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Representation and Conservation of Angular Momentum in the Born-Oppenheimer Theory of Polyatomic Molecules

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This paper concerns the representation of angular momentum operators in the Born-Oppenheimer theory of polyatomic molecules and the various forms of the associated conservation laws. Topics addressed include the question of whether these conservation laws are exactly equivalent or only to some order of the Born-Oppenheimer parameter $\kappa = (m/M)^{1/4}$, and what the correlation is between angular momentum quantum numbers in the various representations. These questions are addressed both in problems involving a single potential energy surface, and those with multiple, strongly coupled surfaces; and both in the electrostatic model and those for which fine structure and electron spin are important. The analysis leads to an examination of the transformation laws under rotations of the electronic Hamiltonian; of the basis states, both adiabatic and diabatic, along with their phase conventions; of the potential energy matrix; and of the derivative couplings. These transformation laws are placed in the geometrical context of the structures in the nuclear configuration space that are induced by rotations, which include the rotational orbits or fibers, the surfaces upon which the orientation of the molecule changes but not its shape; and the section, an initial value surface that cuts transversally through the fibers. Finally, it is suggested that the usual Born-Oppenheimer approximation can be replaced by a dress-ing transformation, that is, a sequence of unitary transformations that block-diagonalize the Hamiltonian. When the dressing transformation is carried out, we find that the angular momentum operator does not change. This is a part of a system of exact equivalences among various representations of angular momentum operators in Born-Oppenheimer theory. Our analysis accommodates large-amplitude motions, and is not dependent on small-amplitude expansions about an equilibrium position. Our analysis applies to the noncollinear configurations of a polyatomic molecule; this covers all but a subset of measure zero (the collinear configurations) in the nuclear configuration space.

I. INTRODUCTION

This article concerns angular momentum and rotations in the Born-Oppenheimer theory of polyatomic molecules. Topics addressed include the relationship among the various representations of angular momentum operators and the corresponding conservation laws, as well as the equivalence among them, and whether that is approximate or exact. We also address the correlation between angular momentum quantum numbers in the various representations. We treat both single-surface and multi-surface problems, and we treat both the simple electrostatic model for the electronic Hamiltonian as well as models that incorporate fine structure and electron spin. We assume the molecule is isolated, so that the Hamiltonian commutes with both rotations and time reversal.

This article relies on basic Born-Oppenheimer theory (Born and Oppenheimer (1927); Born and Huang (1954); Ballhausen and Hansen (1972); Mead (1988); Cederbaum (2004)) and its application to multisurface problems with conical intersections (Herzberg and Longuet-Higgins (1963); Longuet-Higgins (1975); Mead (1979, 1983); Thompson and Mead (1985); and Yarkony (1996, 1997b,a); Gordon, Glezaku, and Yarkony (1998); Yarkony (2001); Adhikari and Billing (2002); Kuppermann and Abrol (2002); Domcke (2004); Yarkony (2004b,a); Jasper *et al.* (2006); Schuurman and Yarkony (2006); Faraji, Gómez-Carrasco, and Köppel (2012); Matsika (2012); Yarkony (2012); Zhu and Yarkony (2016); Gonon *et al.* (2017); Kendrick (2018); Fedorov and Levine (2019); Choi and Vaniček (2020); Bian *et al.* (2021); Wu and Subotnik (2021)). An important role is played by diabatic bases (Smith (1969); Baer (1975); Thomp-son, Truhlar, and Mead (1985); Pacher, Cederbaum, and Köppel (1988); Cederbaum, Schirmer, and Meyer (1989); and Pacher *et al.* (1989); Pacher, Cederbaum, and Köppel (1993); Atchity and Ruedenberg (1997); Matsunaga and Yarkony (1998); Thiel and Köppel (1999); Yarkony (1999, 2000); Abrol and Kuppermann (2002); Köppel (2004); Subotnik *et al.* (2008, 2009); Richings and Worth (2015); Zhu and Yarkony (2015); Venghaus and Eisfeld (2016); Wang, Guan, and Yarkony (2019); Richings and Habershon (2020); Littlejohn, Rawlinson, and Subot-nik (2022)). Extensive attention is devoted to the derivative couplings, which are the components of a Mead-Truhlar-Berry vector potential or connection, part of one of the two gauge theories that appear in molecular Born-Oppenheimer theory (Mead and Truhlar (1979); Mead (1980b); Berry (1984); Moody, Shapere, and Wilczek (1989); Bohm, Boya, and Kendrick (1991); and Bohm *et al.* (1992); Bohm, Kendrick, and Loewe (1992); Mead (1992); Kendrick and Mead (1995);

Kendrick, Mead, and Truhlar (2002); Child (2002); Kendrick (2004); Juanes-Marcos, Althorpe, and Wrede (2005); Althorpe (2006, 2012); Wittig (2012); Choi and Vaniček (2021)). Finally, we treat electron dynamics both in the electrostatic model and also when fine structure and electron spin are important (Mead (1980a, 1987); Yarkony (1992); Koizumi and Sugano (1995); Schön and Köppel (1998); and Matsika and Yarkony (2001, 2002b,a); Wu, Miao, and Subotnik (2020); Sadovskii and Zhilinskii (2022)).

Our analysis requires a careful treatment of the phase and frame conventions of the electronic basis states, both adiabatic and diabatic. We emphasize that the Born-Oppenheimer treatment is not well defined without phase conventions. This analysis takes place within a context that provides geometrical interpretations of our procedures and of the resulting formulas, and that involves geometrical structures in the nuclear configuration space. These include the rotational orbits or fibers, which are the surfaces upon which the orientation of the molecule changes but not its shape, and the section, a kind of initial-value surface that cuts transversally through the fibers. We use rotation operators for assigning phase and frame conventions when moving along the rotational fibers, and other algorithms when moving transversally (along the section). This distinction has appeared between the lines in existing literature but it has not been addressed explicitly, as far as we know, nor has the geometrical context been brought to light.

In the case of fine-structure models with an odd number of electrons, the method of assigning phase and frame conventions by means of rotation operators must be modified, in that an extra spin rotation, applied to the two elements of a Kramers doublet (what we call "pseudo-spin"), is necessary to create a single-valued set of basis states. This observation seems to be new, and it has an important impact down the line on the form of the Born-Oppenheimer Hamiltonian and of the angular momentum. The basic idea is this. If a molecule with an odd number of electrons is subjected to a rigid rotation about some axis by 360°, then the spatial part of the electronic eigenfunctions returns to itself but the spin part suffers a change in sign. Therefore assigning phase conventions purely by rotation operators introduces a discontinuity in the basis states. The situation bears some similarity to the -1 phase shift that real electronic eigenfunctions suffer in the electrostatic model when being continuously carried around a conical intersection. In that case, Mead and Truhlar (1979) suggested introducing a complex phase factor (a $U(1)$ rotation) to smooth out the discontinuity. Similarly, in our case, we suggest introducing an extra spin rotation to remove the discontinuity encountered when rotating the molecule by 360°.

The establishment of phase and frame conventions leads to the derivation of a number of transformation laws of objects under rotations, including the electronic Hamiltonian, its matrix elements, the basis states and the derivative couplings. We have done this in several different models of the electronic Hamiltonian. The resulting explicit formulas seem to be mostly new, although some of them are quite clear intuitively and Yarkony (2001) has derived some closely related re-sults in the case of nondegenerate, adiabatic basis states. Nevertheless, the careful derivation of these results involves some subtleties, for example, some of the results are only valid under certain circumstances which we specify. These transformation laws are necessary to establish the relationship among the various forms of angular momentum operators. We believe our transformation laws for the derivative couplings are new; they are necessary for showing the invariance of the Born-Oppenheimer Hamiltonians (in their various versions) under rotations.

In this article we wish to accommodate large amplitude motions, that is, ones in which the nuclear displacements are of the order of an atomic unit or larger. Such motions occur in isomerization, photoexcitation, scattering and other processes that are of current interest. Therefore we require an understanding of angular momentum and its conservation that allows such motions and that is not dependent on small-amplitude expansions about an equilibrium position.

Although the results presented below are most directly related to the determination of stationary states, many of the lessons derived have implications for time-dependent quantum mechanical simulations as well. There are also semiclassical implications with regards to surface hopping calculations, as will be described in Sec. VIII.

In this article we do not consider the construction of kinetic energy operators in internal or shape coordinates, but several of our results, such as the treatment of phase conventions of electronic ba-sis states by means of rotation operators, the transformation laws of the derivative couplings under rotations, and the derivation of the rotational components of the derivative couplings, are necessary preliminaries for the construction of such operators when multiple surfaces, geometric phases, and/or fine structure are important. The subject of kinetic energy operators is a large one; we just mention Wang and Tucker Carrington (2000); Kendrick (2018), of which the latter reference is notable for its treatment of multiple potential energy surfaces in scattering calculations.

In this article for simplicity we ignore nuclear spin, effectively treating the nuclei as spinless, distinguishable particles.

We turn now to an outline of the paper. The purpose of Sec. II is to place some of the questions raised by this paper into a simple context, as a way of making a hopefully painless introduction to the subject before treating it in all generality. In addition, Sec. II establishes terminology and notation.

Section II treats a polyatomic molecule in the electrostatic model for which motion on a single potential energy surface is a good approximation. There are two descriptions of the dynamics, one, the "molecular," which explicitly incorporates the interactions of all the charged particles, electrons and nuclei; and the other, the "Born-Oppenheimer," in which the electron dynamics is incorporated into the potential energy function. The Hamiltonian in the molecular representation commutes with the total orbital angular momentum of the molecule, nuclear plus electronic, what we write as $\mathrm{L}_n + \mathrm{L}_e$, while the Hamiltonian in the Born-Oppenheimer representation commutes with the nuclear orbital angular momentum L_n alone. These two conservation laws are presumably equivalent somehow, but we may ask whether this equivalence is exact or only valid to some order in the Born-Oppenheimer ordering parameter $\kappa = (m/M)^{1/4}$ (Born and Oppenheimer (1927)). In addition there is the question of the correlation between angular momentum quantum numbers in the two representations.

Section II presents an overview of the answers to these questions, first in the electrostatic model and then generalizing to models that include fine structure and electron spin. Finally, Sec. II presents an overview of the dressing transformation that block-diagonalizes the Born-Oppenheimer Hamiltonian, and its effect on angular momentum operators.

After this overview the paper presents a more detailed and rigorous analysis of questions surrounding angular momentum in Born-Oppenheimer theory. Although the problems addressed in Sec. II concern motion on a single surface, the rest of the paper, starting with Sec. III, treats multiple, strongly interacting surfaces; naturally, single-surface problems are covered as a special case. Multi-surface problems require that diabatic bases be incorporated into the discussion of basis states.

Sections III–V deal with the electrostatic model, presenting results that are later generalized to various fine-structure models. Section III treats phase and frame conventions for the electronic basis states, a necessary topic since the form of operators in the Born-Oppenheimer representation depends on these conventions. The subject of phase and frame conventions is not as well developed in the literature as it might be, perhaps because in simple (single-surface, electrostatic) problems the choice of a phase for the one electronic eigenstate of interest can be reduced to a ± sign, which seems trivial. It is not, actually, even in this case, but when degeneracies, multiple surfaces, diabatic bases and spin are taken into account, phase and frame conventions become a more serious matter.

In Sec. IV, continuing with the electrostatic model, we consider the transformation properties of the basis states under rotations. The basis states can be either adiabatic or diabatic. This leads to a collection of transformation laws under rotations, including (47) for the electronic Hamiltonian, (56) for the basis states and (70) for the derivative couplings. An important consequence of these is (62), which says that the electronic basis functions, with our phase conventions, are invariant under simultaneous rotations of the electronic and nuclear coordinates. In the context of nondegenerate, adiabatic basis states this formula is only a small step away from the results of Yarkony (2001), but the formula is notable for its simplicity and in our treatment it incorporates degeneracies and diabatic bases (and later it is generalized to include spin). This formula is consequential, being important in the establishment of the equivalence of various representations of the angular momentum.

In Sec. V we provide careful definitions of what we call the "molecular representation" and the "Born-Oppenheimer representation" of molecular dynamics, which have been mentioned previously. We discuss the invertible mapping between these two and the corresponding map between linear operators in the two representations. Several operators are considered, including the Hamiltonian and the angular momentum. As far as the latter is concerned, we are able to show, using (62), that $\mathrm{L}_n + \mathrm{L}_e$ in the molecular representation is exactly equivalent to L_n alone in the Born-Oppenheimer representation, that is, in the Born-Oppenheimer representation, the operator that looks like the nuclear orbital angular momentum actually includes the electronic orbital angular momentum.

In Sec. VI we cover the same territory as in Sections III–V but with the fine-structure model for the electronic Hamiltonian. The cases of even and odd numbers of electrons are treated sepa-rately. The case of an even number of electrons is broadly similar to the electrostatic model, with some notable differences such as the fact that the nominal, nuclear orbital angular momentum L_n in the Born-Oppenheimer representation now includes, from a physical standpoint, not only the electronic orbital angular momentum but also the electron spin. The case of an odd number of electrons presents many new features, such as the extra spin rotation required in the phase conventions for the basis states (see (116)) in order to make the basis single-valued.

In Sec. VII we provide a more detailed treatment of the dressing transformation that removes off-block-diagonal terms in the Born-Oppenheimer Hamiltonian. A principal conclusion is that the dressing transformation does not change the form of angular momentum operators. This holds to all orders of the Born-Oppenheimer perturbation parameter κ.

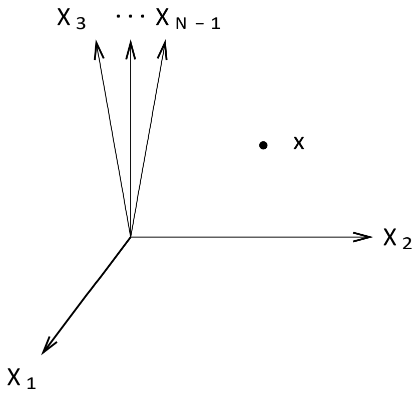

FIG. 1. The nuclear configuration space in the center-of-mass frame is R^{3N-3}, where N is the number of nuclei. This space is indicated schematically by the axes labeled X_α, $\alpha = 1,\dots,N-1$. The notation x stands for a point of configuration space, or, equivalently, the coordinates $(\mathrm{X}_1,\dots,\mathrm{X}_{N-1})$ of that point.

Finally, in Sec. VIII, we present some conclusions.

II. OVERVIEW OF MAIN RESULTS IN A SIMPLE CONTEXT

In this section we discuss the equivalence of different angular momentum operators in a simple context, in order to highlight the issues before getting into a detailed or general analysis. We also establish some notation.

A. Nuclear Configuration Space

We assume our molecule has $N \geq 3$ nuclei. To describe the configuration of the nuclei in the center-of-mass frame we require $N-1$ translationally invariant vectors, X_α, $\alpha = 1,\dots,N-1$, the components of which are coordinates on the nuclear configuration space. Each component ranges from $-\infty$ to $+\infty$, so the nuclear configuration space is R^{3N-3}. This is the parameter space for the electronic Hamiltonian; it is topologically trivial. For brevity we denote the nuclear coordinates collectively by x, so that

$$x = (\mathrm{X}_1,\dots,\mathrm{X}_{N-1}). \tag{1}$$

We also use the symbol x to stand geometrically for a point of the nuclear configuration space, as illustrated in Fig. 1.

We choose the vectors X_α to be Jacobi vectors (Delves (1960); Aquilanti and Cavalli (1986);

Gatti *et al.* (1998)), which cause the nuclear kinetic energy K_n to be diagonal,

$$K_n = \sum_{\alpha=1}^{N-1} \frac{\mathrm{P}_\alpha^2}{2M_\alpha}, \tag{2}$$

where P_α, $\alpha = 1, \ldots, N-1$ are the momenta conjugate to Jacobi vectors X_α, and where the $M_\alpha > 0$ are reduced nuclear masses.

B. Molecular and Electronic Hamiltonians

We write the Hamiltonian for the molecule as

$$H_{\mathrm{mol}} = \sum_{\alpha=1}^{N-1} \frac{\mathrm{P}_\alpha^2}{2M_\alpha} + H_e(x; \mathrm{r}, \mathrm{p}, \mathrm{S}), \tag{3}$$

where $H_e = H_e(x) = H_e(x; \mathrm{r}, \mathrm{p}, \mathrm{S})$ is the electronic Hamiltonian and where $\mathrm{r} = (\mathrm{r}_1, \ldots, \mathrm{r}_{N_e})$, $\mathrm{p} = (\mathrm{p}_1, \ldots, \mathrm{p}_{N_e})$, and $\mathrm{S} = (\mathrm{S}_1, \ldots, \mathrm{S}_{N_e})$ are the electron positions, momenta and spins, respectively. Here N_e is the number of electrons, the electron positions r_i, $i = 1, \ldots, N_e$, are measured relative to the nuclear center of mass, and the electron momenta p_i are conjugate to the positions r_i. The parametric dependence of the electronic Hamiltonian on the nuclear configuration x is set off by a semicolon from the electronic operators $(\mathrm{r}, \mathrm{p}, \mathrm{S})$ upon which it depends.

The molecular Hamiltonian H_{mol} depends on both nuclear and electronic operators,

$$H_{\mathrm{mol}} = H_{\mathrm{mol}}(\mathrm{X}, \mathrm{P}, \mathrm{r}, \mathrm{p}, \mathrm{S}), \tag{4}$$

where $\mathrm{X} = (\mathrm{X}_1, \ldots, \mathrm{X}_{N-1})$ and $\mathrm{P} = (\mathrm{P}_1, \ldots, \mathrm{P}_{N-1})$. The notation X is essentially the same as x, the only difference being one of emphasis (X being used for the Jacobi vectors upon which H_{mol} or a wave function depends, while x stands either for those vectors or a point of nuclear configuration space).

C. Models of the Electronic Hamiltonian

We consider the electronic Hamiltonian in various models. The most basic is the electrostatic, for which the electronic Hamiltonian is

$$H_e(x; \mathrm{r}, \mathrm{p}) = \sum_{i=1}^{N_e} \frac{\mathrm{p}_i^2}{2m_e} + \sum_{i,j=1}^{N_e} \frac{\mathrm{p}_i \cdot \mathrm{p}_j}{2M_n} + V_{\mathrm{Coul}}(\mathrm{X}, \mathrm{r}), \tag{5}$$

where m_e is the electron mass, M_n is the total nuclear mass and where the potential V_{Coul} contains all the Coulomb interactions among all the particles (electrons and nuclei). The second major term is the mass-polarization term, which is due to the fact that the nuclear center of mass, to which the electron coordinates r_i are referred, is not fixed in an inertial frame. In the electrostatic model the electronic Hamiltonian $H_e = H_e(x;\mathrm{r},\mathrm{p})$ is independent of the electron spin, and so can be regarded as an operator acting on the space of purely spatial electronic wave functions $\phi(\mathrm{r})$, that is, with no dependence on spin quantum numbers m.

Other models are obtained by adding fine structure terms to (5) (Bethe and Salpeter (1957); Howard and Moss (1970); Yarkony (1992); Hess and Marian (2000)). In the resulting fine structure models the electronic Hamiltonian $H_e = H_e(x;\mathrm{r},\mathrm{p},\mathrm{S})$ does depend on the spin and the electronic wave function $\phi(\mathrm{r},m)$ depends on the electron spin quantum numbers,

$$m = (m_1,\ldots,m_{N_e}), \tag{6}$$

where $m_i = \pm 1/2$, $i = 1,\ldots,N_e$. There is some latitude in how relativistic corrections are treated, but in fact the only assumptions we shall make about the fine structure model are the symmetries of the electronic Hamiltonian, which apply in all cases.

In the following we use the symbol ϕ for a purely electronic wave function (that is, $\phi(\mathrm{r})$ in the electrostatic model or $\phi(\mathrm{r},m)$ if electron spin is included); ψ for a purely nuclear wave function (that is, $\psi(\mathrm{X})$); and Ψ for a molecular wave function (that is, $\Psi(\mathrm{X},\mathrm{r})$ in the electrostatic model or $\Psi(\mathrm{X},\mathrm{r},m)$ if electron spin is included).

D. Two Conservation Laws

We now pose a set of questions regarding angular momentum conservation in Born-Oppenheimer theory. For simplicity we do this initially in the electrostatic model, generalizing later (in Sec. II G) to the fine structure model. Also, for simplicity, we present our questions in the context of motion on a single potential energy surface, generalizing later (starting in Sec. III) to multisurface problems.

Suppose we wish to find energy eigenfunctions for the whole molecule, that is, wave functions $\Psi(\mathrm{X},\mathrm{r})$ such that

$$H_{\mathrm{mol}}(\mathrm{X},\mathrm{P},\mathrm{r},\mathrm{p})\Psi(\mathrm{X},\mathrm{r}) = E\,\Psi(\mathrm{X},\mathrm{r}), \tag{7}$$

either bound or unbound (see, for example, Cafiero and Adamowicz (2004)). The molecular

Hamiltonian in the electrostatic model (5) commutes with the total orbital angular momentum of the molecule,

$$\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e = \sum_{\alpha=1}^{N-1} \mathrm{X}_\alpha \times \mathrm{P}_\alpha + \sum_{i=1}^{N_e} \mathrm{r}_i \times \mathrm{p}_i, \tag{8}$$

which we have broken into the nuclear and electronic contributions. It does not commute with L_n or L_e separately. Therefore it is possible to organize the energy eigenfunctions (by forming linear combinations of degenerate energy eigenfunctions, if necessary) to be also eigenfunctions of the operators L^2 and L_z.

Instead of (7) one often solves the Born-Oppenheimer version of the Schrödinger equation,

$$H_{\mathrm{BO}}(\mathrm{X}, \mathrm{P})\psi(\mathrm{X}) = E\,\psi(\mathrm{X}), \tag{9}$$

where $\psi = \psi(\mathrm{X})$ is a function of the nuclear coordinates alone. The Born-Oppenheimer version of the Hamiltonian is

$$H_{\mathrm{BO}}(\mathrm{X}, \mathrm{P}) = \sum_{\alpha=1}^{N-1} \frac{\mathrm{P}_\alpha^2}{2M_\alpha} + \varepsilon_k(\mathrm{X}), \tag{10}$$

where $\varepsilon_k(\mathrm{X}) = \varepsilon_k(x)$ is the k-th eigenvalue of $H_e(x)$. This Hamiltonian describes motion on a single potential energy surface k; in practice this is often the ground state. The Born-Oppenheimer Hamiltonian (10) is like the molecular one (3) except that the electronic Hamiltonian $H_e(x)$ has been replaced by one of its eigenvalues $\varepsilon_k(x)$.

The Born-Oppenheimer Hamiltonian (10) commutes with the nuclear orbital angular momentum,

$$\mathrm{L}_n = \sum_{\alpha=1}^{N-1} \mathrm{X}_\alpha \times \mathrm{P}_\alpha, \tag{11}$$

because the electronic eigenvalues are invariant under rotations,

$$\varepsilon_k(x) = \varepsilon_k(Rx), \qquad \forall R \in SO(3), \tag{12}$$

where Rx indicates a rigid rotation of the nuclei about the center of mass,

$$Rx = R(\mathrm{X}_1, \ldots, \mathrm{X}_{N-1}) = (R\mathrm{X}_1, \ldots, R\mathrm{X}_{N-1}). \tag{13}$$

This is because the electronic eigenvalues do not change if the nuclei are subjected to a rigid rotation, that is, one that changes the orientation of the nuclei but not their shape.

Therefore the energy eigenfunctions $\psi(\mathrm{X})$ of (9) can be organized (by forming linear combinations of degenerate eigenfunctions, if necessary) to be simultaneous eigenfunctions of energy, L_n^2 and L_{nz}, the latter of which refer to the nuclear orbital angular momentum L_n.

E. Questions About the Two Conservation Laws

Thus it would appear that the Born-Oppenheimer approximation has replaced one exact conservation law (that of $\mathbf{L} = \mathbf{L}_n + \mathbf{L}_e$) with another (that of just $\mathbf{L}_n$). This leads us to ask, are these conservation laws just approximate versions of one another, or are they somehow exactly equivalent? And how does this come about in detail? There is also the question of the physical interpretation of the solutions of the Born-Oppenheimer equation (9). If we find such a solution $\psi(\mathbf{X})$ that is an eigenfunction of energy, L_n^2 and L_{nz} with quantum numbers (E, l, m_l), then presumably (as is standard in Born-Oppenheimer theory) the corresponding solution of (7) will be approximately

$$\Psi(\mathbf{X}, \mathbf{r}) = \psi(\mathbf{X})\phi_k(\mathbf{X}; \mathbf{r}), \tag{14}$$

where $\phi_k(\mathbf{X}; \mathbf{r})$ is the k-th energy eigenfunction of the electronic Hamiltonian $H_e(x)$. Is this Ψ then an eigenfunction of L^2 and L_z (which refer to the total orbital angular momentum, $\mathbf{L} = \mathbf{L}_n + \mathbf{L}_e$)? If so, is it exactly so or only to some order of the Born-Oppenheimer expansion? And are the angular momentum quantum numbers of the solution $\Psi(\mathbf{X}, \mathbf{r})$ the same as those of $\psi(\mathbf{X})$, what we have called (l, m_l), even though the operators appear to be different?

Finally, how do the answers to these questions change when fine structure effects are included or when multiple potential energy surfaces are strongly coupled?

F. Overview of Some Answers in the Electrostatic Model

It is convenient to introduce ket language for the eigenfunctions $\phi_k(\mathbf{X}; \mathbf{r})$ of the electronic Hamiltonian $H_e(x)$ in the electrostatic model. We denote these eigenkets by $|x; k\rangle$, so that

$$H_e(x)\,|x; k\rangle = \varepsilon_k(x)\,|x; k\rangle, \tag{15}$$

and so that the relation between the kets and wave functions is given by

$$\phi_k(\mathbf{X}; \mathbf{r}) = \langle \mathbf{r}|x; k\rangle. \tag{16}$$

We must also address the derivative couplings, which are defined by

$$\mathrm{F}_{\alpha;kl}(x) = \langle x; k|\partial_\alpha|x; l\rangle, \tag{17}$$

where $\partial_\alpha = \partial/\partial X_\alpha$. If we write simply $\mathrm{F}_\alpha(x)$, we refer to the infinite-dimensional matrix (really a 3-vector of matrices for each value of α) whose kl-th component is $\mathrm{F}_{\alpha;kl}(x)$. It follows from the orthonormality of the basis, $\langle x;k|x;l\rangle = \delta_{kl}$, that the matrix F_α is anti-Hermitian,

$$\mathrm{F}_{\alpha;kl} = -\mathrm{F}^*_{\alpha;lk}. \tag{18}$$

The questions posed can only be answered relative to the phase conventions for the electronic eigenstates $|x;k\rangle$. In the electrostatic model we will require that the energy eigenfunctions $\phi_k(\mathrm{X};\mathrm{r})$ be real, that is, invariant under time reversal. This reduces the phase convention to a choice of a ± sign, a subject that we address more carefully in Sec. III. The reality of the basis functions means that the derivative couplings $\mathrm{F}_{\alpha;kl}$ are real, which, combined with (18), implies that the matrix F_α is real and antisymmetric. This in turn implies that the derivative couplings vanish on the diagonal, $\mathrm{F}_{\alpha;kk} = 0$, which is why those couplings do not appear in our single-surface, Born-Oppenheimer version (10) of the Hamiltonian.

To answer one of our questions in the electrostatic model, it turns out that the two conservation laws are exactly equivalent to one another. We can state the matter by recalling that in quantum mechanics, physical observables are represented by linear operators, but the linear operator representing a given physical observable depends on the representation of the quantum states. If the physical observable is the total orbital angular momentum of the molecule, nuclear plus electronic, then, when acting on molecular wave functions $\Psi(\mathrm{X},\mathrm{r})$, the linear operator is $\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e$, as in (8). But when acting on wave functions $\psi(\mathrm{X})$ in the Born-Oppenheimer representation, the same physical observable is represented by L_n alone. Thus, what appears to be the nuclear orbital angular momentum, when acting on $\psi(\mathrm{X})$, actually includes physically the electronic orbital angular momentum. We emphasize that this is exact.

To answer another of our questions, suppose that $\psi(\mathrm{X})$ is a solution of (9), a simultaneous eigenfunction of $(H_{\mathrm{BO}}, L_n^2, L_{nz})$ with quantum numbers (E, l, m_l). Also, let $\Psi(\mathrm{X},\mathrm{r})$ be defined by (14). Then it turns out that Ψ is automatically an eigenfunction of (L^2, L_z) with the same quantum numbers (l, m_l); and this is exact. (It is, however, only approximately an eigenfunction of the molecular Hamiltonian H_{mol}.)

One may wonder how we can claim something is exact when the Born-Oppenheimer approximation is only an approximation. The brief answer is that the Born-Oppenheimer approximation approximates the Hamiltonian but not the angular momentum. A more sophisticated point of view, in which the Born-Oppenheimer approximation is replaced by a sequence of unitary transformations, will be discussed in Sec. II H and in greater detail in Sec. VII.

G. Answers in the Fine Structure Model

When fine structure effects are included these results generalize in interesting ways. Time reversal plays an important role in this case (see, for example, Mead (1979)). Time reversal T is an antiunitary operator that acts on electronic wave functions $\phi(\mathrm{r}, m)$ according to (A2) or (A4). It commutes with the electronic Hamiltonian,

$$T^{\dagger} H_e(x) T = H_e(x), \tag{19}$$

since our molecule is isolated and not interacting with external fields. The properties of time reversal that we will need are summarized in Appendix A.

In the fine structure model the electronic and molecular Hamiltonians depend on electron spin S, and the molecular Schrödinger equation (7) of the electrostatic model must be replaced by

$$H_{\mathrm{mol}}(\mathrm{X}, \mathrm{P}, \mathrm{r}, \mathrm{p}, \mathrm{S})\, \Psi(\mathrm{X}, \mathrm{r}, m) = E\, \Psi(\mathrm{X}, \mathrm{r}, m), \tag{20}$$

where now the molecular wave function $\Psi(\mathrm{X}, \mathrm{r}, m)$ depends on the electron spin quantum numbers m. The molecular Hamiltonian no longer commutes with L but it does commute with the total angular momentum of the molecule,

$$\mathrm{J} = \mathrm{L} + \mathrm{S} = \mathrm{L}_n + \mathrm{L}_e + \mathrm{S} = \sum_{\alpha=1}^{N-1} \mathrm{X}_\alpha \times \mathrm{P}_\alpha + \sum_{i=1}^{N_e} \mathrm{r}_i \times \mathrm{p}_i + \sum_{i=1}^{N_e} \mathrm{S}_i, \tag{21}$$

that is, including the electron spin. This is one exact conservation law in the case of the fine structure model. Now energy eigenfunctions of the molecule, $\Psi(\mathrm{X}, \mathrm{r}, m)$, solutions of (20), can be organized to be also eigenfunctions of J^2 and J_z.

1. Even Number of Electrons

We treat first the case of an even number of electrons. We denote the electronic energy eigenstates in ket language as $|x;k\rangle$, as in the electrostatic model, so that (15) is still valid, but the electronic eigenfunctions (16) must be replaced by

$$\phi_k(\mathrm{X}; \mathrm{r}, m) = \langle \mathrm{r}, m | x; k \rangle, \tag{22}$$

that is, with an m-dependence. We choose the eigenstates $|x;k\rangle$ to be invariant under time reversal,

$$T|x;k\rangle = |x;k\rangle \tag{23}$$

(see Sec. A 2 for a proof that this can be done). In the case of a nondegenerate energy level this is a matter of a phase convention, which is determined to within a ± sign, as in the electrostatic model. For a single-surface problem, as here, the relevant level is nondegenerate.

The condition (23) is enough to make the derivative couplings vanish on the diagonal, as in the electrostatic model, so the Born-Oppenheimer Hamiltonian is still given by (10), that is, with no derivative couplings. The only difference is that the electronic eigenvalue $\epsilon_k(x)$ now includes fine structure contributions. This Hamiltonian still commutes with L_n, the nominal, nuclear orbital angular momentum (see (11)). Also, the Born-Oppenheimer wave function is still $\psi(\mathrm{X})$.

Now the operator representing the total angular momentum of the molecule, nuclear orbital, electronic orbital, and electronic spin, when acting on molecular wave functions $\Psi(\mathrm{X},\mathrm{r},m)$, is J, given by (21); while the operator representing the same physical observable, when acting on Born-Oppenheimer wave functions $\psi(\mathrm{X})$, is L_n alone, given by (11); and this is exact. In other words, L_n, when acting on Born-Oppenheimer wave functions $\psi(\mathrm{X})$ in the fine structure model with N_e = even, includes physically the electronic angular momentum, both orbital and spin.

In addition, suppose we solve the Born-Oppenheimer version of the Schrödinger equation (9) for a wave function $\psi(\mathrm{X})$ that is a simultaneous eigenfunction of energy, L_n^2 and L_{nz} with quantum numbers (E,l,m_l), and then we define a molecular wave function by

$$\Psi(\mathrm{X},\mathrm{r},m) = \psi(\mathrm{X})\phi_k(\mathrm{X};\mathrm{r},m), \tag{24}$$

a generalization of (14), where k is the surface in question. Then $\Psi(\mathrm{X},\mathrm{r},m)$ is exactly an eigenfunction of J^2 and J_z with the same quantum numbers (l,m_l), and approximately an eigenfunction of energy. Notice that with an even number of electrons the quantum number of J^2 must be an integer, as is the quantum number l of the nuclear orbital angular momentum L_n^2 (otherwise our statements would not make sense).

2. Odd Number of Electrons

In the fine structure model with an odd number of electrons the electronic energy eigenstates are Kramers doublets (Messiah (1966)), that is, they come in pairs $|x;k\mu\rangle$, $\mu = 1,2$, such that

$$H_e(x)|x;k\mu\rangle = \epsilon_k(x)|x;k\mu\rangle, \tag{25}$$

in which the energy $\epsilon_k(x)$ does not depend on μ. We shall think of a Kramers doublet as corresponding to a single potential energy surface, so that k labels the surfaces and each surface corresponds to two degenerate levels. For now for simplicity we treat the problem of a single surface. This is realistic, for example, when fine structure effects are added to a system in a spin doublet state.

Since $H_e(x)$ commutes with time reversal it is possible to choose the eigenstates $|x;k\mu\rangle$ so that $T|x;k1\rangle = |x;k2\rangle$, $T|x;k2\rangle = -|x;k1\rangle$, or, equivalently,

$$T|x;k\mu\rangle = \sum_\nu |x;k\nu\rangle\tau_{\nu\mu}, \tag{26}$$

where τ is given by (A3), as we shall do. Such a basis is said to be *quaternionic* (see Sec. A 3 a). To say that the basis is quaternionic only determines that basis to within an $SU(2)$ transformation (Mead (1987)). We choose the basis so that it transforms under rotations according to (116).

The electronic energy eigenfunction corresponding to $|x;k\mu\rangle$ now has a double index,

$$\phi_{k\mu}(\mathrm{X};\mathrm{r},m) = \langle\mathrm{r},m|x;k\mu\rangle, \tag{27}$$

which replaces (22). The Born-Oppenheimer wave function $\psi_{k\mu}(\mathrm{X})$ carries the same double index, and the molecular wave function is given by

$$\Psi(\mathrm{X},\mathrm{r},m) = \sum_\mu \psi_{k\mu}(\mathrm{X})\,\phi_{k\mu}(\mathrm{X};\mathrm{r},m), \tag{28}$$

that is, with a sum over μ. There is no sum on k because we are working on a single surface.

In the fine structure model with $N_e =$ odd the Born-Oppenheimer Hamiltonian contains derivative couplings, even for a single surface, because there is always more than one level (two, for a single surface). Now the derivative couplings also carry doubled indices,

$$\mathrm{F}_{\alpha;k\mu,l\nu}(x) = \langle x;k\mu|\partial_\alpha|x;l\nu\rangle, \tag{29}$$

which we can break up into minor, 2 × 2 matrices as in Sec. A 3 a. That is, in the context of an odd number of electrons, when we write $\mathrm{F}_{\alpha;kl}$ we mean the minor (2×2) matrix whose $(\mu\nu)$ component is $\mathrm{F}_{\alpha;k\mu,l\nu}$. Because of the orthonormality relations, $\langle x;k\mu|x;l\nu\rangle = \delta_{kl}\,\delta_{\mu\nu}$, the derivative couplings satisfy

$$\mathrm{F}_{\alpha;k\mu,l\nu} = -\mathrm{F}^{*}_{\alpha;l\nu;k\mu}, \tag{30}$$

a generalization of (18), which in the language of minor matrices becomes

$$\mathrm{F}_{\alpha;kl} = -(\mathrm{F}_{\alpha;lk})^\dagger. \tag{31}$$

As for the Born-Oppenheimer Hamiltonian, a standard way of deriving it is to project the molecular Hamiltonian onto a subspace of chosen energy levels (Yarkony (1996); Cederbaum (2004)), which in this case is the subspace spanned by $|x;k\mu\rangle$ for fixed k and $\mu = 1,2$. Doing this we obtain the Born-Oppenheimer version of the Schrödinger equation,

$$\sum_{\nu=1}^{2}\left[\sum_{\alpha=1}^{N-1}\frac{1}{2M_\alpha}\left(\mathrm{P}_\alpha^2\,\delta_{\mu\nu} - 2i\hbar\mathrm{F}_{\alpha;k\mu,k\nu}\cdot\mathrm{P}_\alpha - \hbar^2 G_{\alpha;k\mu,k\nu}\right) + \epsilon_k(\mathrm{X})\,\delta_{\mu\nu}\right]\psi_{k\nu}(\mathrm{X}) = E\,\psi_{k\mu}(\mathrm{X}), \tag{32}$$

which replaces (9) and (10) in the electrostatic model. Here we define

$$G_{\alpha;k\mu,l\nu} = \langle x;k\mu|\nabla_\alpha^2|x;l\nu\rangle, \tag{33}$$

which gives us minor matrices $G_{\alpha;kl}$ (and note that only the diagonal elements $k = l$ of F and G appear in the Hamiltonian in (32)). This notation is close to that used by Cederbaum (2004) in the electrostatic model.

Since the operators ∇_α and ∇_α^2 commute with T, the minor matrices $\mathrm{F}_{\alpha;kl}$ and $G_{\alpha;kl}$ are quaternions (see (A18); ∇_α and ∇_α^2 are not linear operators in the usual sense but the proof goes through just the same). In the language of quaternions (31) becomes

$$\mathrm{F}_{\alpha;kl} = -\overline{\mathrm{F}_{\alpha;lk}}. \tag{34}$$

For our single-surface problem we need only the diagonal elements ($k = l$) of the derivative couplings, which satisfy $\mathrm{F}_{\alpha;kk} = -\overline{\mathrm{F}_{\alpha;kk}}$, that is, they are quaternions whose real part (the a-part of (B1)) vanishes. We see that the derivative couplings for a single surface in the case of an odd number of electrons can be written as a purely imaginary, linear combination of the Pauli matrices (see also Mead (1987)).

We write the i-th component of F_α, for $i = 1,2,3$, as $F_{i\alpha}$, and then define coefficients $A_{ji\alpha;kk}$ by

$$F_{i\alpha;kk} = -\frac{i}{2}\sum_{j=1}^{3}\sigma_j\,A_{ji\alpha;kk}, \tag{35}$$

where σ_j are the Pauli matrices. In this formula we have split off a factor of $-i$ as in the b-part of (B1), which makes the coefficients $A_{ji\alpha;kk}$ real, and introduced a factor of 1/2 for convenience.

The Born-Oppenheimer wave function $\psi_{k\mu}$ for fixed k and $\mu = 1,2$ looks like the wave function of a pseudo-particle with spin 1/2, moving on a multidimensional potential energy surface given by $\epsilon_k(x)$. We define the pseudo-spin operator,

$$\mathrm{K} = \frac{\hbar}{2}\sigma, \tag{36}$$

so that the Born-Oppenheimer Hamiltonian can be written as

$$H_{\mathrm{BO}} = \sum_{\alpha=1}^{N-1} \frac{1}{2M_\alpha}\left(\mathrm{P}_\alpha^2 - 2\mathrm{K}\cdot \mathsf{A}_{\alpha;kk}\cdot \mathrm{P}_\alpha - \hbar^2 G_{\alpha;kk}\right) + \varepsilon_k(\mathrm{X}), \tag{37}$$

where $\mathsf{A}_{\alpha;kk}$ is a real, 3×3 tensor whose ji-component is $A_{ji\alpha;kk}$. This is written in the style common with the Pauli equation, in which all operators are understood to be 2×2 matrices, and scalars are understood to be multiplied by the unit matrix.

Now we can state the main result. The total, physical angular momentum of the molecule, nuclear orbital, electronic orbital plus electronic spin, is represented by the operator J (see (21)) when acting on molecular wave functions $\Psi(\mathrm{X}, \mathrm{r}, m)$; and it is represented by I, defined by

$$\mathrm{I} = \mathrm{L}_n + \mathrm{K}, \tag{38}$$

when acting on Born-Oppenheimer wave functions $\psi_{k\mu}(\mathrm{X})$. The latter is the nominal, nuclear orbital angular momentum plus the pseudo-spin; and this result is exact.

The angular momentum I commutes with the Born-Oppenheimer Hamiltonian (37). We defer the proof of this since it involves the transformation properties of the derivative couplings under rotations, a topic that we take up in Sec. VI B 5. But it means that when we solve the Born-Oppenheimer version of the Schrödinger equation in the case of an odd number of electrons, we can organize the energy eigenfunctions to be also eigenfunctions of the operators I^2 and I_z, with (say) quantum numbers (i, m_i). If we then define a molecular wave function by (28), it turns out be an exact eigenfunction of J^2 and J_z with the same quantum numbers (i, m_i). Notice that both I and J are half-integral (otherwise our statements would not make sense).

H. Dressed Variables

In this article we are drawing a distinction between what we are calling the molecular representation of wave functions and the Born-Oppenheimer representation (for example, in the case of the electrostatic model, this means wave functions $\Psi(\mathrm{X}, \mathrm{r})$ and $\psi(\mathrm{X})$, respectively). Cederbaum (2004) has referred what we call the Born-Oppenheimer representation as a “dressed” representation. The notion of dressing has been used in a different sense by Martinazzo and Burghardt (2022), in connection with electronic friction. We prefer to reserve the term “dressed” for representations that are obtained from the Born-Oppenheimer representation by a sequence of unitary transformations, the purpose of which is to remove the off-diagonal terms in the molecular

Hamiltonian. These unitary transformations take the place of what is usually called the "Born-Oppenheimer approximation," which means simply neglecting those terms on the grounds that they are small.

If we take the point of view that the Born-Oppenheimer version of the Schrödinger equation (for example, (9) and (10) or (32)) is obtained, not by throwing away terms that couple the various levels, but by transforming them away, then the operators that appear in the Born-Oppenheimer Hamiltonian must be interpreted as dressed variables. In particular, the operator X_α no longer represents a Jacobi vector of the nuclei, but rather it has higher order corrections in the Born-Oppenheimer parameter κ. Another consequence is that $|\psi(\mathrm{X})|^2$ no longer represents the probability distribution of the nuclei in nuclear configuration space, not exactly, anyway, since there are higher order corrections in κ. Similar statements can be made about the electric current. Such distinctions can be important in the analysis of matrix elements involved in radiative transitions (see, for example, Mead and Moscowitz (1967); Scherrer *et al.* (2015); Schaupp and Engel (2020)).

These unitary transformations, which diagonalize the molecular Hamiltonian leaving Born-Oppenheimer Hamiltonians for the various surfaces on the diagonal, then create an infinite sequence of dressed representations, as the off-diagonal coupling terms are removed order by order. The question then arises as to what happens to our exact representations of angular momentum operators as the variables are dressed.

The answer is that nothing happens to them, for example, in the electrostatic model the total orbital angular momentum of the molecule, nuclear plus electronic, is represented in each of these dressed representations by the same linear operator L_n given by (11), and this is exact. This is because the generators of the unitary transformations that carry out the diagonalization are scalars, and commute with L_n, and therefore so do the unitary transformations themselves. The dressing of L_n just reproduces L_n. Similar statements hold in the fine structure models.

This concludes the overview of our main results. We turn now to a more detailed development.

III. PHASE AND FRAME CONVENTIONS OF ELECTRONIC BASIS STATES

Energy eigenstates are only determined to within a phase (when nondegenerate) or to within an orthonormal frame in the eigenspace (when degenerate), and these must be carefully specified as our main results depend on them. Notice that a frame in a one-dimensional space is the same as a phase, so phase and frame conventions are the same thing. Similar issues apply to other basis states (diabatic, etc.) that are not energy eigenstates. In this section we explain how phase and frame conventions are related to the geometry of orientation and shape in configuration space. We work in the electrostatic model, deferring fine structure effects until Sec. VI. For generality we treat multisurface problems, which include single surface problems as a special case.

A. Electronic Rotation Operators and the Electronic Hamiltonian

See Appendix C for basic facts about the rotation groups $SO(3)$ and $SU(2)$. Electronic orbital rotation operators, denoted $U_{eo}(R)$, are parameterized by rotations $R \in SO(3)$ and are defined by their action on electronic wave functions,

$$U_{eo}(R)\phi(\mathbf{r}) = \phi\big(R^{-1}\mathbf{r}\big), \tag{39}$$

where $R^{-1}\mathbf{r}$ means $(R^{-1}\mathbf{r}_1, \ldots, R^{-1}\mathbf{r}_{N_e})$. We also write $U_{eo}(\hat{\mathbf{n}},\theta) = U_{eo}\big(R(\hat{\mathbf{n}},\theta)\big)$ for these operators in axis-angle form. They are given in terms of their generators by

$$U_{eo}(\hat{\mathbf{n}},\theta) = \exp\Big(-\frac{i}{\hbar}\theta\,\hat{\mathbf{n}}\cdot\mathbf{L}_e\Big). \tag{40}$$

It follows from (39) that the operators $U_{eo}(R)$ form a representation of $SO(3)$,

$$U_{eo}(R_1)U_{eo}(R_2) = U_{eo}(R_1R_2). \tag{41}$$

The electrostatic, electronic Hamiltonian $H_e(x) = H_e(x;\mathbf{r},\mathbf{p})$, given by (5), is a function of the dot products of the vectors $\mathbf{X}_\alpha$, $\mathbf{r}_i$ and $\mathbf{p}_i$, and is therefore invariant if each of these is rotated by the same rotation,

$$H_e(x;\mathbf{r},\mathbf{p}) = H_e(Rx;R\mathbf{r},R\mathbf{p}), \qquad \forall R \in SO(3), \tag{42}$$

where Rx is given by (13) and where

$$R\mathbf{r} = R(\mathbf{r}_1,\ldots,\mathbf{r}_{N_e}) = (R\mathbf{r}_1,\ldots,R\mathbf{r}_{N_e}), \tag{43}$$

$$R\mathbf{p} = R(\mathbf{p}_1,\ldots,\mathbf{p}_{N_e}) = (R\mathbf{p}_1,\ldots,R\mathbf{p}_{N_e}), \tag{44}$$

Equation (42) is a statement about the functional form of the electronic Hamiltonian in the electrostatic model.

On the other hand, the electronic position and momentum operators transform under conjugation by rotations according to

$$U_{eo}(R)\,\mathbf{r}_i\,U_{eo}(R)^\dagger = R^{-1}\mathbf{r}_i, \qquad U_{eo}(R)\,\mathbf{p}_i\,U_{eo}(R)^\dagger = R^{-1}\mathbf{p}_i, \tag{45}$$

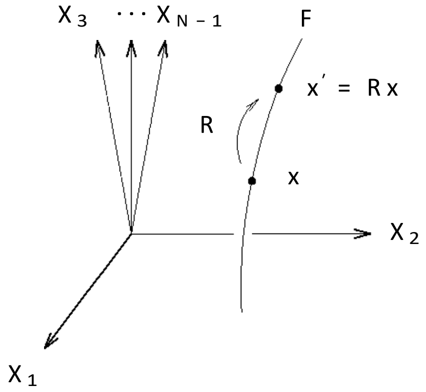

FIG. 2. A proper rotation R acts on a point x of nuclear configuration space and maps it to $x' = Rx$. The set F of all such points x' swept out as R runs over $SO(3)$ is the orbit of x under the action of $SO(3)$. If x is noncollinear, F is a fiber in the rotational fiber bundle.

which is a statement that r_i and p_i are vector operators (Messiah (1966); Varshalovich, Moskalev, and Khersonskii (1988)). Therefore

$$U_{eo}(R)\,H_e(x;\mathrm{r},\mathrm{p})\,U_{eo}(R)^\dagger = H_e\;\; x; R^{-1}\mathrm{r}, R^{-1}\mathrm{p} = H_e(Rx;\mathrm{r},\mathrm{p}), \tag{46}$$

where in the first step the conjugation does nothing to the parameters x which are just c-numbers as far as the rotation operators $U_{eo}(R)$ are concerned, and where in the second step we have multiplied all arguments by R, which according to (42) does not change the answer. Now simplifying the notation by making the replacement $H_e(x;\mathrm{r},\mathrm{p}) \to H_e(x)$, we can summarize the result by writing

$$U_{eo}(R)\,H_e(x)\,U_{eo}(R)^\dagger = H_e(Rx). \tag{47}$$

This is the transformation law for the electrostatic, electronic Hamiltonian under proper rotations.

B. Rotational Orbits and Fibers

The formula (47) has a geometrical interpretation in the nuclear configuration space, which is illustrated in Fig. 2. Given a configuration x as illustrated, the rotated configuration $x' = Rx$ is one with the same shape as x but a different orientation. Equation (47) relates the electronic Hamiltonians at the original point x and the rotated point x'.

Figure 2 calls attention to the surface F, which is the set swept out by $x' = Rx$ for fixed x as R runs over $SO(3)$. This is otherwise the *orbit* of x under the action of $SO(3)$ on the nuclear configuration space. It is the set of all configurations of the same shape as x but different orientations.

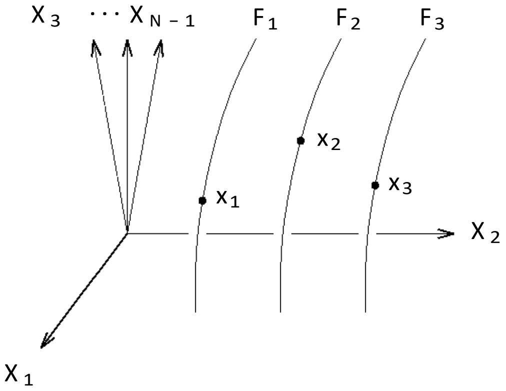

FIG. 3. The action of rotations $R \in SO(3)$ on nuclear configuration space decomposes that space into a disjoint set of orbits.

Other configurations of different shapes have their own orbits, as illustrated in Fig. 3. Two configurations x, x' belong to the same orbit if and only if there exists $R \in SO(3)$ such that $x' = Rx$. Configurations such as x_1, x_2 and x_3 in Fig. 3, which do not belong to the same orbit, have different shapes. The action of $SO(3)$ decomposes nuclear configuration space R^{3N-3} into a disjoint set of orbits, each with its own shape.

The orbits F or F_i illustrated in Figs. 2 and 3 are drawn as if they were one-dimensional, but actually their dimensionality is either 0, 2 or 3. If the configuration is the N-body collision, in which all nuclei are on top of one another, then rotations do nothing to the configuration and the orbit consists of a single point, a zero-dimensional set. If the configuration is collinear but not the N-body collision, then the orientation is specified by a unit vector along the line of collinearity and the orbit is diffeomorphic (see Appendix C) to the 2-sphere S^2, the space of such unit vectors. Finally, if the configuration is noncollinear, then the orbit is diffeomorphic to $SO(3)$ which in turn is diffeomorphic to $\mathrm{R}P^3$ (see Appendix C). This is because two noncollinear configurations of the same shape are related by a unique $R \in SO(3)$.

In polyatomic molecules most configurations are noncollinear (they form a subset of full dimensionality, that is, $3N-3$), while the collinear configurations (and the N-body collision, which we count as collinear) form a subset of measure zero. In this article we ignore the collinear configurations, and work only in regions where all configurations are noncollinear. We do this for simplicity; the collinear configurations are the setting for the Renner-Teller effect (with an extensive literature, including Perić and Peyerimhoff (2002); Jungen (2019); Gamallo, González, and Petrongolo (2021)), which is outside the scope of this article. For the same reason we restrict consideration to polyatomic molecules; all diatomics are collinear, and in some ways are more complicated than polyatomics.

Thus, in the noncollinear subset of nuclear configuration space all orbits are 3-dimensional. This subset is decomposed by rotations into a $(3N-6)$-parameter family of 3-dimensional orbits, each of which is diffeomorphic to $SO(3)$. This gives this subset the structure of a principal fiber bundle (Nakahara (2003); Frankel (1997)), in which the fibers are the rotational orbits. For the noncollinear shapes, the fibers and the rotational orbits are the same thing; in this article we shall usually refer to them as the "rotational fibers."

C. The Strongly Coupled Subspace

A pair of adjacent electronic energy levels is considered strongly coupled if the corresponding energy eigenvalues are degenerate or nearly degenerate. This statement is made more quantitative in Sec. VII. We consider a region of nuclear configuration space in which a chosen subset I of N_l adjacent energy levels,

$$I = \{k_0, \dots, k_0 + N_l - 1\}, \tag{48}$$

is not strongly coupled to levels outside of the set I, that is, level k_0 is not strongly coupled to level $k_0 - 1$ and level $k_0 + N_l - 1$ is not strongly coupled to level $k_0 + N_l$. (Note that if k_0 is the ground state, then there is no level $k_0 - 1$.) Since the energy levels are a function of the nuclear configuration x, these conditions can normally hold only over some region of the nuclear configuration space.

Levels within the set I, however, are allowed to be strongly coupled among themselves, at least somewhere in the region in question. These are the conditions that allow a theoretical treatment of the levels $k \in I$ in isolation from the levels $k \notin I$. In other words, degeneracies or near degeneracies that cross the boundaries of I are not allowed, while internal degeneracies or near degeneracies, those that take place among the levels $k \in I$, are allowed.

As a special case, in a single-surface problem, $N_l = 1$ and I contains the single level k_0. Then internal degeneracies do not occur, and the condition on the region is that k_0 is not degenerate or nearly degenerate with levels $k_0 \pm 1$.

These restrictions on the region may cause it to be topologically nontrivial, either not simply connected or noncontractible, which has implications for the existence of smooth fields of frames.

We define the strongly coupled subspace $S(x)$ as the subspace of the electronic Hilbert space spanned by energy eigenstates for $k \in I$, and we denote the complementary, orthogonal subspace by $\mathcal{S}^{\perp}(x)$.

D. The Adiabatic Basis

It is customary to call the energy eigenbasis the “adiabatic basis” but for reasons discussed in Littlejohn, Rawlinson, and Subotnik (2022) we prefer not to work with energy eigenstates for $k \notin I$. Therefore we define a set of basis states $|ax;k\rangle$ that are energy eigenstates when $k \in I$, while for $k \notin I$ we simply require the states $|ax;k\rangle$ to form a discrete, orthonormal set that spans $\mathcal{S}^{\perp}(x)$. We will call the set $\{|ax;k\rangle\}$ for all k the “adiabatic basis” (hence the a), but we must remember that these are energy eigenstates only for $k \in I$.

In addition, we require the basis states to be invariant under time-reversal, $T|ax;k\rangle = |ax;k\rangle$. In the electrostatic model, this just means that the wave functions corresponding to $|ax;k\rangle$ are real (see (A1)). The energy eigenspaces for $k \in I$ are T-invariant, as is $\mathcal{S}(x)$, the sum of such spaces, as is $\mathcal{S}^{\perp}(x)$, the orthogonal space (see Appendix A). According to Sec. A 2, this guarantees the existence of a T-invariant basis $|ax;k\rangle$. A simpler argument that works in the electrostatic model is that a real Hamiltonian has real eigenfunctions, but the argument as given generalizes to cases involving spin.

The freedom in phase and frame conventions that remains after time-reversal invariance is imposed is the following. For $k \in I$, nondegenerate energy eigenstates $|ax;k\rangle$ are determined to within a ± sign; for n-fold degeneracies inside the strongly coupled subspace the choices are labeled by elements of the orthogonal group $O(n)$; and for $k \notin I$ the choices are labeled by the infinite-dimensional orthogonal group. (Note that in the case $n = 1$, that is, the nondegenerate case, the group $O(1)$ consists of two matrices, (1) and (-1), containing the relevant ± sign.)

Some such choice can be made at each point x of nuclear configuration space, and is implied in the use of the notation $|ax;k\rangle$. We must ask whether these choices can be made in a smooth manner as x is varied, because discontinuities in the basis produce divergences in the derivative couplings, which appear in the Hamiltonian. In addition, perturbation theory generates derivatives of the basis states that must be defined and that must have magnitudes that are under control. This question can be decomposed into what happens when we vary the just the orientation, holding the shape fixed, and what happens when we vary the shape as well.

E. How Phase Conventions Depend on Orientation

Let x_0 be a noncollinear configuration and let us choose definite phase and frame conventions for the basis vectors $|ax_0;k\rangle$, which we assume are T-invariant. Thus we have the adiabatic basis $|ax_0;k\rangle$ at the one point x_0.

Now let $x = Rx_0$ for some $R \in SO(3)$, so that x has the same shape but a different orientation from x_0, and define $|b\rangle = U_{eo}(R)|ax_0;k\rangle$. We note first that since time reversal commutes with rotations, $T|b\rangle = |b\rangle$. Next, if $k \in I$, then

$$\begin{aligned} H_e(x)\,|b\rangle &= U_{eo}(R)\,H_e(x_0)\,U_{eo}(R)^\dagger\,U_{eo}(R)\,|ax_0;k\rangle \\ &= U_{eo}(R)\,\epsilon_k(x_0)\,|ax_0;k\rangle = \epsilon_k(x_0)\,|b\rangle, \end{aligned} \tag{49}$$

where in the first step we use (47). Thus, $U_{eo}(R)$ maps energy eigenstates at x_0 into those at $x = Rx_0$, without changing the eigenvalues. More generally, since $U_{eo}(R)$ is unitary, it maps orthonormal eigenbases inside eigenspaces (degenerate or not) at x_0 into other such bases at x. The fact that the eigenvalues do not change means that they are invariant under rotations, as already noted (see (12)). As for the vectors $k \notin I$, $U_{eo}(R)$ maps the orthonormal, T-invariant frame in S ⌷(x_0) into another such frame in S ⌷(x).

We can think of x_0 as an initial condition on the fiber passing through x_0. Since x_0 is noncollinear, if x lies on this fiber then there is a unique $R \in SO(3)$ such that $x = Rx_0$, and point x can be parameterized by R. This allows us to define basis vectors at x, including their phase conventions, by

$$|ax;k\rangle = U_{eo}(R)\,|ax_0;k\rangle, \tag{50}$$

where $x = Rx_0$. The arbitrarily chosen phase conventions at x_0 are propagated along the rotational fiber by means of rotation operators.

This approach does not work for collinear shapes, for which there is more than one R that maps a configuration x_0 into another one x of the same shape. Phase conventions for collinear shapes are a more complicated matter, which we do not cover in this article.

There are other ways of extending phase conventions from a given point. In the nondegenerate case a T-invariant energy eigenstate $|ax;k\rangle$ for $k \in I$ is determined to within a ± sign, a discrete choice, and the obvious way to extend the phase convention away from a given point x_0 is to demand continuity of the wave function as x is continuously varied along a path. We will call this method, "extension by continuity." It leads to the question of whether the result depends

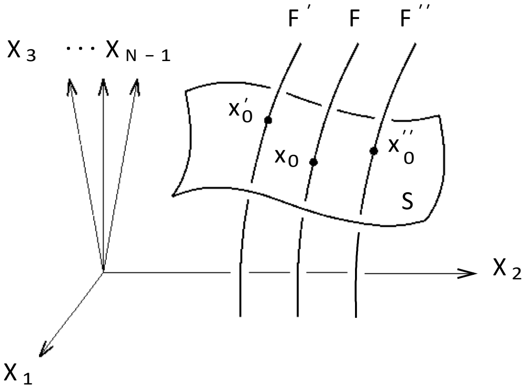

FIG. 4. Initial points x_0 over a family of rotational fibers sweep out a surface S, a section of the rotational fiber bundle.

on the path. The answer can be developed in terms of the fundamental group of the region in question (also called the first homotopy group), as explained by Juanes-Marcos, Althorpe, and Wrede (2005); Althorpe (2006, 2012). If the region is simply connected then the fundamental group is trivial and extension by continuity gives a unique answer that is a smooth function of the final position x. If it is not simply connected then the result may be path-dependent. (A region is simply connected if all loops can be smoothly contracted to a point.)

In fact, $SO(3)$ is not simply connected (its fundamental group is Z_2), so there is a question as to whether extension of phase conventions by continuity gives an answer over a rotational fiber that is path-dependent. This question is answered, however, by our formula (50). Along a noncollinear rotational fiber, for fixed x_0 and variable $x = Rx_0$, R is a smooth function of x, so (50) gives phase conventions over the fiber that are single-valued, smooth functions of x. Since they are smooth, they are the same as the conventions obtained by extension by continuity; and since they are single-valued, the latter method is path-independent.

The method of extension by continuity only works when the choices are discrete, but for degenerate eigenvalues k ⍰ I the choices are continuous, as are the choices for the orthogonal space S ⍰ (which is infinite-dimensional). Equation (50) works in all cases and gives phase and frame conventions that are smooth and single-valued over a rotational fiber.

F. How Phase Conventions Depend on Shape

Now we extend the phase conventions for the basis states to a region in which both shape and orientation are variable. We choose some region of nuclear configuration space consisting of a family of rotational fibers, as illustrated in Fig. 4, and we choose initial points x_0 on each fiber. If the assignment of the initial points x_0 is made in a smooth manner, these points sweep out a smooth surface called a *section* of the fiber bundle, which is denoted S in Fig. 4. If we can make a smooth assignment of phase and frame conventions for our basis along S, then we can use (50) to smoothly extend those conventions along the rotational fibers.

The section should have dimensionality $3N-6$ so that, taken with the 3-dimensional fibers, it covers a region of nuclear configuration space of full dimensionality $3N-3$. As we move along S the shape of the molecule changes, so coordinates on S can be taken to be shape coordinates. These are collections of $3N-6$ rotationally invariant functions of the Jacobi vectors X_α. In practice, bond lengths and angles are common choices for shape coordinates. We require that the section be transverse (not tangent) to the rotational fibers, so that first order displacements along S produce first order changes in shape (this condition makes certain Jacobian matrices well behaved).

Let us now arbitrarily choose phase and frame conventions for the basis states $|ax_0;k\rangle$ at one point x_0 on the section, as in Fig. 4, and ask if those conventions can be extended in a smooth manner to neighboring points on the section such as x'_0 and x''_0 in the figure.

For simplicity let us begin with a single surface problem, for which I contains the single, nondegenerate level k_0. Then the choice of phase convention for $|ax;k_0\rangle$ is that of a ± sign, a discrete choice, and the method of extension by continuity can be applied. This shows that it is possible to make a smooth assignment of phase conventions for the adiabatic basis vector $k = k_0$ in simply connected regions of S.

In some cases, however, the region of interest is not simply connected, as when it encircles a conical intersection. Then it turns out that the nondegenerate energy eigenstate $|ax;k_0\rangle$, when carried continuously as x encircles the conical intersection, undergoes a sign change on returning to its initial point. In this case one can break the region into subregions that are simply connected, with transition rules in the overlaps to connect them together. In practice an equivalent method is preferred, one that employs a single region with an enforced discontinuity (a change in sign) along a boundary surface. This situation is well known and well understood (Herzberg and Longuet-Higgins (1963); Longuet-Higgins (1975); Mead and Truhlar (1979); Mead (1992); Yarkony (1996); and Kuppermann and Abrol (2002); Althorpe (2006)), but the usual discussions pay no attention to the geometry of the rotational orbits and the section, or to the fact that $SO(3)$ is not simply connected.

Given an initial point x_0 on a rotational fiber, other points x on the same fiber can be parameterized by the rotation $R \in SO(3)$ such that $x = Rx_0$, or, equivalently, by the Euler angles of that rotation. Thus Euler angles become coordinates along a rotational fiber. We denote the Euler angles by θ^i, $i = 1, 2, 3$, or just θ for short. Shape or internal coordinates, on the other hand, are rotationally invariant functions of x or X. We denote these by q^μ, $\mu = 1, \ldots, 3N-6$, or just q for short. These can be taken to be coordinates along the section S, but, since they are rotationally invariant, they are defined elsewhere in nuclear configuration space by the fact that they are constant along rotational fibers.

G. Diabatic Bases

In multisurface problems the region of interest may include internal degeneracies, usually conical intersections, and we may choose x_0 to lie on one of these in order to study frames in a corresponding neighborhood. Then small changes in shape as we move along S away from the conical intersection will break the degeneracy and produce an eigenframe (an adiabatic basis) that is well defined but discontinuous. (The frame is smooth as $x \to x_0$ and the limit exists, but the limit depends on the direction of approach.) In such cases the adiabatic basis has singularities regardless of phase or frame conventions, and a smooth assignment of those conventions over a section is impossible. Therefore we must accept that an adiabatic basis can be defined over a section S and extended along rotational fibers by (50), but that it will have discontinuities as we vary the shape. It will, however, be smooth as we vary the orientation, holding the shape fixed.

The discontinuities in the adiabatic basis at degeneracies cause the derivative couplings to diverge, and are the major drawback of this basis. To avoid these we may switch to a diabatic basis, an orthonormal basis denoted $|dx;k\rangle$ with d for "diabatic." The diabatic basis vectors for $k \in I$ are required to span the subspace $\mathcal{S}(x)$, and to span $\mathcal{S}^\perp(x)$ for $k \notin I$. In addition, a diabatic basis is required to be smooth over its domain of definition, something that can be achieved if we do not require the basis vectors $|dx;k\rangle$ to be energy eigenstates for $k \in I$. Finally, we shall require diabatic bases to be invariant under time reversal.

To construct a diabatic basis we begin with points x_0 on a section. (In the following we use x_0 for a variable point in S.) We assume that a T-invariant, adiabatic basis $|ax_0;k\rangle$, including phase and frame conventions, has been established for all x_0 in some region in S. As explained, this basis will have discontinuities, in general. Since sets of basis vectors, $|ax_0;k\rangle$ and $|dx_0;k\rangle$ for $k \in I$, are required to span the same subspace $S(x)$, they must be related by

$$|dx_0;k\rangle = \sum_{l\in I} |ax_0;l\rangle V_{lk}, \tag{51}$$

where V_{kl} is an $N_l \times N_l$, unitary matrix that depends on x_0. Also, since $|dx_0;k\rangle$ is required to be smooth, the matrix V_{kl} must compensate for the singularities of the basis $|ax_0;k\rangle$ and cannot be smooth itself. Similar statements can be made for the subset $k \notin I$ and the complementary subspace $S^{\perp}(x)$.

There are many ways to find the matrix V so that the diabatic basis is smooth. Two of these, the singular-value basis and the parallel-transported basis, have been discussed by us recently (Littlejohn, Rawlinson, and Subotnik (2022)). The construction of both bases takes place in a neighborhood of a fixed reference point x_{00} on S. The construction is most interesting when x_{00} lies on a degeneracy (a seam or conical intersection) but this is not required. The adiabatic and diabatic bases are required to agree at x_{00}, $|a,x_{00};k\rangle = |d,x_{00};k\rangle$. The singular value diabatic basis is due to Pacher, Cederbaum, and Köppel (1988, 1993); it chooses an orthonormal frame inside $S(x_0)$ for each x_0 in the region of S that is as close as possible to the adiabatic frame in $S(x_{00})$, in the space of such frames. The resulting field of frames on S is unique and smooth in a neighborhood of x_{00} and defines the singular-value diabatic basis. The parallel-transported diabatic basis involves radial lines extending out from x_{00} to points $x_0 \in S$, along which the basis is carried by parallel transport. This minimizes the distance in the space of frames between the bases at x_0 and $x_0 + dx_0$ for each infinitesimal step along the curve.

Both the singular-value basis and the parallel-transported basis have the property that if the adiabatic frame at x_{00} is T-invariant, as we assume, then so is the diabatic frame at all points x_0 in its domain. We omit the proofs but they involve the fact the projection operator onto the strongly coupled subspace commutes with T, which follows since that subspace is invariant under T. Thus, for these diabatic bases, the matrix V_{kl} in (51) is real and orthogonal.

Once the diabatic basis has been defined for $x_0 \in S$, we extend the definition along rotational fibers by means of rotation operators, as in (50). Since we are assuming that the adiabatic basis transforms by those same rotation operators, (51) shows that the matrix V_{kl} is independent of position along a rotational fiber, that is, $V_{kl}(x) = V_{kl}(x_0)$, where $x = Rx_0$. Equivalently, the matrix V_{kl} is a function of shape coordinates only and is independent of orientation.

IV. TRANSFORMATION OF BASIS AND DERIVATIVE COUPLINGS UNDER ROTATIONS

In this section we introduce the "working basis," which is either the adiabatic basis or a diabatic basis, whichever meets the smoothness criteria. It is the basis we will use for subsequent calculations. We continue with the electrostatic model. We accumulate a set of transformation laws for various quantities under rotations, which supplement the transformation law (47) for the electronic Hamiltonian and (12) for its eigenvalues, which we have already worked out. The new transformation laws include that for the basis vectors, (56), that for the matrix elements of the Hamiltonian, (54), and that for the derivative couplings, (70). These are required for subsequent work.

A. The Working Basis and its Properties

In the following we write simply $|x;k\rangle$ for a basis that is either the adiabatic basis, in cases where that is smooth (for example, in single-surface problems over a simply connected region), otherwise a diabatic basis. We will call this the "working basis." We assume that it spans $\mathcal{S}(x)$ for $k \in I$ and $\mathcal{S}^{\perp}(x)$ for $k \notin I$; that it is smooth over a section S or a chosen region thereof; that it is propagated along rotational fibers by

$$|Rx_0;k\rangle = U_{eo}(R)\,|x_0;k\rangle; \tag{52}$$

and that it is T-invariant, $T\,|x;k\rangle = |x;k\rangle$.

Some authors, for example, Kendrick (2018), have used a notation in which the basis states are given as functions of the shape coordinates alone, and not the Euler angles. We believe it is worth clarifying this, since it is obvious that the electronic eigenstates do depend on orientation, and, with our phase conventions, (52) shows explicitly how they do. On the other hand, points x_0 on the section are determined by the shape coordinates, that is, $x_0 = x_0(q)$, so the basis states on the section can be regarded as functions of shape coordinates alone. We believe this is the correct interpretation of something that in our notation would look like $|q;k\rangle$, that is, it means $|x_0(q);k\rangle$. There are objects that really are constant along rotational fibers, for example, the energy eigenvalues, which satisfy $\epsilon_k(x) = \epsilon_k(Rx_0) = \epsilon_k(x_0) = \epsilon_k\big(x_0(q)\big) = \epsilon_k(q)$. These are functions of the shape coordinates alone everywhere in nuclear configuration space, not just on the section.

We write the matrix elements of the electronic Hamiltonian in the working basis for $k, l \in I$ as

$$\langle x; k | H_e(x) | x; l \rangle = W_{kl}(x). \tag{53}$$

If the working basis is the adiabatic basis then $W_{kl}(x) = \epsilon_k(x)\,\delta_{kl}$, while in the diabatic basis W_{kl} is a full matrix. In view of the T-invariance of the basis states $|x; k\rangle$ the matrix W_{kl} is real (hence, real and symmetric). In view of the dependence (52) of the basis states along rotational fibers and the transformation law (47) of the Hamiltonian, the matrix W_{kl} is independent of orientation,

$$W_{kl}(Rx_0) = W_{kl}(x_0), \tag{54}$$

that is, W_{kl} depends only on the shape coordinates.

We turn now to the transformation properties of the working basis under rotations. Let $x_0 \in S$ be an initial point on a rotational fiber, let $R_1, R_2 \in SO(3)$, and let $x_1 = R_1 x_0$ and $x_2 = R_2 x_1$. Then

$$\begin{aligned} |x_2; k\rangle = |R_2 x_1; k\rangle = |R_2 R_1 x_0; k\rangle &= U_{eo}(R_2 R_1)\,|x_0; k\rangle \\ &= U_{eo}(R_2)\,U_{eo}(R_1)\,|x_0; k\rangle = U_{eo}(R_2)\,|x_1; k\rangle, \end{aligned} \tag{55}$$

where we use (52) and the representation property (41). Making the notational changes, $x_1 \to x$, $R_2 \to R$, we can write this as

$$|Rx; k\rangle = U_{eo}(R)\,|x; k\rangle. \tag{56}$$

This is the transformation law of the working basis $|x; k\rangle$ under rotations. It is the same as (52) with x_0 replaced by x, but the meaning is quite different. That is, (52) defines the working basis along the rotational fibers, including the phase and frame conventions, given such a definition at an initial point $x_0 \in S$; whereas (56) is a property of those basis vectors, once defined, at any point x on a rotational fiber. (Of course, (52) is a special case of (56).)

Let us now specialize R in (56) to an infinitesimal rotation, that is, one for which the angle θ is infinitesimal, so that

$$R = R(\hat{n}, \theta) = I + \theta\,\hat{n}\times. \tag{57}$$

If we let such an R act on a configuration x, then we can write $Rx = x + \delta x$, where

$$\delta x = \theta\,(\hat{n} \times \mathrm{X}_1, \ldots, \hat{n} \times \mathrm{X}_{N-1}). \tag{58}$$

On the other hand, when θ is small, (40) implies

$$U_{eo}(R) = 1 - \frac{i}{\hbar}\theta\,\hat{n} \cdot \mathrm{L}_e. \tag{59}$$

For such rotations (56) becomes

$$|Rx;k\rangle = |x+\delta x;k\rangle = |x;k\rangle + \sum_{\alpha=1}^{N-1} \theta\,(\hat{n}\times \mathrm{X}_\alpha)\cdot\nabla_\alpha\,|x;k\rangle = |x;k\rangle - \frac{i}{\hbar}\theta\,\hat{n}\cdot\mathrm{L}_e\,|x;k\rangle. \tag{60}$$

In this we write $(\hat{n}\times\mathrm{X}_\alpha)\cdot\nabla_\alpha = \hat{n}\cdot(\mathrm{X}_\alpha\times\nabla_\alpha)$, we cancel leading terms, the factor θ and the factor $\hat{n}$ (which is an arbitrary unit vector). The result can be written as

$$\left[-i\hbar\sum_{\alpha=1}^{N-1}(\mathrm{X}_\alpha\times\nabla_\alpha)+\mathrm{L}_e\right]|x;k\rangle = 0, \tag{61}$$

or,

$$(\mathrm{L}_n+\mathrm{L}_e)\,|x;k\rangle = 0, \tag{62}$$

where L_n is the usual differential operator for the nuclear orbital angular momentum, here acting on the parametric dependence x of the working basis states.

In the case of nondegenerate adiabatic basis states, Yarkony (2001) has shown that the off-diagonal matrix elements of $\mathrm{L}_n+\mathrm{L}_e$ vanish (see Eq. (19abc) of that article). Because of the time-reversal invariance of the basis states, the diagonal elements vanish, too, and Yarkony's results are equivalent to (62). With our phase and frame conventions, however, (62) applies also in the case of degeneracies or diabatic bases.

B. Transformation Properties of Derivative Couplings

We wish to find how the derivative couplings, defined by (17), transform along rotational fibers, that is, how $\mathrm{F}_{\alpha;kl}(Rx)$ depends on $\mathrm{F}_{\alpha;kl}(x)$. The obvious strategy is to work with $\mathrm{F}_{\alpha;kl}(Rx) = \langle Rx;k|\nabla_\alpha|Rx;l\rangle$, but this is notationally awkward (do we rotate first and then differentiate, or the other way around?)

Therefore we propose a different approach. Let ξ be an infinitesimal displacement in nuclear configuration space,

$$\xi = (\xi_1,\ldots,\xi_{N-1}). \tag{63}$$

Then we have

$$|x+\xi;l\rangle = |x;l\rangle + \sum_{\alpha=1}^{N-1}\xi_\alpha\cdot\nabla_\alpha\,|x;l\rangle, \tag{64}$$

which implies

$$\langle x;k|x+\xi;l\rangle = \delta_{kl} + \sum_{\alpha=1}^{N-1}\xi_\alpha\cdot\mathrm{F}_{\alpha;kl}(x). \tag{65}$$

The x in this equation is a dummy variable, and one that is independent of ξ, so we can replace it by Rx, obtaining

$$\langle Rx;k|Rx+\xi;l\rangle = \delta_{kl} + \sum_{\alpha=1}^{N-1} \xi_\alpha \cdot \mathrm{F}_{\alpha;kl}(Rx). \tag{66}$$

On the other hand, we have

$$\begin{aligned} |Rx+\xi;l\rangle &= |R(x+R^{-1}\xi);l\rangle = U_{eo}(R)\,|x+R^{-1}\xi;l\rangle \\ &= U_{eo}(R)\left[\,|x;l\rangle + \sum_{\alpha=1}^{N-1} (R^{-1}\xi_\alpha)\cdot \nabla_\alpha |x;l\rangle\right], \end{aligned} \tag{67}$$

and

$$\langle Rx;k| = \langle x;k|\,U_{eo}(R)^\dagger, \tag{68}$$

where we use (56). Upon taking the product of (68) and (67) the rotation operators cancel and we obtain

$$\langle Rx;k|Rx+\xi;l\rangle = \delta_{kl} + \sum_{\alpha=1}^{N-1} \xi_\alpha \cdot (R\mathrm{F}_{\alpha;kl}(x)), \tag{69}$$

where we have used the fact that for any two vectors A and B and any rotation R, we have $(R^{-1}\mathrm{A})\cdot\mathrm{B} = \mathrm{A}\cdot(R\mathrm{B})$. Comparing this with (66), we obtain finally

$$\mathrm{F}_{\alpha;kl}(Rx) = R\mathrm{F}_{\alpha;kl}(x), \tag{70}$$

since the displacements ξ_α are arbitrary.

Equation (70) is the transformation law of the derivative couplings under rotations; it says, in a sense, that $\mathrm{F}_{\alpha;kl}$ transforms as a vector field on nuclear configuration space under rotations. This result is important for establishing the rotational invariance of the Born-Oppenheimer Hamiltonian for multisurface, electrostatic problems.

Some authors, for example, Yarkony (2001), have used a notation in which the derivative couplings are given as functions of the shape coordinates alone, with no dependence on the Euler angles. It would be as if we wrote $\mathrm{F}_{\alpha;kl}(q)$ in our notation. We believe this means $\mathrm{F}_{\alpha;kl}\big(x_0(q)\big)$, that is, it is the derivative couplings evaluated on the section, where q^μ are coordinates. The derivative couplings elsewhere do depend on the orientation, as shown explicitly by (70).

A subtlety in this matter is that the derivative couplings are really the components of a differential form with respect to the Jacobi vectors, and if the components are taken instead with respect to rotationally invariant vector fields, then those components will be rotationally invariant. This is an issue in the construction of kinetic energy operators in the internal space that incorporate geometric phase effects.

C. Rotational Components of Derivative Couplings

Let R be an infinitesimal rotation with $\theta \ll 1$, and let $Rx = x + \delta x$, as in (57) and (58). Then the component of the derivative couplings in the direction δx is

$$\begin{aligned}\sum_{\alpha=1}^{N-1} \delta \mathbf{X}_\alpha \cdot \mathbf{F}_{\alpha;kl}(x) &= \theta \sum_{\alpha=1}^{N-1} \langle x;k|(\hat{\mathbf{n}}\times\mathbf{X}_\alpha)\cdot\nabla_\alpha|x;l\rangle = \frac{i}{\hbar}\theta\hat{\mathbf{n}}\cdot\sum_{\alpha=1}^{N-1}\langle x;k|\mathbf{X}_\alpha\times\mathbf{P}_\alpha|x;l\rangle\\ &= -\frac{i}{\hbar}\theta\hat{\mathbf{n}}\cdot\langle x;k|\mathbf{L}_e|x;l\rangle,\end{aligned} \tag{71}$$

where in the last step we use (62). Thus, the angular components of the derivative couplings (with our phase and frame conventions) are proportional to the matrix elements of the electronic angular momentum. This result is due to Yarkony (2001); it is important for the construction of kinetic energy operators on the internal space.

V. MOLECULAR AND BORN-OPPENHEIMER REPRESENTATIONS

We now introduce the molecular and Born-Oppenheimer representations for the state space of the molecule, which give us the setting within which our main results concerning angular momentum can be stated. We continue with the electrostatic model, with possibly more than one strongly coupled potential energy surface.

A. Two Representations

In what we call the "molecular representation," the quantum state of the molecule is specified by the wave function $\Psi(\mathbf{X},\mathbf{r})$, which is just standard quantum mechanics on the standard Hilbert space for the molecule. If Ψ is any such wave function, we expand the $\mathbf{r}$ dependence in terms of the x-dependent working basis vectors $|x;k\rangle$, whose wave functions are denoted $\phi_k(\mathbf{X};\mathbf{r})$, as shown in (16). That is, we write

$$\Psi(\mathbf{X},\mathbf{r}) = \sum_k \psi_k(\mathbf{X})\,\phi_k(\mathbf{X};\mathbf{r}), \tag{72}$$

as is standard in Born-Oppenheimer theory. Here $\psi_k(\mathbf{X})$ are the expansion coefficients; we imagine them forming an infinite-dimensional vector of wave functions of $\mathbf{X}$. Equation (72) gives the wave function $\Psi(\mathbf{X},\mathbf{r})$ in terms of the purely nuclear wave functions $\psi_k(\mathbf{X})$; the inverse relation is

$$\psi_k(\mathbf{X}) = \int d\mathbf{r}\,\phi_k(\mathbf{X};\mathbf{r})^*\,\Psi(\mathbf{X},\mathbf{r}). \tag{73}$$

We will refer to the infinite dimensional vector of nuclear wave functions $\psi_k(\mathrm{X})$ as the "Born-Oppenheimer representation" of the quantum state of the molecule, and abbreviate the relationships (72) and (73) between them by writing

$$\Psi(\mathrm{X},\mathrm{r}) \longleftrightarrow \psi_k(\mathrm{X}). \tag{74}$$

The association is one-to-one, and no information is lost by using the Born-Oppenheimer representation.

Similarly, let A be a linear operator that maps molecular wave functions $\Psi(\mathrm{X},\mathrm{r})$ into new such wave functions $\Psi'(\mathrm{X},\mathrm{r})$, something we can write as $\Psi'(\mathrm{X},\mathrm{r}) = (A\Psi)(\mathrm{X},\mathrm{r})$. This is in the molecular representation. In the Born-Oppenheimer representation, A is replaced by an infinite-dimensional matrix A_{kl} of linear operators, each of which acts on wave functions $\psi(\mathrm{X})$, depending on the nuclear coordinates alone. That is, if $\Psi' = A\Psi$ as shown, and if $\Psi \longleftrightarrow \psi_k$ and $\Psi' \longleftrightarrow \psi'_k$, then

$$\psi'_k(\mathrm{X}) = \sum_l (A_{kl}\,\psi_l)(\mathrm{X}). \tag{75}$$

This is equivalent to

$$(A\Psi)(\mathrm{X},\mathrm{r}) = \sum_k \phi_k(\mathrm{X};\mathrm{r}) \sum_l (A_{kl}\,\psi_l)(\mathrm{X}), \tag{76}$$

which gives A in terms of the matrix of operators A_{kl}. The inverse is

$$(A_{kl}\psi)(\mathrm{X}) = \int d\mathrm{r}\,\phi_k(\mathrm{X};\mathrm{r})^*\,(A\Phi_l)(\mathrm{X},\mathrm{r}), \tag{77}$$

where $\Phi_l(\mathrm{X},\mathrm{r}) = \psi(\mathrm{X})\,\phi_l(\mathrm{X};\mathrm{r})$. We write ψ without a subscript in (77) because it is just a dummy function of X that is used to define the operator A_{kl}; it may be the component of a wave function in the Born-Oppenheimer representation, but it need not be. We will summarize the relations (76) and (77) between the operators in the two representations by writing

$$A \longleftrightarrow A_{kl}. \tag{78}$$

Then it is easy to prove some theorems. If $B = A^\dagger$ (in the molecular representation), then in the Born-Oppenheimer representation we have

$$B_{kl} = (A_{lk})^\dagger, \tag{79}$$

where the parentheses make it clear that we form the transpose of the matrix A_{kl} first, and then take the Hermitian conjugate of the elements.

Likewise, if A, B and C are operators in the molecular representation and $C = AB$, then

$$C_{kl} = \sum_p A_{kp} B_{pl}, \tag{80}$$

that is, operator products are mapped into matrix products (but the matrix elements are themselves operators, and their order of multiplication must be respected).

B. Examples of Operators in the Born-Oppenheimer Representation

We present some examples of the transformation of operators from the molecular representation to the Born-Oppenheimer representation. If $A = f(x)$ is a function of x in the molecular representation, that is, a multiplicative operator on wave functions $\Psi(x, \mathrm{r})$, then we find

$$f(x) \longleftrightarrow f(x)\,\delta_{kl}. \tag{81}$$

In particular, this applies when f is one of the components of the Jacobi vectors X_α.

In the following we let P_α stand for the differential operator $-i\hbar\nabla_\alpha$. In the molecular representation, this represents physically the kinetic momentum conjugate to the Jacobi vector X_α. Transforming to the Born-Oppenheimer representation, we find

$$\mathrm{P}_\alpha \longleftrightarrow \mathrm{P}_\alpha\,\delta_{kl} - i\hbar\,\mathrm{F}_{\alpha;kl}(x). \tag{82}$$

The Born-Oppenheimer version of this operator has a well known interpretation as a covariant derivative (Bohm, Boya, and Kendrick (1991)).

For another example, consider a purely electronic operator, for example, L_e. Then we find

$$\mathrm{L}_e \longleftrightarrow \langle x;k|\mathrm{L}_e|x;l\rangle, \tag{83}$$

that is, the matrix of nuclear operators representing L_e in the Born-Oppenheimer representation are purely multiplicative functions of x, which are otherwise the matrix elements of L_e in the working basis. Another purely electronic operator is the electronic Hamiltonian, which, however, depends on x. We have

$$H_e(x) \longleftrightarrow W_{kl}(x), \tag{84}$$

see (53) and (54).

Yet another such operator is the projector onto the strongly coupled subspace $\mathcal{S}(x)$,

$$P(x) = \sum_{k\in I} |x;k\rangle\langle x;k|. \tag{85}$$

This maps into its Born-Oppenheimer version, $P(x) \longleftrightarrow P_{kl}$, where

$$P_{kl} = \begin{cases} \delta_{kl}, & \text{if } k,l \in I \\ 0, & \text{otherwise.} \end{cases} \qquad (86)$$

C. The Molecular Hamiltonian

The molecular Hamiltonian in the electrostatic model and in the molecular representation is

$$H_{\text{mol}} = \sum_{\alpha=1}^{N-1} \frac{\mathrm{P}_\alpha^2}{2M_\alpha} + H_e(x). \qquad (87)$$

Transforming this to the Born-Oppenheimer representation, $H_{\text{mol}} \longleftrightarrow H_{\text{mol},kl}$, we find

$$H_{\text{mol},kl} = \sum_{\alpha=1}^{N-1} \left(\frac{1}{2M_\alpha} \sum_p [\mathrm{P}_\alpha \delta_{kp} - i\hbar \mathrm{F}_{\alpha;kp}(x)] \cdot [\mathrm{P}_\alpha \delta_{pl} - i\hbar \mathrm{F}_{\alpha;pl}(x)] \right) + W_{kl}(x), \qquad (88)$$

where we use the product rule (80), (82) and (84). This style of transforming to the Born-Oppenheimer representation follows Kendrick (2018). The sum on p is the matrix multiplication indicated by (80); notice that this sum runs over the entire Hilbert space, that is, both $p \in I$ and $p \notin I$.

In most physical circumstances of interest the nuclear momentum P_α is large when measured in atomic units, because of the large nuclear mass, while $\mathrm{F}_{\alpha;kl}$ (with our phase conventions and smoothness assumptions) is of order unity in the same units. Therefore the terms of the kinetic energy in (88) decrease in magnitude as the power of P_α decreases. Therefore the diagonal terms $k = l$ are dominated by P_α^2 while the off-diagonal terms $k = l$ are dominated by the terms linear in P_α, which are therefore smaller than the diagonal terms.

We can decouple the strongly coupled levels $k \in I$ from the rest by simply throwing away the off-diagonal terms (kl) of (88) for $k \in I$ and $l \notin I$ or $k \notin I$ and $l \in I$. This replaces the Hamiltonian $H_{\text{mol},kl}$ by a new, block-diagonal, one that we will call $K_{\text{mol},kl}$. The formula for the latter is the same as (88) when $k,l \in I$ or $k,l \notin I$, and 0 otherwise. Alternatively, since we do not care about dynamics outside the strongly coupled subspace, we can define $K_{\text{mol},kl}$ as the same as $H_{\text{mol},kl}$ when $k,l \in I$, and 0 otherwise. This is equivalent to

$$K_{\text{mol}} = P(x) H_{\text{mol}} P(x), \qquad (89)$$

that is, it is just the original molecular Hamiltonian, projected onto the strongly coupled subspace. Most derivations of the Born-Oppenheimer Hamiltonian in the literature amount to carrying out this projection.

In the special case of a single surface problem, where I contains the single level k_0, this procedure gives us the Born-Oppenheimer Hamiltonian (10) with $k \to k_0$. The latter would be writ-ten in the present notation as K_{mol,k_0k_0}. As noted, the derivative couplings $\mathrm{F}_{\alpha;kl}$ vanish on the diagonal $(kl) = (k_0k_0)$. In this context the replacement of H_{mol} by K_{mol} is usually called "the Born-Oppenheimer approximation." Its obvious generalization to multisurface problems is given by (89).

Actually, the "Born-Oppenheimer approximation" is often described (in the context of a single-surface problem) as one in which the wave function is assumed to have the product form seen in (14). But if the Hamiltonian is approximated by throwing away off-diagonal terms, then the new Hamiltonian possesses solutions of the product form. Therefore we regard the usual Born-Oppenheimer approximation as one of approximating the Hamiltonian.

The off-diagonal terms that we throw away to obtain $K_{\text{mol},kl}$ are indeed small compared to the diagonal terms, but beyond this their neglect is *ad hoc* and it is hard to find a deeper justification for the procedure in the literature, at least in the case of large-amplitude motions. This leaves open the question of whether the Born-Oppenheimer Hamiltonians obtained by projection as in (89) are even correct. They certainly are so to first order in small quantities, but it is not obvious that they are correct to second order. In Sec. VII we will discuss Moyal perturbation theory, which is useful for answering these questions. The issue is more important than the small, second order terms in the Hamiltonian, as it involves the dressing of the nuclear variables, which has effects at first order.

D. The Angular Momentum

In the molecular representation the total orbital angular momentum of the molecule is represented by the operator $\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e$, which is given by (8). To find the Born-Oppenheimer representation we allow L to act on a molecular wave function,

$$\begin{aligned} \mathrm{L}\Psi(\mathrm{X},\mathrm{r}) &= (\mathrm{L}_n + \mathrm{L}_e)\sum_k \psi_k(\mathrm{X})\,\phi_k(\mathrm{X};\mathrm{r}) \\ &= \sum_k [(\mathrm{L}_n + \mathrm{L}_e)\psi_k(\mathrm{X})]\,\phi_k(\mathrm{X};\mathrm{r}) + \sum_k \psi_k(\mathrm{X})\,[(\mathrm{L}_n + \mathrm{L}_e)\phi_k(\mathrm{X};\mathrm{r})], \end{aligned} \tag{90}$$

where we distribute $\mathrm{L}_n + \mathrm{L}_e$ using the product or Leibnitz rule, since it is a first-order, linear, differential operator. Then the second major sum on the right vanishes due to (62), while in the first sum on the right the term involving L_e also vanishes, since ψ_k has no dependence on r. The

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result can be written,

$$\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e \longleftrightarrow \mathrm{L}_n\,\delta_{kl}. \tag{91}$$

This justifies and makes precise our earlier statement that in the Born-Oppenheimer representation, the nominal, nuclear orbital angular momentum includes physically both the nuclear and electronic orbital angular momenta, and that this is exact.

The molecular Hamiltonian H_{mol} in the molecular representation commutes with L, due to the overall rotational invariance of the molecule, so in the Born-Oppenheimer representation the matrix $H_{\text{mol},kl}$ must commute with the matrix $\mathrm{L}_n\,\delta_{kl}$. But since the latter is a multiple of the identity, this reduces to

$$[\mathrm{L}_n, H_{\text{mol},kl}] = 0. \tag{92}$$

This is the form that overall angular momentum conservation takes in the Born-Oppenheimer representation; every component of the matrix $H_{\text{mol},kl}$ commutes with L_n, that is, it is a scalar under nuclear orbital rotations.

Nuclear orbital rotations are generated by L_n and are implemented by the operators,

$$U_{no}(R) = U_{no}(\hat{\mathrm{n}},\theta) = \exp\left(-\frac{i}{\hbar}\theta\,\hat{\mathrm{n}}\cdot\mathrm{L}_n\right), \tag{93}$$

which act on nuclear wave functions according to $U_{no}(R)\psi(\mathrm{X}) = \psi\left(R^{-1}\mathrm{X}\right)$. Like the electronic orbital rotation operators $U_{eo}(R)$, nuclear orbital rotation operators form a representation of $SO(3)$, $U_{no}(R_1)\,U_{no}(R_2) = U_{no}(R_1R_2)$. An operator commutes with nuclear orbital angular momentum L_n if and only if it commutes with the rotations $U_{no}(R)$ for all $R \in SO(3)$. Therefore to check (92) we can see how $H_{\text{mol},kl}$ transforms under conjugation by $U_{no}(R)$.

To begin we have

$$U_{no}(R)\,\mathrm{X}_\alpha\,U_{no}(R)^\dagger = R^{-1}\mathrm{X}_\alpha, \tag{94}$$

$$U_{no}(R)\,\mathrm{P}_\alpha\,U_{no}(R)^\dagger = R^{-1}\mathrm{P}_\alpha, \tag{95}$$

which is a statement that X_α and P_α are vector operators. This implies that $\mathrm{P}_\alpha^2 = \mathrm{P}_\alpha\cdot\mathrm{P}_\alpha$ is a scalar. Next, we have

$$U_{no}(R)\,\mathrm{F}_{\alpha;kl}(x)\,U_{no}(R)^\dagger = \mathrm{F}_{\alpha;kl}\left(R^{-1}x\right) = R^{-1}\mathrm{F}_{\alpha;kl}(x), \tag{96}$$

where in the first step we use (94) and in the second, (70). This shows that the derivative couplings, with our choice of basis states and phase conventions, transform under nuclear rotations as a vector operator. Thus, dot products such as $\mathrm{P}_\alpha \cdot \mathrm{F}_{\alpha;kl}$ are scalars. We see that the components $H_{\mathrm{mol},kl}$ are scalars, and that therefore they commute with L_n. The same is true for the components $K_{\mathrm{mol},kl}$, which are either equal to $H_{\mathrm{mol},kl}$ or else are zero.

In single-surface problems it is obvious that the Born-Oppenheimer version of the Hamiltonian, (10), commutes with L_n, because it has the simple kinetic-plus-potential form with a rotationally invariant potential and there are no derivative couplings. This means that energy eigenfunctions can be organized as eigenfunctions also of L_n^2 and L_{nz}, as noted.

In multisurface problems, as we have just shown, the matrix Hamiltonian $K_{\mathrm{mol},kl}$ commutes with the matrix of angular momentum operators, $\mathrm{L}_n\,\delta_{kl}$. This means that the solutions of the Born-Oppenheimer version of the Schrödinger equation, which now reads (for $k \in I$),

$$\sum_{l \in I} K_{\mathrm{mol},kl}\,\psi_l(\mathrm{X}) = E\,\psi_k(\mathrm{X}), \tag{97}$$

can be organized as simultaneous eigenfunctions of the matrix Hamiltonian $K_{\mathrm{mol},kl}$ and the matrix angular momentum operators, $L_n^2\delta_{kl}$ and $L_{nz}\,\delta_{kl}$. But to make the vector wave function ψ_k for $k \in I$ an eigenfunction of those matrix angular momentum operators, each component $\psi_k(\mathrm{X})$ must be an eigenfunction of L_n^2 and L_{nz} with the same quantum numbers. Call these (l, m_l).

We then transform the eigenfunction $\psi_k(\mathrm{X})$, which is nonzero only for $k \in I$, back to the molecular representation, using (72) but only summing over $k \in I$. The resulting molecular wave function $\Psi(\mathrm{X}, \mathrm{r})$ is then an exact eigenfunction of L^2 and L_z, where $\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e$, with the same quantum numbers (l, m_l). Thus we obtain an understanding of angular momentum conservation in multisurface problems.

VI. DETAILS IN FINE STRUCTURE MODELS

Some of the changes required on passing from the electrostatic model to the fine structure model have been discussed at the beginning of Sec. II G. These include the facts that the electronic and molecular wave functions, $\phi(\mathrm{r}, m)$ and $\Psi(\mathrm{X}, \mathrm{r}, m)$, respectively, acquire a dependence on the spin quantum numbers m (see (6)); that the electronic and molecular Hamiltonians, $H_e(x; \mathrm{r}, \mathrm{p}, \mathrm{S})$ and $H_{\mathrm{mol}}(\mathrm{X}, \mathrm{P}, \mathrm{r}, \mathrm{p}, \mathrm{S})$, respectively, acquire a dependence on the electron spin S; and that the definition of time reversal changes, from (A1) to (A4).

The electronic Hamiltonian $H_e(x; \mathrm{r}, \mathrm{p}, \mathrm{S})$ now depends on the dot products and triple products of the vectors $\mathbf{X}_\alpha$, $\mathbf{r}_i$, $\mathbf{p}_i$ and $\mathbf{S}_i$, so (42) is replaced by

$$H_e(x;\mathbf{r},\mathbf{p},\mathbf{S}) = H_e(Rx;R\mathbf{r},R\mathbf{p},R\mathbf{S}) \qquad \forall R \in SO(3), \tag{98}$$

where $R\mathbf{S} = (R\mathbf{S}_1,\ldots,R\mathbf{S}_{N_e})$. This is a statement about the functional form of the electronic Hamiltonian.

To connect this with rotation operators we cannot use orbital rotations as in (47) but rather we must introduce total electron rotation operators that include the spin. We denote these by $U_e(u)$; they are parameterized by an element $u \in SU(2)$ or by the equivalent axis and angle, $U_e(\mathbf{n},\theta) = U_e\big(u(\mathbf{n},\theta)\big)$, and are defined by their action on electronic wave functions,

$$U_e(u)\phi(\mathbf{r},m) = \sum_{m'}(u\ldots u)_{mm'}\,\phi\big(R^{-1}\mathbf{r},m'\big), \tag{99}$$

where the notation for the sum is the same as in (A4) and where R means $R(u)$, defined by (C2). It follows from (99) that the operators $U_e(u)$ form a representation of $SU(2)$,

$$U_e(u_1)U_e(u_2) = U_e(u_1u_2). \tag{100}$$

These operators are given in terms of their generators by

$$U_e(u) = U_e(\hat{\mathbf{n}},\theta) = \exp\left(-\frac{i}{\hbar}\theta\,\hat{\mathbf{n}}\cdot(\mathbf{L}_e+\mathbf{S})\right). \tag{101}$$

Now all of $\mathbf{r}$, $\mathbf{p}$ and $\mathbf{S}$ transform as vector operators under conjugation by $U_e(u)$, for example, we have

$$U_e(u)\,\mathbf{S}_i\,U_e(u)^\dagger = R^{-1}\mathbf{S}_i, \tag{102}$$

where in formulas like this it is understood that $R = R(u)$. Therefore the electronic Hamiltonian transforms according to

$$U_e(u)\,H_e(x;\mathbf{r},\mathbf{p},\mathbf{S})\,U_e(u)^\dagger = H_e\big(x;R^{-1}\mathbf{r},R^{-1}\mathbf{p},R^{-1}\mathbf{S}\big) = H_e(Rx;\mathbf{r},\mathbf{p},\mathbf{S}), \tag{103}$$

just as in the derivation of (46). With the abbreviation $H_e(x;\mathbf{r},\mathbf{p},\mathbf{S}) \to H_e(x)$ this becomes

$$U_e(u)\,H_e(x)\,U_e(u)^\dagger = H_e(Rx), \tag{104}$$

which may be compared to its electrostatic counterpart, (47). They are the same except that $U_{eo}(R)$ has been replaced by $U_e(u)$. This is the transformation law of the electronic Hamiltonian along rotational fibers in the fine structure model.

A. Fine Structure Details, Even Number of Electrons

Most of the results in the fine structure model with $N_e =$ even have the same form as in the electrostatic model, since the main conclusions follow from $T^2 = +1$ which holds in both cases (although the definitions of T are not the same). We begin with rotation operators.

The function $R(u)$ (see (C2)) has the property $R(u) = R(-u)$ and if the number of electrons is even then the number of factors of u in (99) is also even. Thus $U_e(u) = U_e(-u)$ and U_e might as well be parameterized by $R = R(u) \in SO(3)$. Then the operators $U_e(R)$ form a representation of $SO(3)$, $U_e(R_1)U_e(R_2) = U_e(R_1R_2)$. The definition of $U_e(R)$ is still (99), but with $U_e(R)$ instead of $U_e(u)$ on the left hand side and with the understanding that u on the right hand side is one of the two elements of $SU(2)$ that correspond to the given $R \in SO(3)$ according to (C2). These differ by a sign, which the answer does not depend on.

Thus, the transformation law for the Hamiltonian along rotational fibers in the fine structure model with an even number of electrons is $U_e(R)\,H_e(x)\,U_e(R)^\dagger = H_e(Rx)$, which may be compared to (47) in the electrostatic model (they are the same, except the rotation operator now includes spin).

As for the basis states, we still have $T^2 = +1$ as in the electrostatic model and T still commutes with $H_e(x)$, which together imply the existence of T-invariant bases (adiabatic first, and then diabatic). These can be defined along a section S, smoothly, in the case of the diabatic basis, and then propagated along noncollinear rotational fibers by

$$|Rx_0; k\rangle = U_e(R)\,|x_0; k\rangle. \tag{105}$$

This may be compared to its electrostatic counterpart, (52); the only difference is that the rotation operator now includes spin.

With these (smooth) phase and frame conventions we can define a smooth working basis, as in the electrostatic model. This basis transforms under rotations according to

$$|Rx; k\rangle = U_e(R)\,|x; k\rangle, \tag{106}$$

which is just like (56) and proved in the same way, except that the rotation now involves spin. By making R infinitesimal in this, we obtain

$$(\mathrm{L}_n + \mathrm{L}_e + \mathrm{S})\,|x; k\rangle = 0, \tag{107}$$

just like (62) except that now the spin is included. The operator that appears is the total angular momentum J of the molecule.

We then find that the derivative coupling transform under rotations according to (70), the same formula as in the electrostatic model. As for the rotational components of the derivative couplings, they are now given by

$$\sum_{\alpha=1}^{N-1} \delta \mathrm{X}_\alpha \cdot \mathrm{F}_{\alpha;kl}(x) = -\frac{i}{\hbar}\theta\hat{\mathrm{n}}\cdot\langle x;k|(\mathrm{L}_e+\mathrm{S})|x;l\rangle, \tag{108}$$

where $\delta\mathrm{X}_\alpha = \theta\hat{\mathrm{n}}\times\mathrm{X}_\alpha$ and where the matrix elements of the total electronic angular momentum appear (orbital plus spin).

The potential energy matrix $W_{kl}(x)$ is defined by (53) and it is still rotationally invariant as shown by (54), exactly as in the electrostatic model. The only difference is that W_{kl} now contains contributions to the energy from the fine structure. Likewise, the molecular Hamiltonian in the Born-Oppenheimer representation, $H_{\mathrm{mol},kl}$, is (88), the same as in the electrostatic model, as is the projected Hamiltonian $K_{\mathrm{mol},kl}$.

As for the angular momentum, it is more interesting to work with $\mathrm{J} = \mathrm{L}+\mathrm{S}$ than with $\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e$ alone. We follow the steps of (90) in converting J to the Born-Oppenheimer representation,

$$\begin{aligned}\mathrm{J}\Psi(\mathrm{X},\mathrm{r},m) = (\mathrm{L}_n+\mathrm{L}_e+\mathrm{S})\sum_k \psi_k(\mathrm{X})\,\phi_k(\mathrm{X};\mathrm{r},m) &= \sum_k [(\mathrm{L}_n+\mathrm{L}_e)\psi_k(\mathrm{X})]\,\phi_k(\mathrm{X};\mathrm{r},m)\\ &+\sum_k \psi_k(\mathrm{X})\,[(\mathrm{L}_n+\mathrm{L}_e+\mathrm{S})\phi_k(\mathrm{X};\mathrm{r},m)],\end{aligned} \tag{109}$$

where the differential operator $\mathrm{L}_n+\mathrm{L}_e$ is distributed as before, while the operator S only acts on the second factor (which depends on the spin quantum numbers m). But by (107) the second major sum vanishes, as does the term involving L_e in the first sum. The result is

$$\mathrm{J} = \mathrm{L}+\mathrm{S} = \mathrm{L}_n+\mathrm{L}_e+\mathrm{S} \longleftrightarrow \mathrm{L}_n\,\delta_{kl}. \tag{110}$$

Thus, in the fine structure model with $N_e =$ even, in the Born-Oppenheimer representation, the nominal, orbital angular momentum of the nuclei alone represents physically the total angular momentum of the molecule, both nuclear and electronic, including the electron spin. This is exact.

Thus conservation of angular momentum is represented in the Born-Oppenheimer representation by (92), exactly as in the electrostatic model. That is, the components of $H_{\mathrm{mol},kl}$ must be scalars under nuclear orbital rotations. That they are follows from the transformation property of the derivative couplings, (96), which is the same as in the electrostatic model.

Finally, consider a solution ψ_k for $k \in I$ of the Born-Oppenheimer version of the Schrödinger equation, (97), that is also an eigenfunction of the matrix operators $L_n^2\,\delta_{kl}$ and $L_{nz}\,\delta_{kl}$ with quantum numbers (l, m_l). Every component $k \in I$ of such a solution is an eigenfunction of L_n^2 and L_{nz} with the same quantum numbers. When this is converted to a molecular wave function by (72) it is automatically an eigenfunction of J^2 and J_z with the same quantum numbers, and this is exact.

B. Fine Structure Details, Odd Number of Electrons

1. Basis States

In the fine structure model with $N_e =$ odd the energy levels are Kramers doublets. See Sec. II G 2 for terminology regarding "levels" and "surfaces." We define a subset of strongly coupled surfaces

$$I = \{k_0, k_0+1, \ldots, k_0+N_s-1\}, \tag{111}$$

where N_s is the number of surfaces, which replaces (48). Now the number of levels is $N_l = 2N_s$. We denote the adiabatic basis vectors by $|ax;k\mu\rangle$, $\mu = 1,2$, which are energy eigenstates for $k \in I$,

$$H_e(x)\,|ax;k\mu\rangle = \varepsilon_k(x)\,|ax;k\mu\rangle, \qquad k \in I, \tag{112}$$

where the energy depends on k but not μ (this is the Kramers degeneracy). For $k \in I$ the vectors $|ax;k\mu\rangle$ form a discrete, orthonormal basis that spans $S(x)$. Because $H_e(x)$ commutes with T, these basis vectors can be chosen to be quaternionic, as we assume (see (A10)).

Initially we make some assignment of these vectors along a section S, that is, of phase and frame conventions so that the basis is quaternionic. This assignment cannot be smooth when S contains a degeneracy, that is, a crossing of two or more surfaces or Kramers doublets. The codimension of such degeneracies is different from the case of the electrostatic model (generically 5 or sometimes 3 instead of 2, see Mead (1980a, 1987); Matsika and Yarkony (2001, 2002a)), but the fact remains that in general a continuous assignment of adiabatic basis states on S is impossible. We accept the discontinuities and extend the definitions of the basis vectors along rotational fibers by means of a modified rule, see (115) below, which differs from the ones (52) or (105) used previously. This rule guarantees that the adiabatic basis, so extended, remains quaternionic.

Given the adiabatic basis there are various algorithms for defining a diabatic basis, which is free of the singularities of the adiabatic basis. We denote the diabatic basis by $|dx;k\mu\rangle$. If the adiabatic basis is quaternionic, we must ask whether the diabatic basis so constructed is too. The answer depends on the algorithm, but we have checked both the singular-value diabatic basis, which is due to Pacher, Cederbaum, and Köppel (1988, 1993), and the parallel-transported diabatic basis. These bases were the subject of a recent study of ours (Littlejohn, Rawlinson, and Subotnik (2022)). It turns out that if the adiabatic basis is quaternionic, then the diabatic basis, constructed by either of these two algorithms, is also quaternionic. In this way we can construct a diabatic basis on S that is quaternionic; this can then be propagated along rotation fibers by (115), giving us a smooth, quaternionic, diabatic basis in a region of full dimensionality.

The two bases are connected by a unitary transformation,

$$|dx;k\mu\rangle = \sum_{l,\nu} |ax;l\nu\rangle V_{l\nu,k\mu}(x) \tag{113}$$

the analog of (51) in the electrostatic model. Since the two bases are quaternionic, the matrix $V_{l\nu,k\mu}$ is both unitary and quaternionic, that is, the minor, 2 × 2 matrices V_{kl}, whose $(\nu\mu)$ components are $V_{l\nu,k\mu}$, are quaternions. See Appendix B. The $N_s \times N_s$ block of this matrix of quaternions corresponding to the strongly coupled subspace belongs to the unitary, quaternionic group $U(N_s, \mathbb{H})$. Unlike the electrostatic case, the matrix $V_{l\nu,k\mu}$ is not constant along rotational fibers, but rather satisfies

$$V_{kl}(Rx_0) = u\,V_{kl}(x_0)\,u^{-1}, \tag{114}$$

where $R = R(u)$. This is written in terms of the minor matrices or quaternions that make up V.

2. Working Basis and Its Properties

Thus we obtain a working basis, which we denote by simply $|x;k\mu\rangle$, which is either the adiabatic basis $|ax;k\mu\rangle$ when that is smooth or else the diabatic basis $|dx;k\mu\rangle$. The vectors of the working basis are propagated along rotational fibers by the rule,

$$|Rx_0;k\mu\rangle = \sum_{\nu} U_e(u)\,|x_0;k\nu\rangle \, \big(u^{-1}\big)_{\nu\mu}. \tag{115}$$

which gives the basis vectors at $x = Rx_0$ in terms of those at x_0. In this equation, u on the right hand side means one of the two elements of $SU(2)$ that satisfies $R = R(u)$, which differ by a sign. Because there is an odd number of factors of u contained in the operator $U_e(u)$ and an extra one in the factor of u^{-1}, the total number is even and the right hand side does not depend on which of the two u's is chosen. This was one reason for introducing the factor of u^{-1} on the right hand side;

without it, the formula would not define a single-valued basis set along a rotational fiber. This factor evidently causes a mixing among the Kramers pair as the molecule is rotated.

The rule (115) has several important properties. The first is that if $|x_0;k\mu\rangle$ is quaternionic at x_0, then $|Rx_0;k\mu\rangle$ is quaternionic at $x = Rx_0$. The second is that if $|x_0;k\mu\rangle$ is an electronic eigenstate at x_0 (which is the case for $k \in I$ in the adiabatic basis), then $|Rx_0;k\mu\rangle$ is an electronic eigenstate at $x = Rx_0$, with the same eigenvalue. The proofs are given in Appendix D.

Another important property is the transformation law,

$$|Rx;k\mu\rangle = \sum_{\nu} U_e(u)\,|x;k\nu\rangle\; u^{-1}{}_{\nu\mu} \tag{116}$$

which is like (115) but with x_0 replaced by x. Compare (52) and (56) in the electrostatic model, and see the discussion below (56). In particular, notice that (115) defines the basis states along a rotation fiber, and (116) is a property of those basis states, once defined. The proof of (116) is given in Appendix D.

If we had chosen u instead of u^{-1} in (115) then we would have a single-valued definition of phase and frame conventions along a rotational fiber, but (116) would not be valid, with either u or u^{-1}. This was the main reason we chose u^{-1} in (115), which we believe is the most satisfactory definition of phase and frame conventions along rotational fibers in the fine structure model with N_e = odd. This choice leads to a simple interpretation of the wave function $\psi_{k\mu}(\mathrm{X})$ for fixed k and $\mu = 1,2$ as belonging to a particle of pseudo-spin 1/2, moving on a multidimensional, potential energy surface.

Given our basis states $|x;k\mu\rangle$ we define basis wave functions $\phi_{k\mu}(\mathrm{X};\mathrm{r},m)$ by (27), that is, with the double index $(k\mu)$. The transformation to the Born-Oppenheimer representation is given by

$$\Psi(\mathrm{X},\mathrm{r},m) = \sum_{k\mu} \psi_{k\mu}(\mathrm{X})\,\phi_{k\mu}(\mathrm{X};\mathrm{r},m), \tag{117}$$

which we can also write as

$$\Psi(\mathrm{X},\mathrm{r},m) \longleftrightarrow \psi_{k\mu}(\mathrm{X}). \tag{118}$$

Equation (117) involves a sum on both k and μ and is the exact representation of the wave functions $\Psi(\mathrm{X},\mathrm{r},m)$ (and is not to be confused with (28) which applies to a single-surface problem). Double indices also appear in the Born-Oppenheimer representation of operators,

$$A \longleftrightarrow A_{k\mu,l\nu}, \tag{119}$$

where the right hand side can also be written in terms of minor matrices A_{kl}.

3. Representation of Angular Momentum

We now let R in (116) be infinitesimal, and proceed as in the derivation of (62) or (107). We invoke the infinitesimal version of u^{-1},

$$u^{-1} = 1 + \frac{i}{2}\theta\,\hat{n}\cdot\sigma, \tag{120}$$

and follow the steps leading to (62), finding

$$\mathrm{J}|x;k\mu\rangle = (\mathrm{L}_n + \mathrm{L}_e + \mathrm{S})|x;k\mu\rangle = \frac{\hbar}{2}\sum_{\nu}|x;k\nu\rangle(\sigma)_{\nu\mu}, \tag{121}$$

which takes the place of (62) in the electrostatic model or (107) in the fine structure model with N_e = even. The nonzero result on the right hand side comes from the factor of u^{-1} that was inserted into the transformation law (115).

This allows us to find the total angular momentum of the molecule in the Born-Oppenheimer representation. We proceed as in (109) using the expansion (117), finding

$$\begin{aligned}\mathrm{J}\Psi(\mathrm{X},\mathrm{r},m) &= (\mathrm{L}_n + \mathrm{L}_e + \mathrm{S})\sum_{k\mu}\psi_{k\mu}(\mathrm{X})\,\phi_{k\mu}(\mathrm{X};\mathrm{r},m)\\ &= \sum_{k\mu}[(\mathrm{L}_n + \mathrm{L}_e)\psi_{k\mu}(\mathrm{X})]\,\phi_{k\mu}(\mathrm{X};\mathrm{r},m)\\ &\quad + \sum_{k\mu}\psi_{k\mu}(\mathrm{X})\,[(\mathrm{L}_n + \mathrm{L}_e + \mathrm{S})\phi_{k\mu}(\mathrm{X};\mathrm{r},m)].\end{aligned} \tag{122}$$

In the first major sum on the right the contribution from L_e vanishes as before but now in view of (121) the second major sum is nonzero. Altogether we find

$$\mathrm{J}\Psi(\mathrm{X},\mathrm{r},m) = \sum_{k\mu}[\mathrm{L}_n\psi_{k\mu}(\mathrm{X})]\,\phi_{k\mu}(\mathrm{X};\mathrm{r},m) + \sum_{k\mu\nu}\psi_{k\mu}(\mathrm{X})\,\phi_{k\nu}(\mathrm{X};\mathrm{r},m)\left(\frac{\hbar}{2}\sigma\right)_{\nu\mu}. \tag{123}$$

Swapping μ and ν in the second term makes both sums a linear combination of $\phi_{k\mu}(\mathrm{X};\mathrm{r},m)$, so that the result can be written,

$$\mathrm{J} \longleftrightarrow \mathrm{L}_n\,\delta_{kl}\,\delta_{\mu\nu} + \delta_{kl}\left(\frac{\hbar}{2}\sigma\right)_{\mu\nu}, \tag{124}$$

or, in terms of minor matrices,

$$\mathrm{J} \longleftrightarrow \delta_{kl}\,(\mathrm{L}_n + \mathrm{K}). \tag{125}$$

Here $\mathrm{K} = (\hbar/2)\sigma$ is a vector of minor matrices which act on a Born-Oppenheimer wave function $\psi_{k\mu}$ just by matrix multiplication in the pseudo-spin index μ.

This motivates the definition $\mathrm{I} = \mathrm{L}_n + \mathrm{K}$ made earlier (see (38)). The angular momentum I is associated with rotation operators that are parameterized by $u \in SU(2)$ and that we denote by $U_i(u)$. They are defined by

$$U_i(u) = U_i(\hat{n}, \theta) = \exp \; -\frac{i}{\hbar}\theta \hat{n} \cdot \mathrm{I} \; , \tag{126}$$

and their action on wave functions $\psi_\mu(\mathrm{X})$ is given by

$$U_i(u)\psi_\mu(\mathrm{X}) = \sum_\nu u_{\mu\nu}\, \psi_\nu \; R^{-1}\mathrm{X}. \tag{127}$$

This implies the representation property, $U_i(u_1)U_i(u_2) = U_i(u_1u_2)$. In (127) we write $\psi_\mu(\mathrm{X})$ without a k-index because it is useful to think of this as the wave function of a pseudoparticle of spin 1/2. The Born-Oppenheimer wave function $\psi_{k\mu}(\mathrm{X})$ can be thought of as an infinite-dimensional vector of such wave functions, indexed by k.

4. Derivative Couplings

The fine structure derivative couplings when $N_e =$ odd have been defined in (29). They are denoted $\mathrm{F}_{\alpha;k\mu,l\nu}(x)$, or, as minor matrices which turn out to be quaternions, as $\mathrm{F}_{\alpha;kl}(x)$. These form an anti-Hermitian matrix of quaternions, as noted in (34).

These transform along rotational fibers according to

$$\mathrm{F}_{\alpha;kl}(Rx) = u[R\mathrm{F}_{\alpha;kl}(x)]u^{-1}, \tag{128}$$

where $R = R(u)$. This may be compared to (70), which applies both in the electrostatic model and in the fine structure model with $N_e =$ even. The derivation is similar if slightly more complicated.

We also require the transformation of the derivative couplings under conjugation by $U_i(u)$. A purely spatial vector like X_α transforms as a vector operator,

$$U_i(u)\,\mathrm{X}_\alpha\, U_i(u)^\dagger = R^{-1}\mathrm{X}_\alpha, \tag{129}$$

since the pseudo-spin part of $U_i(u)$ does nothing, while in the case of a minor matrix ω with no spatial dependence we have

$$U_i(u)\,\omega\, U_i(u)^\dagger = u\omega u^{-1}, \tag{130}$$

since the spatial part does nothing. Therefore

$$U_i(u)\,\mathrm{F}_{\alpha;kl}(x)\,U_i(u)^\dagger = u\mathrm{F}_{\alpha;kl} \; R^{-1}xu^{-1} = R^{-1}\mathrm{F}_{\alpha;kl}(x), \tag{131}$$

where in the last step we use a version of (128) with $R \to R^{-1}$ and $u \to u^{-1}$. This may be compared to (96) which applies both in the electrostatic model and in the fine structure model with N_e = even.

Finally, we compute the components of the derivative couplings in a purely rotational direction, defining δx and $\delta \mathrm{X}_\alpha$ as in (57) and (58). Then we find

$$\sum_{\alpha=1}^{N-1} \delta \mathrm{X}_\alpha \cdot \mathrm{F}_{\alpha;k\mu,l\nu}(x) = \frac{i}{\hbar}\theta \hat{\mathbf{n}} \cdot \left(-\langle x;k\mu|(\mathrm{L}_e + \mathrm{S})|x;l\nu\rangle + \frac{\hbar}{2}\delta_{kl}\,\sigma_{\mu\nu} \right), \tag{132}$$

where we use (121). This may be compared to (71) in the electrostatic model or (108) in the fine structure model with $N_e =$ even.

5. The Hamiltonian

When the electronic Hamiltonian $H_e(x)$ is converted to the Born-Oppenheimer representation, it becomes a matrix,

$$W_{k\mu,l\nu}(x) = \langle x;k\mu|H_e(x)|x;l\nu\rangle, \tag{133}$$

which can be interpreted in terms of minor matrices denoted $W_{kl}(x)$. Since $H_e(x)$ commutes with time reversal, these minor matrices are quaternions; and since $H_e(x)$ is Hermitian, these quaternions satisfy $W_{kl}(x) = \overline{W_{lk}(x)}$. It then follows from (104) and (116) that

$$W_{kl}(Rx) = uW_{kl}(x)u^{-1}. \tag{134}$$

In the case of the fine structure model with $N_e =$ odd, the matrix $W_{kl}(x)$ is not constant along rotational fibers. An exception is the diagonal elements; these are real quaternions, $W_{kk} = \overline{W_{kk}}$, that is, as minor matrices they are a multiple of the identity, so the factors of u and u^{-1} in (134) cancel. In particular, for a single surface problem $W_{k_0k_0}(x)$ is the Kramers degenerate eigenvalue $\varepsilon_{k_0}(x)$.

To transform the molecular Hamiltonian to the Born-Oppenheimer representation we start with the momentum, which transforms according to

$$\mathrm{P}_\alpha \longleftrightarrow \mathrm{P}_\alpha\,\delta_{kl}\,\delta_{\mu\nu} - i\hbar \mathrm{F}_{\alpha;k\mu,l\nu}(x). \tag{135}$$

This simplifies in the language of minor matrices,

$$\mathrm{P}_\alpha \longleftrightarrow \mathrm{P}_\alpha\,\delta_{kl} - i\hbar \mathrm{F}_{\alpha;kl}(x), \tag{136}$$

where now it is understood that P_α is multiplied by the unit minor matrix. The result (136) looks exactly the same as (82) in the electrostatic model except that now the operator in the Born-Oppenheimer representation is interpreted as a minor matrix.

Similarly, the molecular Hamiltonian H_{mol} becomes a matrix of minor matrices $H_{\text{mol},kl}$ in the Born-Oppenheimer representation, the formula for which is (88), exactly as in the electrostatic model but now reinterpreted as a relation among minor matrices. Of course, one must respect the order of multiplication of minor matrices when expanding the products shown.

Since in the molecular representation H_{mol} commutes with J, in the Born-Oppenheimer representation we expect the matrix $H_{\text{mol},kl}$ of minor matrices to commute with $\mathrm{I}\,\delta_{kl} = (\mathrm{L}_n + \mathrm{K})\delta_{kl}$, another such matrix. See (125). But since the latter matrix is a multiple of the identity δ_{kl}, we expect

$$[\mathrm{I}, H_{\text{mol},kl}] = [\mathrm{L}_n + \mathrm{K}, H_{\text{mol},kl}] = 0, \tag{137}$$

which takes the place of (92) in the electrostatic model or the fine structure model with an even number of electrons. That is, there is now a contribution K to the angular momentum, and everything is interpreted as minor matrices.

Equation (137) holds if and only if every component $H_{\text{mol},kl}$ of the Hamiltonian commutes with $U_i(u)$, defined by (126) or (127), that is, if every such component transforms as a scalar under conjugation by $U_i(u)$. To show that they do we start with the fact that P_α transforms as a vector operator, just like X_α (see (129)), and so does $\mathrm{F}_{\alpha;kl}$ (see (131)). Therefore dot products that look like $\mathrm{P}\cdot\mathrm{P}$, $\mathrm{P}\cdot\mathrm{F}$ or $\mathrm{F}\cdot\mathrm{F}$ are scalars. As for the potential energy matrix $W_{kl}(x)$, we have

$$U_i(u)\, W_{kl}(x)\, U_i(u)^\dagger = u W_{kl}\ R^{-1} x u^{-1} = W_{kl}(x), \tag{138}$$

where in the last step we use (134) with R and u swapped with R^{-1} and u^{-1}. Thus we check (137).

In the Born-Oppenheimer approximation $H_{\text{mol},kl}$ is replaced by its projected version $K_{\text{mol},kl}$, which is the same when $k, l \in I$ and zero otherwise. Therefore, just as in the other models, $K_{\text{mol},kl}$ commutes with I since $H_{\text{mol},kl}$ does. The Born-Oppenheimer approximation to the Schrödinger equation can be written exactly as in (97), except that now $K_{\text{mol},kl}$ is a minor matrix of operators and ψ_k must be understood as a 2-component pseudo-spinor with components $\psi_{k\mu}$, $\mu = 1, 2$. A solution of this equation will also be an eigenfunction of $I^2\,\delta_{kl}$ and $I_z\,\delta_{kl}$ with quantum num-bers (i, m_i) if each spinor component ψ_k is an eigenfunction of I^2 and I_z with the same quantum numbers. Such an eigenfunction, when converted to the molecular representation via (117), will automatically be an eigenfunction of J^2 and J_z with the same quantum numbers (i, m_i).

VII. THE DRESSING TRANSFORMATION

As explained, the Born-Oppenheimer approximation or its generalization to multisurface problems can be described as just throwing away off block-diagonal elements of $H_{\mathrm{mol},kl}$, that is, for $k \in I$ and $l \notin I$ or $k \notin I$ and $l \in I$. A more satisfactory procedure, however, is to remove these off-diagonal terms by means of unitary transformations. This is conveniently done in the Born-Oppenheimer representation by mapping operators into their Weyl transforms (McDonald (1988)), and using a version of the Moyal bracket (Moyal (1949)) for carrying out the perturbation expansion. The main ideas of this approach are given by Littlejohn and Flynn (1991), and applied to the Born-Oppenheimer approximation by Weigert and Littlejohn (1993). See also Panati, Spohn, and Teufel (2002); Teufel (2003). In this section we shall briefly summarize the ideas and conclusions, enough to show their relevance to the subject of angular momentum. For simplicity we shall describe the situation in the electrostatic model.

The method generates a power series in κ^2, where $\kappa = (m/M)^{1/4}$ is the usual Born-Oppenheimer ordering parameter. When we refer to "first order," we shall mean, first order in κ^2, while "second order" means order κ^4, etc.

In the first step we transform the molecular Hamiltonian,

$$\bar{H}_{\mathrm{mol},1} = U_1 \, H_{\mathrm{mol}} \, U_1^{\dagger}, \tag{139}$$

where U_1 is a unitary transformation that is designed make the off-diagonal terms of $\bar{H}_{\mathrm{mol},1}$ vanish to lowest order in κ^2. All operators are expressed in the Born-Oppenheimer representation, that is, as matrices (thus, for example, $\bar{H}_{\mathrm{mol},1kl}$ and $U_{1,kl}$), but the subscripts are suppressed in (139). The unitary operator U_1 is expressed in terms of an anti-Hermitian generator G_1, $U_1 = \exp(G_1)$, so that, for any operator A, we have

$$U_1 A U_1^{\dagger} = A + [G_1, A] + \frac{1}{2!}[G_1, [G_1, A]] + \ldots \tag{140}$$

This series of iterated commutators turns into a power series in κ^2.

A single unitary transformation of the type shown in (139) is capable of removing the off-diagonal terms only to first order, but there will remain second-order terms. We can apply a second unitary transformation to remove these, leaving behind third-order, off-diagonal terms. Thus to fully remove these terms we must contemplate an infinite number of unitary transformations, for which we write, $U = \ldots U_3 U_2 U_1$, where each U_n has a generator G_n. The generators G_n turn out to be of order κ^{2n}. In practice, the first generator G_1 is the most important, and is responsible for most of what is described in the literature as "nonadiabatic corrections" to the Born-Oppenheimer approximation.

It turns out that G_1 contains energy denominators of the form $\varepsilon_k(x) - \varepsilon_l(x)$, where $k \in I$ and $l \notin I$. Thus when this energy difference is of order κ^2 or smaller, the expansion (140) breaks down and levels cannot be separated by adiabatic means. This gives some quantitative meaning to the notion of "strongly coupled" levels, which were discussed in Sec. III C.

This sequence of unitary transformations produces Hamiltonians $\bar{H}_{\text{mol},1}$, $\bar{H}_{\text{mol},2}$, etc. We will write simply $\bar{H}_{\text{mol}}$ for $\bar{H}_{\text{mol},\infty}$, so that $\bar{H}_{\text{mol}} = UH_{\text{mol}}U^\dagger$. We will refer to U as the "dressing transformation" and $\bar{H}_{\text{mol}}$ as the "dressed Hamiltonian." The latter is block-diagonal to all orders in κ^2.

We can now distinguish what we will call the "original Born-Oppenheimer representation," what was called in Sec. V simply the "Born-Oppenheimer representation," from the "dressed Born-Oppenheimer representation." There is, of course, also the molecular representation, which was described in Sec. V. Physical observables have different operators representing them in the different representations. For example, the physical observables which are the Jacobi vectors are represented by the operators X_α in the molecular representation, that is, the operators are multiplication by X_α. As described in Sec. V, these physical observables are represented by the matrices $\mathrm{X}_\alpha\,\delta_{kl}$ in the original Born-Oppenheimer representation, which we can write simply as X_α if we remember that an identity matrix is implied. In the dressed Born-Oppenheimer representation, however, they are represented by the operators $\bar{\mathrm{X}}_\alpha = U\mathrm{X}_\alpha U^\dagger$, which are not the same as X_α. In fact, to first order in κ^2, we have

$$\bar{\mathrm{X}}_\alpha = \mathrm{X}_\alpha + [G_1, \mathrm{X}_\alpha] + \ldots. \tag{141}$$

Similar statements can be made about the nuclear momenta, which in the original Born-Oppenheimer representation involve the derivative couplings (see (82)).

As for the total orbital angular momentum of the molecule, we have seen that it is represented by $\mathrm{L} = \mathrm{L}_n + \mathrm{L}_e$ in the molecular representation and $\mathrm{L}_n\,\delta_{kl}$ in the original Born-Oppenheimer representation, which we can abbreviate as simply L_n if we remember that it is multiplied by the identity matrix. As for the dressed Born-Oppenheimer representation, the same physical observable is represented by

$$U \mathrm{L}_n U^\dagger = U \sum_{\alpha=1}^{N-1} \mathrm{X}_\alpha \times \mathrm{P}_\alpha \, U^\dagger = \sum_{\alpha=1}^{N-1} \bar{\mathrm{X}}_\alpha \times \bar{\mathrm{P}}_\alpha \, . \tag{142}$$

But the dressing of L_n involves a series of commutators with the generators G_n, such as shown in (140). The generators G_n are responsible for transforming the rotationally invariant Hamiltonian H_{mol} to its diagonalized version, $\bar{H}_{\mathrm{mol}}$, which is also rotationally invariant. The generators G_n that do this are themselves rotationally invariant, so they commute with angular momentum and all the correction terms in power series like (140) vanish. Thus we have

$$\sum_{\alpha=1}^{N-1} \mathrm{X}_\alpha \times \mathrm{P}_\alpha = \sum_{\alpha=1}^{N-1} \bar{\mathrm{X}}_\alpha \times \bar{\mathrm{P}}_\alpha \, , \tag{143}$$

to all orders of the Born-Oppenheimer expansion. The dressing does nothing to the angular momentum L_n, which represents physically the total angular momentum of the molecule in both the original Born-Oppenheimer representation and the dressed version of it.

In the case of single-surface problems the dressing transformation creates a 1×1 block $\bar{H}_{\mathrm{mol},k_0k_0}$ on the diagonal, that is decoupled from all other levels to all orders of κ. Thus in the dressed Born-Oppenheimer representation the solution of the Schrödinger equation is a simple product form as seen in (14), to all orders of κ^2. For this reason we suspect that there is a connection between Moyal perturbation theory, as discussed here, and the method of "exact factorization" (Abedi, Maitra, and Gross (2010, 2012); Cederbaum (2013); Scherrer *et al.* (2015); Schild, Agostini, and Gross (2016); and Requist, Tandetzky, and Gross (2016); Martinazzo and Burghardt (2022)). The possibility of such a connection is a project for the future.

The dressed Hamiltonian $\bar{H}_{\mathrm{mol}}$ may be compared to K_{mol}, which was obtained in Sec. V C by throwing away off-diagonal terms. Both are block-diagonal, but they are not the same Hamiltonians. This is because the dressing transformation modifies the diagonal block, adding extra terms to it. The first such term appears at second order. This term has evidently been discovered independently several times (Moody, Shapere, and Wilczek (1989); Weigert and Littlejohn (1993); Goldhaber (2005)), but it has had no impact on the chemical literature. It is of order κ^4 and is therefore small, but it is of the same order as terms that are routinely discussed in connection with Born-Oppenheimer theory. We will say more about this term in future publications.

VIII. DISCUSSION AND CONCLUSIONS

We have presented an in-depth analysis of angular momentum in the Born-Oppenheimer theory of polyatomic molecules, revealing exact equivalences among its various representations. We have done this both in the electrostatic model and when fine structure effects and electron spin are included. Several new results are reported regarding the transformation laws under rotations of the Hamiltonian, basis states and derivative couplings. A dressing transformation that replaces the Born-Oppenheimer approximation reveals further exact equivalences among representations of angular momentum.

These findings are general and should be applicable even when one does not have an exact diagonalization of the electronic Hamiltonian, as is usual in practice. On the other hand, one will need to use caution when applying some of the formalism above to non-Hermitian electronic structure methods (e.g., coupled-cluster methods), where it is known that derivative couplings must be calculated delicately because the Hellman-Feynman theorem is not easily applied (Ichino, Gauss, and Stanton (2009); Tajti and Szalay (2009); Faraji, Matsika, and Krylov (2018)).

Finally, note that we have not made any semiclassical approximations above, and the exact equivalences described above hold rigorously. That being said, the results do have clear implications for semiclassical calculations. In particular, within surface hopping calculations (Fatehi *et al.* (2011)), there has been a long literature regarding questions of how to treat electronic momentum and how to conserve momentum with electron translation factors (Bates and McCarroll (1958); Schneiderman and Russek (1969); Delos (1981); Illescas and Riera (1998)). These questions arise because the electronic momentum is hidden in the phase conventions of the Born-Oppenheimer representation. To that extent this article has pointed out that similar questions can also be raised in the context of rotations and angular momentum. This line of study will be pursued in a subsequent publication as well.

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Appendix A: Time Reversal

Time reversal is covered in texts (Messiah (1966); Sakurai and Napolitano (2011)) and specifically in molecular theory (Mead (1979, 1980a); Rösch (1983); Mead (1987); Koizumi and Sugano (1995); and Johnsson and Aitchison (1997); Schön and Köppel (1998); Matsika and Yarkony (2001, 2002b,a)). We prefer an approach based on invariant subspaces.

There are at least two distinct time reversal operators relevant to this article: the one that acts on electronic wave functions $\phi(\mathrm{r})$, relevant in the electrostatic model, and the one that acts on wave functions $\phi(\mathrm{r}, m)$, relevant in the fine structure model. In the electrostatic model time reversal acts on electronic wave functions according to

$$(T\phi)(\mathrm{r}) = \phi(\mathrm{r})^{*}, \tag{A1}$$

that is, by simple complex conjugation, so $T^2 = +1$. In the fine structure model the wave function $\phi(\mathrm{r}, m)$ depends on spin and time reversal acts according to

$$(T\phi)(\mathrm{r}, m) = \sum_{m_1} \ldots \sum_{m_{N_e}} \tau_{m_1 m'_1} \ldots \tau_{m_{N_e} m'_{N_e}} \phi(\mathrm{r}, m')^{*}, \tag{A2}$$

where m' is a primed version of (6), where each magnetic quantum number m'_i, $i = 1, \ldots, N_e$ ranges over $\pm 1/2$, and where τ is the matrix

$$\tau = e^{-i\pi\sigma_y/2} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{A3}$$

The matrix τ is the spin rotation $u(\hat{y}, \pi)$ in the notation (C1). We abbreviate an equation like (A2) by writing

$$(T\phi)(\mathrm{r}, m) = \sum_{m'} (\tau \ldots \tau)_{mm'} \phi(\mathrm{r}, m')^{*}. \tag{A4}$$

1. Properties of T

Time reversal T is an antiunitary operator, $T^{\dagger}T = TT^{\dagger} = 1$, that satisfies $T^2 = +1$ in the electrostatic model or in the fine structure model with $N_e =$ even, and $T^2 = -1$ in the fine structure model with $N_e =$ odd. These are the only properties of T that are needed for the rest of this appendix.

If $\mathcal{H}$ is a Hilbert space upon which T acts and $\mathcal{S} \subset \mathcal{H}$ is a subspace, then we say that $\mathcal{S}$ is *invariant* under T if for every $|\psi\rangle \in \mathcal{S}$, $T|\psi\rangle \in \mathcal{S}$ (that is, T maps $\mathcal{S}$ into itself). Important examples of invariant subspaces include the entire Hilbert space ($\mathcal{S} = \mathcal{H}$) and eigenspaces (possibly degenerate) of a Hamiltonian that commutes with T. Many other examples appear in this article. As for energy eigenspaces, note that if $H|\psi\rangle = E|\psi\rangle$, $T^{\dagger}HT = H$, and $|\phi\rangle = T|\psi\rangle$, then $H|\phi\rangle = E|\phi\rangle$. That is, T maps energy eigenstates into other energy eigenstates of the same energy. This does not say whether $|\phi\rangle$ is linearly independent of $|\psi\rangle$.

Antiunitary operators map scalar products into their complex conjugates, that is, if $|\psi'\rangle = T|\psi\rangle$ and $|\phi'\rangle = T|\phi\rangle$, then $\langle\phi'|\psi'\rangle = \langle\phi|\psi\rangle^{*} = \langle\psi|\phi\rangle$. This in turn means that time reversal maps orthonormal frames into other orthonormal frames, that is, if $\{|n\rangle, n = 1, \ldots, N\}$ is an orthonormal frame, $\langle n|m\rangle = \delta_{nm}$, and if $|n'\rangle = T|n\rangle$, then $\langle n'|m'\rangle = \delta_{nm}$. The frame $\{|n\rangle\}$ need not be complete (it need not span the whole Hilbert space). This does not say whether the new frame $\{|n'\rangle\}$ is linearly independent of the old one $\{|n\rangle\}$.

In the following we will take subspaces that are invariant under T and break them down into smaller, mutually orthogonal subspaces that are also invariant under T. First we note that if $\mathcal{S}$ is invariant under T, then it is also invariant under $T^{\dagger}$, as follows from the fact that $T^{\dagger} = \pm T$ (the same sign as in $T^2 = \pm 1$).

Now let $\mathcal{S} \subset \mathcal{H}$ be an invariant subspace under T, let $\mathcal{A} \subset \mathcal{S}$ be a subspace of $\mathcal{S}$ that is also invariant under T, and let $\mathcal{B} \subset \mathcal{S}$ be the space orthogonal to $\mathcal{A}$ inside $\mathcal{S}$, so that

$$\mathcal{S} = \mathcal{A} \oplus \mathcal{B}. \tag{A5}$$

Then $\mathcal{B}$ is invariant under T. To prove this we note that a vector $|\phi\rangle \in \mathcal{B}$ if and only if $|\phi\rangle \in \mathcal{S}$ and $\langle\phi|\psi\rangle = 0$ for all $|\psi\rangle \in \mathcal{A}$. Now let $|\phi\rangle \in \mathcal{B} \subset \mathcal{S}$ and let $|\phi'\rangle = T|\phi\rangle$, so that $|\phi'\rangle \in \mathcal{S}$. We wish to show that $|\phi'\rangle$ is orthogonal to all $|\psi\rangle \in \mathcal{A}$, hence $|\phi'\rangle \in \mathcal{B}$. First we note that $\langle\phi'|\psi\rangle = (\langle\phi|T^{\dagger})|\psi\rangle = [\langle\phi|(T^{\dagger}|\psi\rangle)]^{*} = \langle\phi|\psi'\rangle^{*}$, where $|\psi'\rangle = T^{\dagger}|\psi\rangle$. But $|\psi'\rangle \in \mathcal{A}$ since $\mathcal{A}$ is invariant under $T^{\dagger}$, and therefore the scalar product vanishes. Therefore $|\phi'\rangle \in \mathcal{B}$, and $\mathcal{B}$ is invariant under T.

2. Case $T^2 = +1$

Now we specialize to the case $T^2 = +1$. Let $\mathcal{S}$ be a subspace invariant under T, with $\dim \mathcal{S} \geq 1$. Then $\mathcal{S}$ possesses a 1-dimensional, invariant subspace. To prove this let $|\psi\rangle \in \mathcal{S}$ be a nonzero vector and consider the two vectors $|\psi\rangle$ and $T|\psi\rangle$. If these are linearly dependent, then $|\psi\rangle$ spans a 1-dimensional, invariant subspace of $\mathcal{S}$. If they are linearly independent then $|\psi\rangle + T|\psi\rangle$ is nonzero and spans a 1-dimensional, invariant subspace.

Then the space inside $\mathcal{S}$, complementary and orthogonal to this 1-dimensional, invariant subspace, is also invariant under T, so, if its dimensionality is ≥ 1, it also possesses an invariant, 1-dimensional subspace. Proceeding by induction, we see that if $\mathcal{S}$ is finite-dimensional, then it can be decomposed into a set of mutually orthogonal, 1-dimensional subspaces, each invariant under T. We will assume that the same holds when $\mathcal{S}$ is infinite-dimensional.

Now let $|e\rangle$ be a unit vector inside a 1-dimensional, invariant subspace. Then $T|e\rangle = e^{i\alpha}|e\rangle$ for some phase factor $e^{i\alpha}$, since both $|e\rangle$ and $T|e\rangle$ are bases inside the 1-dimensional subspace. Then defining $|\phi\rangle = e^{i\alpha/2}|\psi\rangle$, we have

$$T|\phi\rangle = e^{-i\alpha/2}\,T|\psi\rangle = |\phi\rangle, \tag{A6}$$

and $|\phi\rangle$ is invariant under T. That is, by a phase convention we can make the basis in a 1-dimensional, invariant subspace invariant under time reversal. This applies to each of the subspaces into which $\mathcal{S}$ of the previous paragraph was decomposed, so we see that in the case $T^2 = +1$, a T-invariant subspace $\mathcal{S}$ always possesses a T-invariant orthonormal basis.

In particular, bases can be chosen inside the eigenspaces of a Hamiltonian that commutes with T that are T-invariant, that is, such a Hamiltonian always possesses a T-invariant energy eigenbasis.

It is easy to show that the matrix elements of a T-invariant operator such as the Hamiltonian in a T-invariant basis are real.

Now let $\mathcal{S} \subset \mathcal{H}$ be a subspace of a Hilbert space and let $\{|e_n\rangle\}$ and $\{|f_n\rangle\}$ be two orthonormal bases in $\mathcal{S}$. Then these bases are connected by a unitary transformation,

$$|f_n\rangle = \sum_m |e_m\rangle U_{mn}, \tag{A7}$$

where $U^\dagger U = UU^\dagger = 1$. If however $\mathcal{S}$ is T-invariant, as are the two bases, $T|e_n\rangle = |e_n\rangle$, $|f_n\rangle = T|f_n\rangle$, then it is easy to show that $U_{mn} = U^*_{mn}$, that is, U is a real, orthogonal matrix. If $N = \dim \mathcal{S}$, then $U \in O(N)$, the latter being the group that connects choices of T-invariant, orthonormal bases in the case $T^2 = +1$. Conversely, if the basis $|e_n\rangle$ in (A7) is T-invariant and if U is real orthogonal, then the basis $|f_n\rangle$ is also T-invariant.

As a special case, if $N = 1$, the group $O(1)$ consists of just two matrices $(+1)$ and (-1), so the choice of a T-invariant basis reduces to the choice of a ± sign.

3. Case $T^2 = -1$

Now let $T^2 = -1$ and, as before, let $\mathcal{S}$ be a subspace invariant under T such that $\dim\mathcal{S} \geq 1$. Then $\mathcal{S}$ does not possess any 1-dimensional, invariant subspaces but it does possess a 2-dimensional invariant subspace. To prove this let $|\psi\rangle \neq 0$ be a vector in $\mathcal{S}$ and notice that $|\phi\rangle = T|\psi\rangle$ is also a nonzero vector in $\mathcal{S}$ since $\mathcal{S}$ is T-invariant and T preserves norms. These vectors are orthogonal,

$$\langle\phi|\psi\rangle = (\langle\psi|T^\dagger)|\psi\rangle = [\langle\psi|(T^\dagger|\psi\rangle)]^* = -[\langle\psi|(T|\psi\rangle)]^* = -\langle\psi|\phi\rangle^* = -\langle\phi|\psi\rangle = 0, \tag{A8}$$

where we use $T^\dagger = -T$, and therefore linearly independent. They span a 2-dimensional, invariant subspace of $\mathcal{S}$, since

$$T(a|\psi\rangle + b|\phi\rangle) = a^*|\phi\rangle - b^*|\psi\rangle, \tag{A9}$$

where we use $T|\phi\rangle = T^2|\psi\rangle = -|\psi\rangle$.

Thus $\dim\mathcal{S} \geq 2$ and $\mathcal{S}$ possesses a 2-dimensional, invariant subspace. If $\mathcal{S}$ is the eigenspace of a T-invariant Hamiltonian, then this implies that all eigenvalues are at least 2-fold degenerate (the usual statement of Kramers degeneracy). But this means that the space inside $\mathcal{S}$ that is orthogonal and complementary to this 2-dimensional, invariant subspace is also invariant, so, by induction, we can continue to split off 2-dimensional, invariant subspaces until $\mathcal{S}$ is exhausted (if ever). If $\mathcal{S}$ is finite-dimensional, this implies that $\mathcal{S}$ can be decomposed into a set of mutually orthogonal, 2-dimensional, invariant subspaces; and we will assume that this can also be done when $\mathcal{S}$ is infinite-dimensional. If $\mathcal{S}$ is finite-dimensional, then $\dim\mathcal{S} = 2N$ is even.

a. Quaternionic bases

If the vector $|\psi\rangle$ of the preceding paragraphs is a unit vector then we may call it $|1\rangle$; and then $|\phi\rangle = T|\psi\rangle = T|1\rangle$ is also a unit vector, call it $|2\rangle$. Then the set $\{|1\rangle, |2\rangle\}$ forms an orthonormal basis in the invariant subspace that they span, such that $T|1\rangle = |2\rangle$ and $T|2\rangle = -|1\rangle$. Doing the same for each of the 2-dimensional, invariant subspaces into which an invariant subspace $\mathcal{S}$ is decomposed, we obtain an orthonormal basis inside $\mathcal{S}$, $\{|k\mu\rangle, k = 1, \ldots, N, \mu = 1, 2\}$, such that

$$T|k\mu\rangle = \sum_\nu |k\nu\rangle\tau_{\nu\mu}, \tag{A10}$$

where τ is given by (A3) and where $\dim\mathcal{S} = 2N$. We shall call such a basis *quaternionic*. (In equations like this we label the rows and columns of τ by $1, 2$; in other places by $1/2, -1/2$.)

Now let $|e;k\mu\rangle$ and $|f;l\nu\rangle$ be two quaternionic bases on a T-invariant subspace S. (The symbols e and f just distinguish the two bases.) Since the bases are orthonormal, they must be connected by a unitary matrix,

$$|f;l\nu\rangle = \sum_{k\mu} |e;k\mu\rangle U_{k\mu,l\nu}, \tag{A11}$$

where

$$\sum_{n\sigma} U_{k\mu,n\sigma} U^{*}_{l\nu,n\sigma} = \delta_{kl}\,\delta_{\mu\nu} = \sum_{n\sigma} U^{*}_{n\sigma,k\mu} U_{n\sigma,l\nu}. \tag{A12}$$

In cases like this we shall view the matrix $U_{k\mu,l\nu}$ as a "major" matrix that is composed of 2 × 2 blocks that we will call "minor" matrices. If we write simply U_{kl}, we shall mean the minor matrix whose $(\mu\nu)$ component is $U_{k\mu,l\nu}$. With this understanding, (A12) can be written,

$$\sum_{n} U_{kn}(U_{ln})^{\dagger} = \delta_{kl} = \sum_{n} (U_{nk})^{\dagger} U_{nl}, \tag{A13}$$

where we use parentheses to make it clear, for example, that $(U_{nk})^{\dagger}$ is the Hermitian conjugate of the minor matrix U_{nk}, and where δ_{kl} is understood to be multiplied by the identity minor matrix.

Now applying T to both sides of (A11) we obtain

$$\sum_{\nu'} |f;l\nu'\rangle \tau_{\nu'\nu} = \sum_{k\mu\mu'} |e;k\mu'\rangle \tau_{\mu'\mu} U^{*}_{k\mu,l\nu}. \tag{A14}$$

We multiply this by $(\tau^{\dagger})_{\nu\sigma}$ and sum over ν, to obtain

$$|f;l\sigma\rangle = \sum_{k\mu\mu'\nu} |e;k\mu'\rangle \tau_{\mu'\mu} U^{*}_{k\mu,l\nu} (\tau^{\dagger})_{\nu\sigma} = \sum_{k\mu'} |e;k\mu'\rangle \left(\tau U^{*}_{kl}\tau^{\dagger}\right)_{\mu'\sigma} = \sum_{k\mu'} |e;k\mu'\rangle U_{k\mu',l\sigma}, \tag{A15}$$

where in the last step we have used (A11) again. Then, since the vectors $|e;k\mu'\rangle$ are linearly independent, we obtain $U_{kl} = \tau U^{*}_{kl}\tau^{\dagger}$, an equation connecting minor matrices. Multiplying this on the left by $\tau^{\dagger}$ and on the right by τ, we obtain

$$\tau^{\dagger} U_{kl} \tau = U^{*}_{kl}, \tag{A16}$$

showing that the minor matrices of U are quaternions (see (B3)).

Thus, U belongs to the group $U(N,\mathbb{H})$, the set of $N \times N$ unitary matrices of quaternions. These matrices satisfy

$$\sum_{n} U_{kn} \overline{U_{ln}} = \delta_{kl} = \sum_{n} \overline{U_{nk}} U_{nl}, \tag{A17}$$

which is (A13) written in quaternionic language. Conversely we can show that if the basis $|e;k\mu\rangle$ is quaternionic and $U \in U(N,\mathbb{H})$, then the basis $|f;l\nu\rangle$ defined by (A11) is also quaternionic.

In the special case $N = 1$, which applies to a single surface problem with an odd number of electrons (a single Kramers doublet), the group $U(1,\mathbb{H})$ consists of unit quaternions, those for which $U_{11}\overline{U_{11}} = 1$. As noted in Appendix B this is the group $SU(2)$. Its role in this context was appreciated by Mead (1987).

b. Quaternionic matrix elements

Finally, let A be a linear operator that commutes with time reversal, $T^\dagger AT = A$. Then the matrix elements of A in a quaternionic basis form minor matrices that are quaternions. To prove this we consider the matrix elements of A with respect to a quaternionic basis $\{|k\mu\rangle\}$,

$$\begin{aligned} A_{k\mu,l\nu} &= \langle k\mu|A|l\nu\rangle = \langle k\mu|(T^\dagger AT|l\nu\rangle) = [(\langle k\mu|T^\dagger)A(T|l\nu\rangle)]^* \\ &= \left[\sum_{\mu'\nu'}(\langle k\mu'|\tau^*_{\mu'\mu})A(|l\nu'\rangle\tau_{\nu'\nu})\right]^* = \left[\sum_{\mu'\nu'}(\tau^\dagger)_{\mu\mu'}A_{k\mu',l\nu'}\tau_{\nu'\nu}\right]^*, \end{aligned} \tag{A18}$$

or, in terms of minor matrices, $A_{kl} = (\tau^\dagger A_{kl}\tau)^*$. Now taking the complex conjugate of both sides and comparing to (B3) we see that A_{kl} is a quaternion.

Appendix B: Quaternions

It is well known that the quantum mechanics of systems with an odd number of fermions is conveniently described in terms of quaternions (Dyson (1962); Finkelstein *et al.* (1962); Rösch (1983); Avron *et al.* (1988); Johnsson and Aitchison (1997); and Zhang (1997); Saue and Aa Jensen (1999); De Leo and Scolarici (2000); Sadovskii and Zhilinskii (2022)). Quaternions also play an important role in representation theory (Simon (1996)). In this appendix we summa-rize what is needed for this article. Our treatment is similar to that of Rösch (1983).

For the purposes of this article a quaternion is a 2 × 2 matrix of the form

$$q = a - i\mathbf{b}\cdot\boldsymbol{\sigma}, \tag{B1}$$

where a and $\mathbf{b} = (b_1, b_2, b_3)$ are real. We denote the set of quaternions by $\mathbb{H}$. Hamilton's unit quaternions i, j, k are identified with the matrices $-i\sigma_i$, $i = 1,2,3$. By this definition the matrices (B1) form a representation of the algebra of quaternions (matrix multiplication and inversion are equivalent to the same operations on quaternions, etc).

The quaternion conjugate to q, denoted $\bar{q}$, is obtained from q by the replacement $\mathbf{b} \to -\mathbf{b}$. Interpreted as a matrix, this is the same as forming the Hermitian conjugate; therefore we will write $\bar{q} = q^\dagger$, and note that $\overline{q_1 q_2} = \bar{q}_2 \bar{q}_1$. A quaternion q is said to be *real* if $\mathbf{b} = 0$, that is, $\bar{q} = q$. The square magnitude of a quaternion is

$$|q|^2 = \bar{q}q = q\bar{q} = a^2 + b_1^2 + b_2^2 + b_3^2 = \det q. \tag{B2}$$

As for complex conjugation, by q^* we mean the complex conjugate of the 2×2 matrix (B1).

A 2×2 matrix q is a quaternion, according to (B1), if and only if

$$\tau^\dagger q \tau = q^*, \tag{B3}$$

where τ is given by (A3). Notice that τ is the basis quaternion $\mathbf{j}$.

A unit quaternion q is one for which $|q|^2 = 1$. The set of unit quaternions, interpreted as matrices, is the group $SU(2)$. An arbitrary quaternion can be written as $q = \rho u$, where $\rho \geq 0$ is real and u is an element of $SU(2)$, which is unique if $\rho > 0$.

Appendix C: Rotation Groups $SO(3)$ and $SU(2)$

We let $R \in SO(3)$ be a proper rotation, which we parameterize in axis-angle form, $R = R(\hat{\mathbf{n}}, \theta)$, where the unit vector $\hat{\mathbf{n}}$ is the axis of the rotation and θ is the angle. All proper rotations are covered if $\hat{\mathbf{n}}$ runs over the unit sphere and $0 \leq \theta \leq \pi$. If $0 < \theta < \pi$ the axis-angle representation is unique, but if $\theta = 0$ then $R(\hat{\mathbf{n}}, 0) = I$ (the identity) for all axes $\hat{\mathbf{n}}$, and if $\theta = \pi$ then $R(\hat{\mathbf{n}}, \pi) = R(-\hat{\mathbf{n}}, \pi)$. This shows that the space of proper rotations, the group manifold $SO(3)$, is diffeomorphic to the real projective space $\mathbb{R}P^3$. (Two spaces are diffeomorphic if their points can be placed in a one-to-one correspondence in a smooth manner. It means that the spaces are identical from a differentiable or topological standpoint. The space $\mathbb{R}P^3$ is the 3-sphere S^3 with antipodal points identified.)

The group $SU(2)$ consists of matrices that can be parameterized in axis-angle form,

$$u(\hat{\mathbf{n}}, \theta) = e^{-i\theta\,\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}/2} = \cos(\theta/2) - i\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\sin(\theta/2), \tag{C1}$$

where $\boldsymbol{\sigma}$ is the vector of Pauli matrices. All of $SU(2)$ is covered if the axis $\hat{\mathbf{n}}$ runs over the unit sphere and $0 \leq \theta \leq 2\pi$. The representation is unique if $0 < \theta < 2\pi$ but when $\theta = 0$, $u(\hat{\mathbf{n}}, 0) = 1$ for all $\hat{\mathbf{n}}$, and when $\theta = 2\pi$, $u(\hat{\mathbf{n}}, 2\pi) = -1$ for all $\hat{\mathbf{n}}$. This means that the group manifold $SU(2)$ is diffeomorphic to the 3-sphere S^3.

The projection from $SU(2)$ to $SO(3)$ is given by

$$R_{ij} = \frac{1}{2}\mathrm{tr}(u^{\dagger}\sigma_i u \sigma_j). \tag{C2}$$

One can show that the matrix R defined by this equation belongs to $SO(3)$ if $u \in SU(2)$, so it defines a map or function : $SU(2) \to SO(3)$. We will denote the function by $R(u)$; it is a group homomorphism,

$$R(u_1)R(u_2) = R(u_1 u_2), \tag{C3}$$

and thus $SO(3)$ forms a representation of $SU(2)$. The map (C3) is two-to-one, since $R(u) = R(-u)$. The map preserves the axis and angle, that is, $R\;u(\hat{n},\theta)\; = R(\hat{n},\theta)$.

Sometimes it is desirable to invert (C2), that is, given $R \in SO(3)$ we wish to find u. The answer can be given by using the axis-angle parameterization; if we write $R = R(\hat{n},\theta)$, then the two elements of $SU(2)$ that satisfy (C2) are $\pm u(\hat{n},\theta)$.

Appendix D: Some Proofs

We prove the statements made below (115), which concern the consequences of that formula. First, suppose a basis is quaternionic at x_0,

$$T|x_0;k\mu\rangle = \sum_{\nu} |x_0;k\nu\rangle\tau_{\nu\mu}, \tag{D1}$$

see (A10), and suppose that $|Rx_0;k\mu\rangle$ is given by (115). Then we have

$$\begin{aligned} T|Rx_0;k\mu\rangle &= \sum_{\nu} U_e(u)\; T|x_0;k\nu\rangle\; (u^{-1})^{*}_{\nu\mu} = \sum_{\nu\sigma} U_e(u)\,|x_0;k\sigma\rangle\tau_{\sigma\nu}\; (u^{-1})^{*}_{\nu\mu} \\ &= \sum_{\sigma} U_e(u)\,|x_0;k\sigma\rangle\; \tau u^{-1*}\; {}_{\sigma\mu}, \end{aligned} \tag{D2}$$

where in the first step we use the fact that T commutes with rotations. But since $u^{-1} \in SU(2)$ it is a quaternion and satisfies $u^{-1*} = \tau^{\dagger}u^{-1}\tau$, see (B3). Thus $\tau u^{-1*} = u^{-1}\tau$, and (D2) becomes

$$\sum_{\nu\sigma} U_e(u)\,|x_0;k\sigma\rangle\; (u^{-1})_{\sigma\nu}\,\tau_{\nu\mu} = \sum_{\nu} |Rx_0;k\nu\rangle\tau_{\nu\mu}. \tag{D3}$$

Thus, the basis $|Rx_0;k\mu\rangle$ at the rotated point $x = Rx_0$ is also quaternionic.

Next, suppose a basis vector at x_0 is an energy eigenvector,

$$H_e(x_0)\,|x_0;k\mu\rangle = \epsilon_k(x_0)\,|x_0;k\mu\rangle, \tag{D4}$$

where the energy does not depend on μ as indicated. Then

$$\begin{aligned} H_e(Rx_0)\,|Rx_0;k\mu\rangle &= U_e(u)H_e(x_0)U_e(u)^\dagger \sum_\nu U_e(u)\,|x_0;k\nu\rangle \left(u^{-1}\right)_{\nu\mu} \\ &= \varepsilon_k(x_0) \sum_\nu U_e(u)\,|x_0;k\nu\rangle \left(u^{-1}\right)_{\nu\mu} = \varepsilon_k(x_0)\,|Rx_0;k\mu\rangle, \end{aligned} \tag{D5}$$

where in the first step we use (104) and (115). Thus, the rule (115) maps energy eigenbases at x_0 into those at $x = Rx_0$, without changing the eigenvalues.

To prove (116) we let $R_1, R_2 \in SO(3)$, corresponding to $u_1, u_2 \in SU(2)$, and we write $x_1 = R_1x_0$ and $x_2 = R_2x_1$. Then we have

$$\begin{aligned} |x_2;k\mu\rangle = |R_2x_1;k\mu\rangle = |R_2R_1x_0;k\mu\rangle &= \sum_\nu U_e(u_2u_1)\,|x_0;k\nu\rangle (u_2u_1)^{-1}_{\nu\mu} \\ &= \sum_{\nu\sigma} U_e(u_2)U_e(u_1)\,|x_0;k\nu\rangle \left(u_1^{-1}\right)_{\nu\sigma} \left(u_2^{-1}\right)_{\sigma\mu} \\ &= \sum_\sigma U_e(u_2)\,|x_1;k\sigma\rangle \left(u_2^{-1}\right)_{\sigma\mu}. \end{aligned} \tag{D6}$$

Now making the replacements $x_1 \to x$, $R_2 \to R$ and $u_2 \to u$, we obtain (116). The proof would not work if we had used u instead of u^{-1} in (116).

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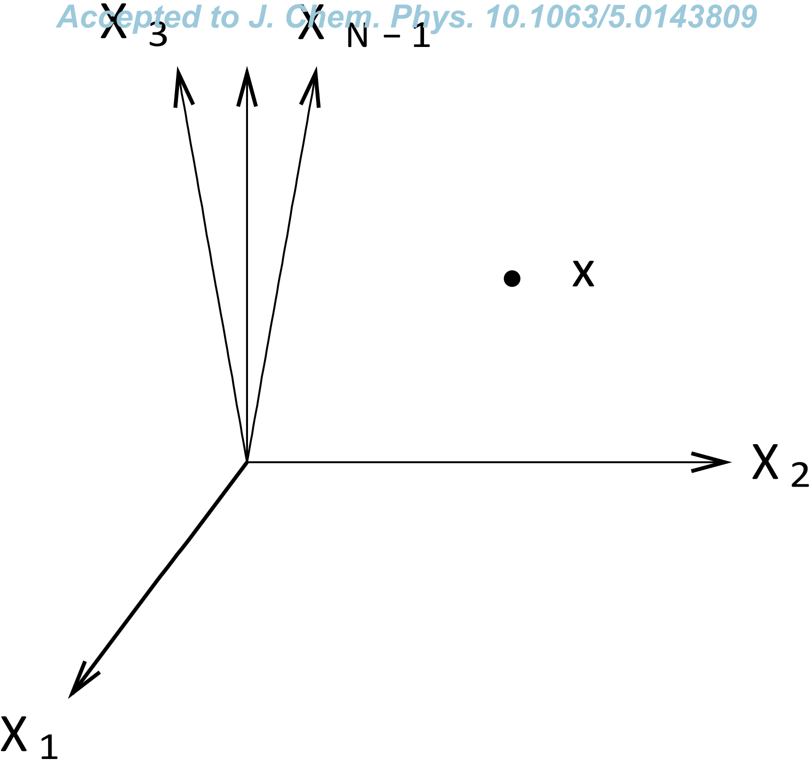
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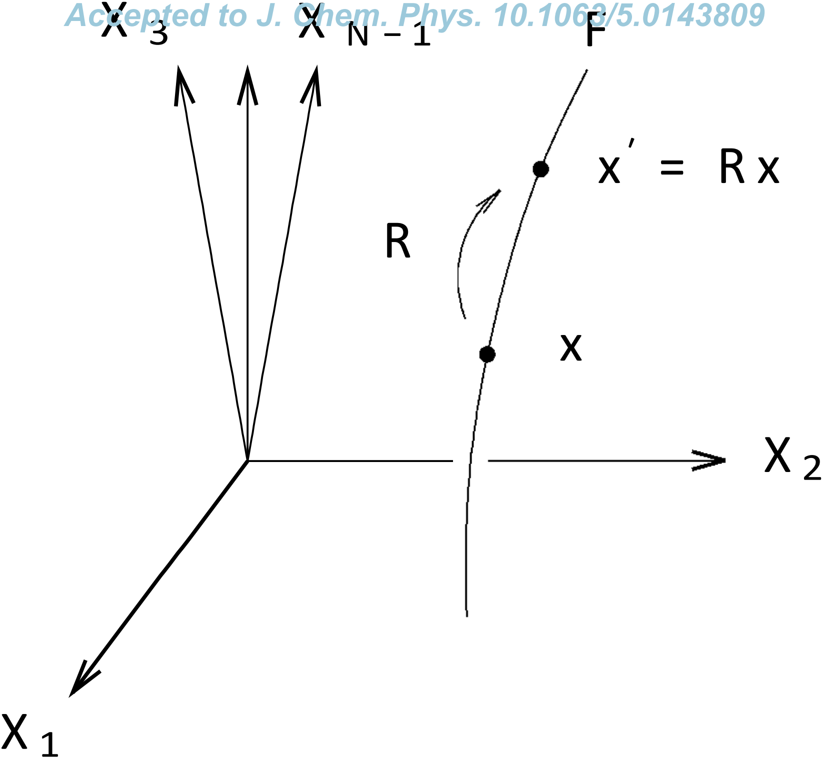
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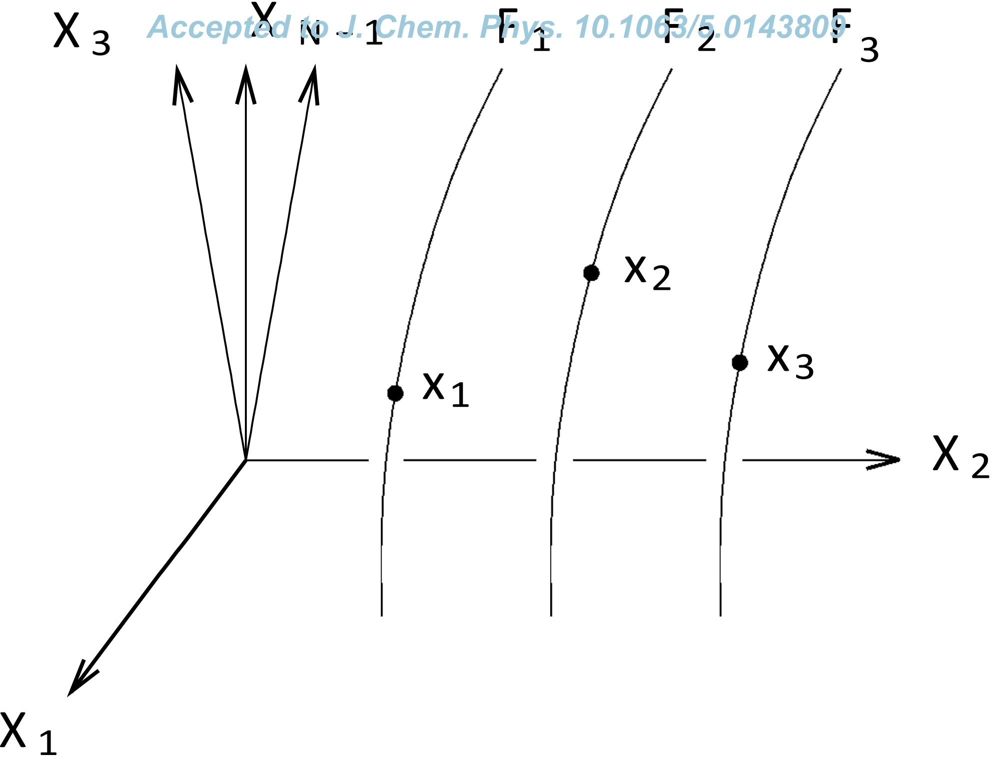
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X_{N-1}
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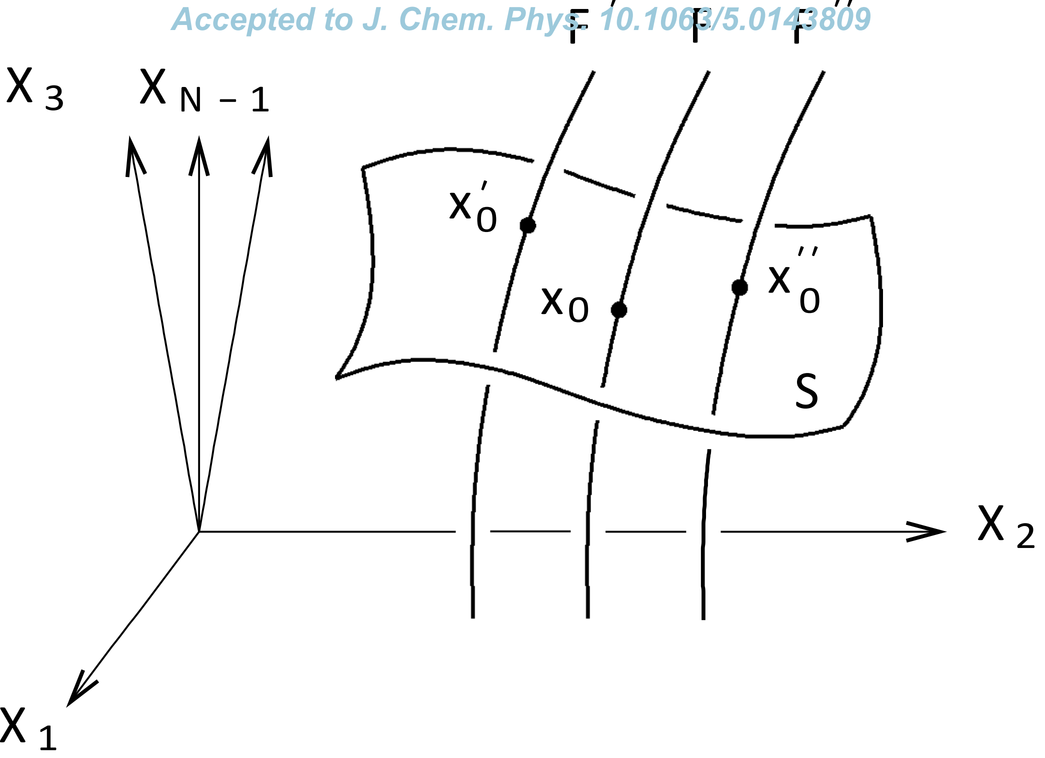
F′
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X_3
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x_0'
x_0
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X_2
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