated with each nucleus $\gamma$. In a uniform external magnetic field $\mathbf{B}$, the Hamiltonian (4.1) becomes

$$\hat{\mathcal{H}}=\sum_j \frac{1}{2M_\gamma}\left[\frac{1}{i}\nabla_\gamma - Z_\gamma \alpha \mathcal{A}_\gamma\right]^2 + \hat{H} \ , \tag{6.1}$$

where $M_\gamma$ and $Z_\gamma$ are mass and charge number, respectively, of nucleus $\gamma$, and $\alpha=e^2/\hbar c\approx 1/137$ is the dimensionless fine-structure constant.[3] The vector potential $\mathcal{A}_\gamma$ experienced by nucleus $\gamma$ due to the external field is given by

$$\mathcal{A}_\gamma=\tfrac{1}{2}\mathbf{B}\times\mathbf{r}_\gamma \ . \tag{6.2}$$

The electronic Hamiltonian $\hat{H}$, of course, also contains the interaction of the electrons with the external magnetic field.

The operators $\hat{g}_\mu$ representing the change of electronic eigenket with nuclear coordinate are now conveniently thought of as consisting of a vector $\hat{\mathbf{g}}_\gamma$ associated with each nucleus $\gamma$. Similarly, there will be a geometric vector potential $\mathbf{A}_\gamma$ associated with nucleus $\gamma$. The equation obeyed by $\mathbf{A}_\gamma$ is obtained from Eqs. (3.45) and (3.42), noting that, since we are dealing with the Abelian case, the commutator on the left side of Eq. (3.45) vanishes. For instance, we have

$$\frac{\partial A_{\gamma y}}{\partial x_\gamma}-\frac{\partial A_{\gamma x}}{\partial y_\gamma}=\frac{1}{i}\langle\chi|[\hat{g}_{\gamma x},\hat{g}_{\gamma y}]|\chi\rangle \ , \tag{6.3}$$

or in a convenient shorthand

$$\nabla\times\mathbf{A}_\gamma=\frac{1}{i}\langle\chi|\hat{\mathbf{g}}_\gamma\times\hat{\mathbf{g}}_\gamma|\chi\rangle \ , \tag{6.4}$$

[3]The unit of vector potential is $e/a=me^3/\hbar^2$, the unit of magnetic field strength is thus $e/a^2$.

where $|\chi\rangle$, of course, is the electronic eigenket. Equation (6.4) gives the effective magnetic field due to the geometric vector potential for nucleus $\gamma$.

According to Eq. (4.19), the operator $\hat{\mathbf{g}}_\gamma$ obeys

$$-\hat{\mathbf{g}}_\gamma=(\hat{\mathbf{F}}_\gamma)_{\rm od}\ , \tag{6.5}$$

where $\hat{\mathbf{F}}_\gamma$ is the force exerted on all the electrons by nucleus $\gamma$. Actually, since we shall only be using $\hat{\mathbf{g}}_\gamma$ in Eq. (6.4), where any diagonal part will not contribute anyway, we can omit the subscript (od) in Eq. (6.5) and simply use

$$-\hat{\mathbf{g}}_\gamma=(\hat{\mathbf{F}}_\gamma)\ . \tag{6.6}$$

Now, the total force, on the electrons consists of (a) the electrostatic attraction to the nuclei, (b) the forces they exert on each other, and finally (c) the force due to the external magnetic field. Of these, contribution (b) vanishes when summed over all electrons, so we can express the force $\hat{\mathbf{F}}_\gamma$ as

$$\hat{\mathbf{F}}_\gamma=\hat{\mathbf{F}}_{\rm tot}-\hat{\mathbf{F}}_{\rm mag}-\hat{\mathbf{F}}'_\gamma\ , \tag{6.7}$$

where

$$\hat{\mathbf{F}}'_\gamma=\sum_{\lambda\neq\gamma}\hat{\mathbf{F}}_\lambda\ . \tag{6.8}$$

The utility of Eq. (6.7) lies in the fact that the first two terms are easily written as a time derivative:

$$\begin{aligned}\mathbf{F}_{\rm tot}-\mathbf{F}_{\rm mag}&=\sum_\sigma\left[\frac{d}{dt}(\hat{\mathbf{p}}_\sigma+\alpha\mathcal{A}_\sigma)+\alpha\dot{\mathbf{r}}_\sigma\times\mathbf{B}\right]\\&=\frac{d}{dt}\sum_\sigma(\hat{\mathbf{p}}_\sigma-\alpha\mathcal{A}_\sigma)\ ,\end{aligned}$$

where the sum goes over the electrons, whose negative charge determines the signs of the terms involving external field and vector potential.

Combining Eq. (6.9) with (6.5), we can write

$$\hat{\mathbf{g}}_\gamma=-\sum_\sigma(\hat{\mathbf{p}}_\sigma-\alpha\mathcal{A}_\sigma)-\hat{\mathbf{g}}'_\gamma\ , \tag{6.10}$$

where

$$\hat{\mathbf{g}}'_\gamma=-\hat{\mathbf{F}}'_\gamma\ . \tag{6.11}$$

The first term on the right side of Eq. (6.10) looks like minus the electronic contribution to the conserved total pseudomomentum (Avron *et al.*, 1978). One must keep in mind, though, that Eq. (6.10) refers to the electronic system with fixed nuclei, for which this pseudomomentum is not conserved. Of course, Eq. (6.10) is useful only to the extent that $\hat{\mathbf{g}}'_\gamma$ can be evaluated, or at least estimated. The simplest case, which is nevertheless instructive, is that of a single atom, so that there is only one nucleus, $\hat{\mathbf{g}}'_\gamma=0$, and there is no need for the subscript $\gamma$. Omitting the subscript and the vanishing term from Eq. (6.10), and inserting the result into (6.4), we immediately find

$$\nabla\times\mathbf{A}=\alpha\sum_\sigma(\nabla\times\mathcal{A}_\sigma)=N\alpha\mathbf{B}\ , \tag{6.12}$$

where $N$ is the number of electrons in the atom. Thus the curl of the geometric vector potential is opposite to that of the external vector-potential term in Eq. (6.1), and the net effect of both is that the external field acts on a body whose charge is that of the entire atom, not that of the bare nucleus. This is, of course, just what one would expect, but it does not appear in the usual Born-Oppenheimer treatment if the geometric vector potential is ignored. Thus the fact that a neutral atom is not deflected by a uniform magnetic field may be considered as an experimental observation of the geometric gauge potential!

Yin and Mead (1992) have extended the above approach to treat the translational motion of atoms and molecules in nonuniform magnetic fields and to obtain the modification of the effective magnetic moment of a diatomic molecule rotating in a uniform field.

In the general case, of course, the evaluation of $\hat{\mathbf{g}}_\gamma$ is not so simple because of the contribution from $\hat{\mathbf{g}}'_\gamma$. Nevertheless, one can get an intuitive, nonrigorous idea by postulating that $\hat{\mathbf{F}}_\gamma$ represents some fraction, say $b_\gamma$, of the total electrostatic force exerted on the electrons by the nuclei. The "fudge factor" $b_\gamma$ would presumably be some measure of the fraction of the electrons that follow nucleus $\gamma$. Within this assumption, one can repeat the above process and conclude that nucleus $\gamma$ is screened by a fraction $b_\gamma$ of the electrons. To make this rigorous, however, one would have to resort to Eq. (4.22) and a numerical calculation.

It is worthwhile to point out that the correction to the vector-potential effect considered here does *not* affect the interaction of the external field with the nuclear spin, and that it does *not* represent the magnetic field produced at the nucleus by the motion of the electrons, an effect that we have left out completely. What the effect treated here represents is that, in Born-Oppenheimer approximation, the electrons are dragged along by the nuclei, so that an external field acts not on the bare nuclei, but on nuclei with their charges effectively modified by their accompanying electrons. There is, however, another effect in which electronic degrees of freedom and nuclear spin interact: The anisotropic shielding of the nuclear spin from an adiabatically rotated external field by the electrons (via the magnetic field produced by the electrons, *not* via the geometric phase) can affect the solid angle subtended by the rotating field and hence also the geometric phase experienced by the nuclear-spin state. This topic has been considered by Cina and Schofield (1989).

### B. Spin systems (case B)

The presence of an external magnetic field, which removes the time-reversal invariance, also makes possible magnetic-resonance experiments. In his first paper on the subject, Berry (1984) proposed a magnetic-resonance experiment that might serve as a test. Cina (1986) pointed out that a classical magnet in a slowly rotating magnetic field should acquire a geometric phase in addition

to its precession phase.

The first experiment to test this was performed by Suter *et al.* (1987), who observed the phase acquired by the magnetization of protons in a water-acetone sample subjected to a rotating magnetic field in addition to a stronger constant field. The results were in excellent agreement with theory. Suter *et al.* (1988) took this a step further by measuring the phase change acquired by a spin system carried around a closed circuit, but too rapidly for the motion to be considered adiabatic. Their results confirmed the prediction of Aharonov and Anandan (1987), and discussed in Sec. II.C.1 of the present article, that the phase change should depend only on the path in Hilbert space, regardless of whether the motion is adiabatic. In related theoretical work, Kobe *et al.* (1990) have presented an exact solution, not subject to the adiabatic assumption, for a spin-$\frac{1}{2}$ particle in a uniformly rotating magnetic field, while Wang (1990) has extended this to arbitrary spin. Analogous two-level atomic systems have been considered by Tewari (1989) and by Datta *et al.* (1989). A very general discussion of spin systems (and more general systems) undergoing continuous unitary transformations has been presented by Jordan (1988a).

A related and very interesting phenomenon is that of the geometric contribution to the *transition probability* in a two-level system driven by a time-dependent, but not adiabatic, Hamiltonian. Berry (1990a) predicted that the transition probability, which vanishes in the limit of a slow, adiabatic evolution of the Hamiltonian, should contain a geometric factor depending only on the path and not on the rapidity with which the path is traversed. In a magnetic-resonance experiment involving $^{13}C$ in a time-varying magnetic field, this effect has recently been observed by Zwanziger *et al.* (1991).

## VII. NON-ABELIAN CASE: DEGENERATE PARAMETRIC HAMILTONIAN

### A. Molecular systems (case A)

It was first pointed out by Wilczek and Zee (1984) that a set of degenerate states propagated around a closed path could produce a non-Abelian geometric phase, and that a single-valuedness requirement results in a multidimensional gauge potential instead of an ordinary vector potential. The appearance of such a gauge potential is of interest because of the analogy with the gauge potentials used in elementary-particle theory (Cheng and Li, 1984). Li (1987) examined the non-Abelian phase in a simple model of a Born-Oppenheimer system, while Moody *et al.* (1986) considered the degenerate levels other than $^1\Sigma$ of diatomic molecules, showing that these lead to a non-Abelian gauge potential if the total projection of angular momentum along the molecular axis is $\frac{1}{2}$. The diatomic molecule has been further considered by Zygelman (1987, 1990) and by Bohm, Kendrick, and Loewe (1991).

Mead (1987) pointed out that any molecular system with an odd number of electrons is capable of exhibiting a non-Abelian gauge potential because of the twofold Kramers degeneracy (Gottfried, 1966; Truhlar *et al.*, 1975) that is a consequence of the time-reversal invariance of the electronic Hamiltonian for all configurations of the nuclei. The topological invariants of such a system have been discussed by Avron *et al.* (1988). Thus non-Abelian gauge potentials should be present in many molecular systems, but the study of them is at present in its infancy. Under normal circumstances, where it is a good approximation to neglect spin-orbit interaction and to treat the electronic eigenket as a direct product of a space part with a constant-spin part, the gauge potential would be expected to be small, induced by the weak spin-orbit interaction. Certainly, the non-Abelian gauge potential can be studied only in a theory in which spin-orbit interaction is included. The effect of spin-orbit interaction on the geometric gauge potential has been considered by Mead (1980b) and most elegantly by A. Stone (1976), but not in the context of degeneracy.

As in the Abelian case, the non-Abelian gauge potential is expected to be largest in the vicinity of an intersection between two electronic levels; now, however, an intersection means an intersection of two Kramers doublets, and this requires that the nuclear coordinates satisfy five conditions instead of two (Mead, 1979). To satisfy five conditions, one needs at least four nuclei, since the number of internal coordinates for $n$ nuclei remains $(3n-6)$. To show how non-Abelian gauge potentials can arise, we consider a model of the $CH_4^+$ ion near the $T_d$ configuration. For simplicity, the only distortions for $T_d$ that we shall consider will be the five bending modes. While this is an oversimplification, it does include five independent motions that split the degeneracy, the maximum number since the vanishing of five appropriately defined coordinates defines the intersection. Thus our model, which does not pretend to numerical accuracy, will be capable of exhibiting the fundamental properties of the non-Abelian gauge potential. We are not claiming that it gives numerically accurate results for actual $CH_4^+$, although it could presumably be modified so as to do so.

The ground state of $CH_4^+$ is a spin doublet. At the $T_d$ configuration, the orbital energy becomes triply degenerate, with the three degenerate states transforming as the polar vector $F_2$ representation of $T_d$ (Frey and Davidson, 1988). If spin is included for counting purposes, with spin-orbit interaction still neglected, the degeneracy becomes sixfold. To consider spin-orbit interaction, one needs to use the $T_d$ double group (Hamermesh, 1962; Salthouse and Ware, 1972). The approximately sixfold-degenerate state transforms according to the direct product of $F_2$ with $E_{1/2}$, the representation of the double group corresponding to a $\frac{1}{2}$-spinor. This decomposes into two irreducible parts. The first of these is $E_{5/2}$, a two-dimensional representation which is a direct product of $E_{1/2}$ with $A_2$, the totally antisymmetric representation of $T_d$. The other irreducible part is $U_{3/2}$,

which is four dimensional and transforms like the angular momentum eigenkets corresponding to quantum number $\frac{3}{2}$. This representation, being fourfold degenerate, represents the intersection of two Kramers doublets. Given the equality of the four CH distances, we note that five conditions on the bending modes are necessary for $T_d$ symmetry, which is the same as the number required for degeneracy; any distortion from $T_d$, therefore, will remove the degeneracy. Distortions that do not preserve a lower symmetry such as $C_{3v}$ or $D_{2d}$ will also in general move the two $U_{3/2}$ doublets further away from the $E_{5/2}$ doublet and mix $U_{3/2}$ with $E_{5/2}$. At first, we consider small distortions, with distortion energies smaller than the spin-orbit splitting, so that the $U_{3/2}$ quartet is split, but not appreciably mixed with the $E_{5/2}$ doublet. We now proceed to construct a consistent model to describe the splitting of the $U_{3/2}$ quartet and the accompanying gauge potential. Afterwards, we take up the more common opposite extreme, where the distortion splittings are large compared with spin-orbit effects.

The five bending distortions belong to two irreducible representations of $T_d$: the two-dimensional representation $E$ and the three-dimensional $F_2$. We need to construct a consistent model to represent the effect of these distortions on the four nearly degenerate states of the $U_{3/2}$ quartet. To do this, we shall find it convenient to define the following four-dimensional matrices, each represented as made up of two-by-two blocks:

$$\mathsf{I}_z=\begin{bmatrix}1&0\\0&-1\end{bmatrix},\quad \mathsf{I}_x=\begin{bmatrix}0&1\\1&0\end{bmatrix},$$
$$\mathsf{I}_y=\begin{bmatrix}0&-i\\i&0\end{bmatrix},\quad \boldsymbol{\sigma}=\begin{bmatrix}\sigma&0\\0&\sigma\end{bmatrix}, \tag{7.1}$$

where each entry stands for a two-by-two matrix and the last definition has three components, one for each of the usual Pauli matrices. In Eq. (7.1), the subscripts $x,y,z$ correspond to the usual notation for Pauli matrices and have no significance in terms of directions in space. In four dimensions, there are fifteen independent traceless, Hermitian matrices, and these can be taken to be the six matrices defined by Eq. (7.1) together with the nine products of an $\mathsf{I}$ matrix with a $\sigma$ matrix. Further details are to be found in Appendix B.

The time-reversal operator operating on a column vector can always be represented as the complex conjugation of all components ($\bar{K}$) followed by a unitary matrix $\mathsf{b}$:

$$\hat{T}=\mathsf{b}\bar{K}\ . \tag{7.2}$$

The four basis kets for $U_{3/2}$ transform like angular momentum eigenkets with total angular momentum quantum number $\frac{3}{2}$. Denoting these by their $z$ components and using normal conventions, we find that the operation of $\hat{T}$ on them is given by

$$\hat{T}|\tfrac{3}{2}\rangle=-|-\tfrac{3}{2}\rangle\ ,\quad \hat{T}|-\tfrac{3}{2}\rangle=|\tfrac{3}{2}\rangle\ ,$$
$$\hat{T}|\tfrac{1}{2}\rangle=|-\tfrac{1}{2}\rangle\ ,\quad \hat{T}|-\tfrac{1}{2}\rangle=-|\tfrac{1}{2}\rangle\ , \tag{7.3}$$

which, if columns and rows are labeled in the order $\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2}$, corresponds to

$$\mathsf{b}=\begin{bmatrix}0&0&0&1\\0&0&-1&0\\0&1&0&0\\-1&0&0&0\end{bmatrix}=i\mathsf{I}_x\sigma_y\ . \tag{7.4}$$

Instead of the eigenkets of $z$ components of angular momentum, we find it convenient to introduce the basis kets

$$|a\rangle=\frac{1}{\sqrt{2}}(|\tfrac{1}{2}\rangle-i|-\tfrac{3}{2}\rangle)\ ,$$
$$|b\rangle=\frac{1}{\sqrt{2}}(i|\tfrac{3}{2}\rangle-|-\tfrac{1}{2}\rangle)\ ,$$
$$|c\rangle=\hat{T}|b\rangle=\frac{1}{\sqrt{2}}(|\tfrac{1}{2}\rangle+i|-\tfrac{3}{2}\rangle)\ , \tag{7.5}$$
$$|d\rangle=-\hat{T}|a\rangle=\frac{1}{\sqrt{2}}(-i|\tfrac{3}{2}\rangle-|-\tfrac{1}{2}\rangle)\ .$$

In terms of these kets, and labeling rows and columns in the order $a,b,c,d$, we see that Eq. (7.4) is still satisfied.

When the molecule is distorted from $T_d$ symmetry, the electronic Hamiltonian, in addition to terms proportional to the unit matrix, may contain additional terms proportional to the distortion coordinates multiplied by traceless, Hermitian matrices. Any such matrix $\mathsf{Q}$, however, must commute with time reversal, which means it must satisfy (Gottfried, 1966; Truhlar *et al.*, 1975)

$$\mathsf{Q}\mathsf{b}=\mathsf{b}\mathsf{Q}^*\ , \tag{7.6}$$

where the asterisk denotes complex conjugation, not Hermitian conjugation. Of the fifteen fundamental traceless Hermitian matrices that we have defined, only the following five satisfy Eq. (7.6):

$$\mathsf{I}_x\ ,\ \mathsf{I}_y\ ,\ \mathsf{I}_z\sigma_x\ ,\ \mathsf{I}_z\sigma_y\ ,\ \mathsf{I}_z\sigma_z\ . \tag{7.7}$$

Moreover, our basis kets have been chosen so as to lead to simple relations between the matrices of Eq. (7.7) and the bending distortions. For the $F_2$ and $E$ distortions, we choose as coordinates three-dimensional and two-dimensional vectors, respectively, as follows:

$$F_2\text{: }\mathbf{r}=(x,y,z)\ ,\quad E\text{: }\rho=(u,v)\ . \tag{7.8}$$

For $\mathbf{r}$, we shall make use of spherical polar coordinates defined in the usual way; for $\rho$, we use plane polar coordinates $(\rho,\varepsilon)$ with

$$u=\rho\cos\varepsilon\ ,\quad v=\rho\sin\varepsilon\ . \tag{7.9}$$

We shall also make use of the "total" displacement $R$ and angle $\kappa$, with range $0\le\kappa\le\pi/2$, defined by

$$\rho=R\cos\kappa\ ,\quad r=R\sin\kappa\ . \tag{7.10}$$

In terms of these coordinates, scaled in an appropriate way, a self-consistent model of the electronic Hamiltonian is

$$\hat{H}=\tfrac{1}{2}(\omega_r^2 r^2+\omega_\rho^2\rho^2)-(u\mathsf{I}_x+v\mathsf{I}_y+\mathsf{I}_z\sigma\cdot\mathbf{r}) . \tag{7.11}$$

For further details, the reader is referred to Appendix B.

We concentrate on the lower energy level of this Hamiltonian, which in our model represents the ground electronic state of the Jahn-Teller distorted molecule. The eigenvalue is $\frac{1}{2}(\omega_r^2 r^2+\omega_\rho^2\rho^2)-R$. The two degenerate eigenkets can of course be chosen in many ways, corresponding to the infinite variety of allowable gauges. A gauge that leads to convenient gauge potentials corresponds to the following choice of single-valued eigenkets:

$$|\alpha\rangle=\frac{\sin\frac{\kappa}{2}}{\sqrt{2}}\begin{bmatrix}\cos\theta\\ \sin\theta e^{i\phi}\\ \cos\theta e^{i\varepsilon}\\ \sin\theta e^{i(\phi+\varepsilon)}\end{bmatrix}+\frac{\cos\frac{\kappa}{2}}{\sqrt{2}}\begin{bmatrix}-1\\ 0\\ e^{i\varepsilon}\\ 0\end{bmatrix} , \tag{7.12}$$

$$|\beta\rangle=e^{i\varepsilon\hat{T}}|\alpha\rangle=\frac{\sin\frac{\kappa}{2}}{\sqrt{2}}\begin{bmatrix}\sin\theta e^{-i\phi}\\ -\cos\theta\\ \sin\theta e^{i(\varepsilon-\phi)}\\ -\cos\theta e^{i\varepsilon}\end{bmatrix}+\frac{\cos\frac{\kappa}{2}}{\sqrt{2}}\begin{bmatrix}0\\ -1\\ 0\\ e^{i\varepsilon}\end{bmatrix} . \tag{7.13}$$

It is now a straightforward matter to insert Eqs. (7.12) and (7.13) into (3.44) to calculate the gauge potentials. In our notation, we shall now find it convenient to use Pauli matrices with respect to the kets $|\alpha\rangle$ and $|\beta\rangle$: $\sigma_z=|\alpha\rangle\langle\alpha|-|\beta\rangle\langle\beta|$, etc. The gauge potentials corresponding to the three components of $\mathbf{r}$ can be summed up as

$$\mathsf{A}_r=-\frac{1-\cos\kappa}{2r^2}(\mathbf{r}\times\boldsymbol{\sigma}) , \tag{7.14}$$

while the polar component corresponding to $\rho,\varepsilon$, are

$$\mathsf{A}_\rho=0 ;\quad \mathsf{A}_\varepsilon=\tfrac{1}{2}\left[1+\frac{\mathbf{r}\cdot\boldsymbol{\sigma}}{R}\right] . \tag{7.15}$$

To demonstrate that this is a truly non-Abelian situation, we calculate some field strengths, using Eq. (3.45) along with (7.14), (7.15). For $\mathbf{r}$, we can use three-dimensional vector notation, replacing $\mathsf{Z}_{xy}$ by $\mathsf{Z}_z$, etc. We find the result

$$\mathsf{Z}_r=\frac{1}{2R^2}\left[\boldsymbol{\sigma}\cos\kappa+\frac{\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\sigma})}{r^2}(1-\cos\kappa)\right] . \tag{7.16}$$

For $\mathsf{Z}_{\rho\varepsilon}$, we find

$$\mathsf{Z}_{\rho\varepsilon}=-\frac{\rho}{2R^2}(\mathbf{r}\cdot\boldsymbol{\sigma}) . \tag{7.17}$$

One could also calculate $\mathsf{Z}_{x\rho}$, $\mathsf{Z}_{y\varepsilon}$, etc., but one can already see from Eqs. (7.16) and (7.17) that different field strengths taken at different points in configuration space do not in general commute, demonstrating that this is a true non-Abelian case.

Introducing effective masses for the $E$ and $F_2$ coordinates, we can insert Eqs. (7.14) and (7.15) into the nuclear kinetic-energy operator, arriving at the effective nuclear Hamiltonian

$$\begin{aligned}\hat{H}_{\rm nuc}=&-\frac{1}{2M_r}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]-\frac{1}{2M_\rho}\frac{1}{\rho}\frac{\partial}{\partial\rho}\left[\rho\frac{\partial}{\partial\rho}\right]\\ &+\frac{1}{2M_r r^2}\left[\hat{L}^2+(1-\cos\kappa)\hat{\mathbf{L}}\cdot\boldsymbol{\sigma}+\frac{(1-\cos\kappa)^2}{2}\right]\\ &+\frac{1}{2M_\rho\rho^2}\left[(\hat{L}_\varepsilon+\tfrac{1}{2})^2+(\hat{L}_\varepsilon+\tfrac{1}{2})\frac{\mathbf{r}\cdot\boldsymbol{\sigma}}{R}+\frac{r^2}{4R^2}\right]\\ &+\tfrac{1}{2}(\omega_r^2 r^2+\omega_\rho^2\rho^2)-R ,\end{aligned} \tag{7.18}$$

where we have defined the pseudoangular momentum operators

$$\hat{\mathbf{L}}=\frac{1}{i}\mathbf{r}\times\nabla_r \tag{7.19}$$

and

$$\hat{L}_\varepsilon=\frac{1}{i}\frac{\partial}{\partial\varepsilon} . \tag{7.20}$$

In Eq. (7.18), we have ignored the G matrix term appearing in Eq. (4.6). It is a multiple of the unit matrix, which can be considered as an extra term in the potential energy.

We note that, because of Eq. (7.13), the time-reversal operator operates on our eigenkets as

$$\hat{T}|\alpha\rangle=e^{-i\varepsilon}|\beta\rangle ;\quad \hat{T}|\beta\rangle=-e^{-i\varepsilon}|\alpha\rangle , \tag{7.21}$$

which can be summarized as

$$\hat{T}=-ie^{-i\varepsilon}\sigma_y\bar{K} . \tag{7.22}$$

With the aid of Eq. (7.22), one can show that $\hat{T}$ reverses $\sigma$, $\hat{\mathbf{L}}$, and $\hat{\mathbf{p}}_r$, while replacing $\hat{L}_\varepsilon$ by $(-\hat{L}_\varepsilon-1)$, meaning that $(\hat{L}_\varepsilon+\frac{1}{2})$ is reversed in sign. The Hamiltonian (7.18) is thus invariant under time reversal.

The terms in Eq. (7.18) containing $\hat{\mathbf{L}}\cdot\boldsymbol{\sigma}$ and $(\hat{L}_\varepsilon+\frac{1}{2})\mathbf{r}\cdot\boldsymbol{\sigma}$ are true gauge-potential terms. They are *not* the spin-orbit interaction, which was included at the very beginning, and split the $U_{3/2}$ from the $E_{5/2}$ levels. If only the first term were present, it could be handled formally like a spin-orbit interaction. In general, however, both terms are of the same order of magnitude and should be treated on an even footing. The gauge potential couples the $E$ and $F_2$ modes, which otherwise would be uncoupled in this model.

The above treatment represents the most interesting case from the purely theoretical point of view, but unfortunately it is correct only in the limit where the distortion splitting is small compared with the spin-orbit energy, that is, only very close to the $T_d$ configuration. In the opposite extreme, the electronic eigenkets are represented to good approximation by products of real electronic space kets with independent spin states. These are perturbed by the spin-orbit interaction. We now examine how this can lead to a gauge potential induced by the

spin-orbit interaction.

To avoid overburdening the notation, we represent the spin-orbit interaction through an effective perturbing Hamiltonian for a single unpaired electron. The explicit inclusion of all electrons would change nothing essential. The spin-orbit Hamiltonian we shall use is

$$\hat{H}_{\rm so}=\frac{e\hbar}{2mc^2}\hat{\mathbf{s}}\cdot(\mathbf{E}\times\hat{\mathbf{v}}) , \tag{7.23}$$

where $\hat{\mathbf{s}}$ is electronic spin, $\mathbf{E}$ is the electric field seen by the unpaired electron due to the nuclei and all other electrons, and $\hat{\mathbf{v}}$ is velocity of the electron. We denote the two unperturbed single-valued eigenkets by the ket row $\{|X_0\rangle|$, and the perturbed ket row, through first order in the spin-orbit interaction, by

$$\{|X\rangle|=(1+i\hat{\tau})\{|X_0\rangle . \tag{7.24}$$

The eigenvalue problem can now be written

$$(\hat{H}_0+\hat{H}_{\rm so})(1+i\hat{\tau})\{|X_0\rangle|=(U_0+\delta U)(1+i\hat{\tau})\{|X_0\rangle| , \tag{7.25}$$

where $\hat{H}_0$ is the unperturbed electronic Hamiltonian. Because the space part of Eq. (7.23) changes sign under time reversal, while the space part of $\{|\chi_0\rangle|$ is time-reversal invariant, $\hat{H}_{\rm so}$ is entirely off block and the first-order shift $\delta U$ in the eigenvalue is zero. Making use of this, and keeping only first-order terms in Eq. (7.25), we see that a solution is found if $\hat{\tau}$ satisfies

$$i[\hat{\tau},\ \hat{H}_0]=-\hbar\dot{\hat{\tau}}=\hat{H}_{\rm so} . \tag{7.26}$$

From Eq. (7.23), we see that (7.26) is satisfied formally by

$$\hat{\tau}=\hat{\mathbf{s}}\cdot\hat{\boldsymbol{\omega}} , \tag{7.27}$$

with the space operator $\hat{\omega}$ given by

$$\hat{\boldsymbol{\omega}}=-\frac{e}{2mc^2}\int\mathbf{E}\times d\mathbf{r} . \tag{7.28}$$

To obtain the gauge potential, we use Eqs. (3.44) and (3.37), noting that there may be an Abelian vector potential $A_\mu$ already present. Through first order in the spin-order interaction, we find

$$\mathsf{A}_\mu=A_\mu-i\mathbf{s}\cdot|\langle X_0|\}[\hat{g}_\mu,\ \hat{\boldsymbol{\omega}}]\{|X_0\rangle| , \tag{7.29}$$

where $\mathbf{s}$ is the matrix representation of the spin.

Although the spin-orbit effect shifts the electronic energy only in second order, we see that it produces a first-order gauge potential in the Hamiltonian for nuclear motion. Like the magnetic screening discussed in Sec. VI, this effect would not appear if the Born-Oppenheimer procedure were to be applied without regard for the geometric gauge potential.

### B. Spin systems (case B)

The study of the effects of the non-Abelian geometric gauge potential in molecules is, as mentioned earlier, in its infancy, and to date no experiments have been done which measure effects of terms such as those found in Eqs. (7.18) and (7.29). For spin systems, however, precise theoretical predictions are more easily obtained, and there has been one relevant experimental study. It was pointed out by Mead (1987) that a half-odd integer spin with quantum number $\frac{3}{2}$ or greater in an electric field should exhibit a non-Abelian phase change when the field is rotated. When the field is rotated, the Kramers doublet with angular momentum component $\pm\frac{1}{2}$ evolves according to the parallel connection, leading to the possibility of a change in angular momentum component when the field returns to its original orientation. A similar idea is that of Segert (1987b), who considers accidental degeneracy produced in an atomic system by parallel electric and magnetic fields, which are then rotated adiabatically so as to produce transitions between the degenerate states. Segert (1987c) has proposed an experiment to observe this phenomenon, in which Pb is optically pumped into the metastable $^3P_1$ state. A further theoretical treatment of the atomic system in parallel magnetic and electric fields has been given by Ligare (1990).

The nuclear quadrupole resonance experiment of Tycko (1987), in which a spin follows the quadrupole field of a crystal in which it is embedded, is in the spirit of the situation considered by Mead (1987), but is so designed as to measure only an Abelian phase change. Zee (1988) pointed out that a more complicated modification of Tycko's experiment should be capable of exhibiting a non-Abelian gauge structure. Zwanziger *et al.* (1990b) have carried out such a modified experiment, in which a $^{35}$Cl nucleus in a $NaClO_4$ crystal is simultaneously rotated about two axes and the nuclear quadrupole resonance spectrum observed. Their results agreed perfectly with predictions based on a non-Abelian geometric phase change, which in the relatively simple spin system could be calculated. So far, this is the only direct observation of a non-Abelian geometric phase or gauge potential at the atomic or molecular level. It is to be hoped that there will be more experimental observations in the future. In particular, it is interesting to speculate as to whether the change of angular momentum component predicted for half-odd integer spins in rotating electric fields can produce population inversions useful in magnetic resonance.

## VIII. NON-ABELIAN CASE: NONDEGENERATE ELECTRONIC STATES

It frequently happens in molecular quantum mechanics that, although two or more Born-Oppenheimer electronic states are nondegenerate, they are strongly enough coupled, or close enough in energy, that it becomes a poor approximation to limit oneself to a single electronic eigenket. In this case, using the procedure outlined in Sec. IV, one includes not just one state, but $n$, where $n$ is deemed large enough to give a good approximation, while still small enough to lead to a tractable problem.

Zygelman (1987, 1990) has demonstrated the utility of this for diatomic systems, especially in collision problems where two or more states that are nondegenerate at small internuclear separations become degenerate asymptotically.

If there is no degeneracy, the matrix U in Eq. (4.9) is no longer a multiple of the unit matrix. U will be diagonal if the basis kets are the eigenkets of the electronic Hamiltonian, but a gauge transformation will now in general lead to a U matrix that is no longer diagonal. Because the gauge-potential terms like $\mathsf{A}_\mu\partial_\mu|\psi\}$ in Eq. (4.9) are considered more troublesome than a nondiagonal U, attempts were made in the past to construct so-called "diabatic" representations in which the gauge-potential terms are absent ("strictly diabatic") or small enough to be neglected in some useful approximation ("approximately diabatic" or "quasidiabatic"), and the coupling between different electronic states is represented, at least approximately, by a nondiagonal U matrix. In our language, this would correspond to finding a gauge transformation that makes the gauge potentials zero (strictly diabatic), or at least small (quasidiabatic).

It has been known for some time (McLachlan, 1961; Mead and Truhlar, 1982) that strictly diabatic representations do not exist except perhaps in exceptional cases. From our point of view, a nonvanishing field strength calculated from Eq. (3.42) guarantees the nonexistence of a strictly diabatic representation. Nevertheless, one can sometimes obtain a useful model by assuming an approximately diabatic representation and hoping that the gauge-potential terms can be made sufficiently small for the purpose, and/or that their effect on the phenomenon under consideration can be mimicked by a nondiagonal U matrix. A number of studies of various molecular phenomena involving more than one electronic state have been carried out using such models (Köppel *et al.*, 1980; Cederbaum *et al.*, 1981; Domcke *et al.*, 1981; Cederbaum and Köppel, 1982; Köppel *et al.*, 1982; Meyer and Köppel, 1984; Köppel *et al.*, 1984; Desouter-Lecomte *et al.*, 1985; Thompson, Truhlar, and Mead, 1985; Estrada *et al.*, 1986; Köppel *et al.*, 1988).

In this article, however, we are interested not in ignoring the gauge potential, but in studying its properties. Of course, all the properties of non-Abelian gauge potentials discussed in Secs. III and IV hold for this case. We first make a few remarks on the size of the couplings, then discuss the question of finding the best possible quasidiabatic representation.

Since the magnitude of the gauge potential itself is different in different gauges, an idea of what might be called the unavoidable magnitude is best obtained by studying the field strengths $\mathsf{Z}_{\mu\nu}$, defined by Eq. (3.34). According to Eq. (3.45), derivatives and/or products of the potential components $\mathsf{A}_\mu$ must be at least of the order of magnitude of the field strengths. We are particularly interested in the question of the existence of a gauge in which all potentials are zero, or at least sufficiently small. According to Eq. (3.45), such a gauge will exist only if all the field strengths are zero or small.

We first consider the possibility that the field strengths might vanish identically because of a symmetry property. For them to vanish on a submanifold of more than zero measure in the nuclear configuration space, this symmetry must be one that holds everywhere, since there are no examples in molecular quantum theory of symmetries that hold on a submanifold of nonzero measure that is not the whole space. The examples already discussed show that time-reversal symmetry does not ensure the vanishing of the field strengths. The only other symmetries that exist for the *entire* nuclear configuration space in molecular systems are the $D_{\infty h}$ or $C_{\infty v}$ symmetry holding for diatomic molecules and the $C_s$ symmetry arising from the omnipresent reflection plane in triatomics. In a diatomic system, using spherical polar coordinates for the nuclear relative motion, if the electronic states under consideration are all of the same symmetry, only $\mathsf{A}_r$ can be different from zero, and it can depend only on $r$. It follows from Eq. (3.45) that the field strengths $\mathsf{Z}_{r\theta},\mathsf{Z}_{r\phi},\mathsf{Z}_{\theta\varphi}$, must all vanish, and for this system these are the only field strengths. This conclusion was also reached by Mead and Truhlar (1982). For the triatomic system, similar considerations apply to field strengths $\mathsf{Z}_{\mu\nu}$ if the electronic states considered all have the same symmetry and if $\mu$ and/or $\nu$ refer to the out-of-plane rotations. For the triatomic system, however, as we have already seen, there are other field strengths that do not vanish. For all other systems, field strengths can vanish by symmetry at most on a zero-measure submanifold of the nuclear configuration space. We now investigate the possibility that they may be zero or small without the help of symmetry.

For simplicity, we consider the case $n=2$, with nondegenerate, time-reversal-invariant electronic eigenkets. It will be clear that the qualitative results do not depend on this restriction. Let $\hat{P}$ be the projection on the space of the two eigenkets, and $\hat{P}'=1-\hat{P}$. According to Eq. (3.34), for each of the two kets $|\chi_j\rangle (j=1,2)$ we have

$$\hat{g}_\mu|\chi_j\rangle=-i\hat{P}'\partial_\mu|\chi_j\rangle\ . \tag{8.1}$$

Now, the characteristic length over which an electronic wave function changes appreciably is a Bohr radius, or one atomic unit. When a nuclear coordinate changes by $\sim 1$ au, therefore, there will be a change of order unity in any electronic eigenket, and, apart from highly unlikely coincidences, projection onto a space of small dimensionality, not chosen for the purpose of minimizing the magnitude of $\partial_\mu|\chi_j\rangle$, will not greatly change this. In atomic units, therefore, the magnitude of the right side of Eq. (8.1) will nearly always be of order unity in atomic units. In our example, the eigenkets can be taken as real because of the time-reversal invariance, as discussed in Sec. II.D, which has as a consequence that $\mathsf{Z}_{\mu\nu}$ is imaginary and antisymmetric in this gauge, having only one nonvanishing matrix element, $\langle 1|\mathsf{Z}_{\mu\nu}|2\rangle=-\langle 2|\mathsf{Z}_{\mu\nu}|1\rangle$. Because of the covariant property of $\mathsf{Z}_{\mu\nu}$, moreover, $\mathrm{Det}\mathsf{Z}_{\mu\nu}=\langle 1|\mathsf{Z}_{\mu\nu}|2\rangle^2$ in this or any other gauge, so we

can get an idea of the magnitude of the field strength by looking at this matrix element. From Eqs. (8.1) and (3.34), we find

$$\langle 1|Z_{\mu\nu}|2\rangle=\frac{1}{i}\{\langle\partial_\mu\chi_1|\hat{P}'|\partial_\nu\chi_2\rangle-\langle\partial_\nu\chi_1|\hat{P}'|\partial_\mu\chi_2\rangle\} \tag{8.2}$$

Since we know that the kets involved in the right side of Eq. (8.2) are almost certainly of order of magnitude unity, there are only two ways in which the whole expression could be of magnitude much less than unity: The first possibility is that both terms in brackets on the right side of Eq. (8.2) are small, i.e., that $\hat{P}'|\partial_\nu\chi_1\rangle$ and $\hat{P}'|\partial_\mu\chi_2\rangle$ are fortuitously nearly orthogonal, and that the same applies to $\hat{P}'|\partial_\mu\chi_1\rangle$ and $\hat{P}'|\partial_\nu\chi_2\rangle$. The second possibility is that the two terms fortuitously cancel, or nearly cancel. We use the word "fortuitously" for both cases because there is no reason of symmetry for the desired property to hold, so it clearly requires a coincidence. Even if one component of the field strength happens to be small in a given region, there is no guarantee that the same will hold for the other components. Apart from extraordinary coincidences, therefore, the field strengths will be of order unity in atomic units, and hence, according to Eq. (3.45), if the potentials are small their derivatives must be of order unity so that the potentials themselves will become of order unity within a distance of $\sim 1$ au. The general result is that gauge potentials cannot be made small compared with unity in atomic units except perhaps in regions whose extent is much less than unity. Exceptions to this rule depend on things like fortuitous cancellations over sizable regions and will be exceedingly rare, apart from the diatomic system and certain field-strength components for the triatomic system discussed above. This conclusion does not necessarily mean that models based on an assumed diabatic basis cannot be useful for certain problems, but it does mean that their limitations must be kept in mind.

Despite the impossibility of getting the gauge potentials to be small over large regions, it is still useful to ask how to make them, in some sense, as small as possible. To address this question, one has to have a criterion of smallness, such as a property of the gauge potentials that is to be minimized. Pacher *et al.* (1989) have taken up this question, using the smallness criterion

$$\Xi=\int\left[\sum_\mu \mathrm{Tr}(A_\mu^2)\right]d\tau=\min\ , \tag{8.3}$$

where the integral goes over the whole nuclear configuration space, assumed to be defined by Cartesian coordinates. While it would be wrong to assert that this is the only possible criterion, it has the advantage of being simple and of leading easily to an answer.

The meaning of the minimum criterion (8.3), of course, is in terms of gauge transformations: The minimum has been attained if there is no gauge transformation that would result in a decrease of the integral. This has as a consequence that the integral in (8.3) must be stationary under infinitesimal gauge transformations:

$$\delta\Xi=\delta\int\left[\sum_\mu \mathrm{Tr}(A_\mu^2)\right]d\tau=0\ , \tag{8.4}$$

where the variation is with respect to an arbitrary infinitesimal gauge transformation. For an infinitesimal gauge transformation defined by the infinitesimal matrix e, we find with the help of Eq. (3.58)

$$\begin{aligned}\delta\Xi&=\int\left[\sum_\mu \mathrm{Tr}(iA_\mu[A_\mu,\mathrm{e}]\right.\\&\qquad\left.+i[A_\mu,\mathrm{e}]A_\mu+A_\mu\partial_\mu\mathrm{e}+(\partial_\mu\mathrm{e})A_\mu)\right]d\tau\\&=\int\left[\sum_\mu \mathrm{Tr}(i[A_\mu^2,\mathrm{e}]-\mathrm{e}\partial_\mu A_\mu-(\partial_\mu A_\mu)\mathrm{e})\right]d\tau\ ,\end{aligned} \tag{8.5}$$

where the second equality comes from a well-known identity involving commutators, and integration by parts discarding the surface term. The trace of a commutator is zero, so the commutator term in (8.5) contributes nothing. Since e is arbitrary, it follows that the variation will be zero if and only if

$$\sum_\mu \partial_\mu A_\mu=0\ . \tag{8.6}$$

Pacher *et al.* (1989) refer to the condition (8.6) as a Lorentz gauge condition. In lowest order in a small region about a given origin, it can be achieved by means of the block diagonalization procedure of Cederbaum *et al.* (1989) and Pacher *et al.* (1988), discussed in Sec. III.A.3. It is *not* always, or even usually, easy to find a gauge in which Eq. (8.6) is satisfied. Nevertheless, it furnishes a criterion for a quasidiabatic basis which has a solid theoretical foundation.

## IX. DISCUSSION

The geometric phase is a subject of fundamental importance and interest in many areas of physics, which is inherent in the basic laws of classical and quantum mechanics; nevertheless, it has been recognized only recently as a general phenomenon, although special cases had been treated earlier. This is a fundamental area in which the chemical physicist may make a legitimate (though not undisputable) claim to have been ahead of his more pure colleagues, at least in the quantum-mechanical realm. Now, however, when the geometric phase has taken the rest of physics by storm, it remains somewhat outside the mainstream of chemical physics, with many theoreticians in the area being only vaguely aware of it.

The geometric phase does have implications for molecular systems, though, as we hope to have shown in this review, and much work remains to be done before these implications are fully understood. Particularly interesting and challenging problems, in the author's opinion, are the correct handling of permutation symmetry for more than four identical nuclei and the full understanding of the effects of non-Abelian gauge potentials, includ-

ing their effect on the permutation symmetry problem. It is also unclear at this point what role, if any, the geometric phase may play in the properties of large molecules such as polymers, and of bulk matter.

The future should see more theoretical developments and also more experimental verifications of the predictions of geometric phase theory, in both spin and molecular systems. There has been a rapid development in this area in the years since 1984. The period of such explosive growth may be coming to an end, but the period of useful work in this area is by no means over. It is hoped that this article will make a contribution to the dissemination of understanding of this most interesting topic.

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## APPENDIX A: LIMITING PROCESS FOR ABRUPT SIGN CHANGE

Consider a portion of a path $C$ in parameter space in which the coefficient of one basis ket, say $|0\rangle$, passes through zero. We represent this by a limiting process in which the coefficient, instead of passing through zero, circles the origin in the complex plane. We need only consider an infinitesimally small portion of the path, during which there is negligible change except for the change in sign of the one component. Accordingly, for this portion of the path, we can represent the ket by

$$|\chi\rangle = |0\rangle \varepsilon e^{i\theta} + |1\rangle \sqrt{1-\varepsilon^2}\ , \tag{A1}$$

where $\varepsilon$ is a small positive number, to be held constant along the small portion of the path, and the sign change is represented by $\theta$ going from zero to $\pi$. At the end, the limit $\varepsilon \to 0$ is to be taken. For the projection and its differential, we have

$$\hat{P} = \begin{bmatrix} \varepsilon^2 & \varepsilon\sqrt{1-\varepsilon^2}\,e^{i\theta} \\ \varepsilon\sqrt{1-\varepsilon^2}\,e^{-i\theta} & 1-\varepsilon^2 \end{bmatrix}, \tag{A2}$$

$$d\hat{P} = i\,d\theta \begin{bmatrix} 0 & \varepsilon\sqrt{1-\varepsilon^2}\,e^{i\theta} \\ -\varepsilon\sqrt{1-\varepsilon^2}\,e^{-i\theta} & 0 \end{bmatrix}. \tag{A3}$$

Using Eqs. (A2) and (A3), we find for the integrand in (2.23) for this portion of the path

$$\frac{\langle 0|[\hat{P},\, d\hat{P}]|0\rangle}{\langle 0|\hat{P}|0\rangle} = -2i(1-\varepsilon^2)d\theta\ . \tag{A4}$$

The contribution of this portion of the path to the flux (2.23) is thus

$$-(1-\varepsilon^2)\int_0^{\pi} d\theta = -\pi(1-\varepsilon^2)\ , \tag{A5}$$

which becomes just $-\pi$ in the limit $\varepsilon \to 0$. Another choice of limiting path would have given $+\pi$, but the difference does not affect the flux modulo $2\pi$.

## APPENDIX B: MATRICES AND INTERACTIONS FOR $CH_4^+$ SYSTEM

Written out, the matrices defined in (7.1) are

$$I_z = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}, \tag{B1}$$

$$I_x = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \tag{B2}$$

$$I_y = \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}, \tag{B3}$$

$$\sigma_z = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}, \tag{B4}$$

$$\sigma_x = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \tag{B5}$$

$$\sigma_y = \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}. \tag{B6}$$

It is a simple consequence of the Wigner-Eckart theorem (Roman, 1965; Wybourne, 1974; Thompson and Mead, 1985) that any contribution $\hat{H}_{\rm lin}$ to the electronic Hamiltonian within the $U_{3/2}$ quartet which is linear with respect to the coordinates defined in (7.8) must be of the form

$$\hat{H}_{\rm lin}=\boldsymbol{\rho}\cdot\hat{\mathbf{Q}}_\rho+\mathbf{r}\cdot\hat{\mathbf{Q}}_r\ , \tag{B7}$$

where the two components of $\hat{\mathbf{Q}}_\rho$ and the three of $\hat{\mathbf{Q}}_r$ transform, respectively, according to the $E$ and $F_2$ representations of $T_d$, and all commute with time reversal. Of the five traceless Hermitian operators in the space of $U_{3/2}$ that commute with time reversal, the following (in an arbitrary but convenient normalization) transform according to $E$:

$$\hat{Q}_u=\tfrac{1}{3}(2\hat{L}_z^2-\hat{L}_x^2-\hat{L}_y^2)\ ,\quad \hat{Q}_v=\frac{1}{\sqrt{3}}(\hat{L}_x^2-\hat{L}_y^2)\ . \tag{B8}$$

Also in an arbitrary normalization, the operators transforming according to $F_2$ are

$$\begin{aligned}\hat{Q}_z&=\frac{1}{\sqrt{3}}(\hat{L}_x\hat{L}_y+\hat{L}_y\hat{L}_x)\ ,\\ \hat{Q}_x&=\frac{1}{\sqrt{3}}(\hat{L}_y\hat{L}_z+\hat{L}_z\hat{L}_y)\ ,\\ \hat{Q}_y&=\frac{1}{\sqrt{3}}(\hat{L}_z\hat{L}_x+\hat{L}_x\hat{L}_z)\ .\end{aligned} \tag{B9}$$

In terms of the basis kets defined by Eq. (7.5), and also using Eqs. (B1)–(B6), it is straightforward to verify that the matrix forms of the operators of (B8) and (B9) are

$$\mathsf{Q}_u=-\mathsf{I}_x\ ,\quad \mathsf{Q}_v=-\mathsf{I}_y\ , \tag{B10}$$

and

$$\mathsf{Q}_z=-\mathsf{I}_z\sigma_z\ ,\quad \mathsf{Q}_x=-\mathsf{I}_z\sigma_x\ ,\quad \mathsf{Q}_y=-\mathsf{I}_z\sigma_y\ . \tag{B11}$$

Inserting Eqs. (B10) and (B11) into (B7), one verifies the model Hamiltonian (7.11).

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