

Detecting Level Crossings without Looking at the Spectrum

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In many physical systems it is important to be aware of the crossings and avoided crossings which occur when eigenvalues of a physical observable are varied using an external parameter. We have discovered a powerful algebraic method of finding such crossings via a mapping to the problem of locating the roots of a polynomial in that parameter. We demonstrate our method on atoms and molecules in a magnetic field, where it has implications in the search for Feshbach resonances. In the atomic case our method allows us to point out a new class of invariants of the Breit-Rabi Hamiltonian of magnetic resonance. In the case of molecules, it enables us to find curve crossings with practically no knowledge of the corresponding Born-Oppenheimer potentials.

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Curve crossing is a universal phenomenon with examples in many branches of both pure and applied sciences. It is responsible for electron transfer in proteins [1], underlies stability analysis in mechanical engineering [2], and determines Nash equilibria [3]. Mathematically, it arises naturally in the subject of algebraic geometry [4]. In physics, the discovery of a crossing between two energy levels, for example, signals degeneracy in the energy spectrum and the existence of an underlying symmetry in the problem. Since the initial pioneering works by Hamilton [5], von Neumann and Wigner [6], Landau [7] and Zener [8], many interesting physical phenomena have been associated with crossings. These include Berry's phase in adiabatic quantum mechanics [9], the hidden symmetries of the Hubbard model in condensed matter physics [10], and the onset of quantum chaos in nonlinear dynamics [11]. In contemporary atomic and molecular physics an avoided crossing that has come into intense focus is the Feshbach resonance. Such a resonance provides unique experimental control over interactions in a quantum degenerate atomic gas, realizing collapsing condensates [12], ultracold molecules [13], and the crossover from BEC to BCS pairing in degenerate Fermi gases [14].

In this Letter we present a versatile theoretical technique for detecting the presence of level crossings in physical systems. Our technique is algebraic in nature, as the underlying Hamiltonian (or other physical quantity) can often be represented as a parameter-dependent matrix. Our method is powerful and general, as we extract essential information simply from the matrix elements without having to compute the spectrum, and remarkably, works even in cases where the Hamiltonian is not fully known. We demonstrate our technique on atoms and molecules in a magnetic field. Apart from being interesting in themselves, these physical systems are of relevance to Feshbach resonances, a topic of current experimental and theoretical concern [12]. We present specific results for the atom pair ^{23}Na - ^{85}Rb , which is of current interest as a candidate for Feshbach reso-

nances [15], but our analysis can be readily extended to other atoms.

The essence of our algebraic approach can be demonstrated using the following simple example. Let us consider a real symmetric 2×2 matrix,

$$M(T) = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix} \quad (1)$$

which may represent the Hamiltonian of a two-state system. The notation implies that every matrix element is a function of the tunable parameter T , which could be an external field. The eigenvalues E of $M(T)$, labeled λ_1 and λ_2 , may be found from the characteristic polynomial $|M(T) - E| = E^2 + C_1E + C_0$, where $C_0 = E_1E_2 - V^2$ and $C_1 = -(E_1 + E_2)$. However, since the eigenvalues are themselves roots of this polynomial, i.e., $(E - \lambda_1) \times (E - \lambda_2) = 0$, the coefficients may equivalently be written in terms of the eigenvalues: $C_0 = \lambda_1\lambda_2$ and $C_1 = -(\lambda_1 + \lambda_2)$. It should be noted that we did not explicitly calculate the eigenvalues to arrive at this conclusion.

Since we are interested in curve crossings, we would like to know if the eigenvalues are degenerate, i.e., if $\lambda_1 = \lambda_2$, at some value of the parameter T . To this end, we introduce the *discriminant* $\Delta \equiv (\lambda_1 - \lambda_2)^2$ of the characteristic polynomial of $M(T)$ which can be written purely in terms of its coefficients $\Delta = C_1^2 - 4C_0$. If we now choose a simple parametrization for $M(T)$, say $E_{1,2} = 2T$ and $V = T$, we find $\Delta = 4T^2$, a polynomial in T . The root of Δ , $T = 0$ corresponds to the only crossing in the spectrum of $M(T)$, as may be verified by explicitly calculating the eigenvalues $\lambda_{1,2} = T, 3T$. The point of this example is to show how use of the discriminant maps the problem of finding spectral crossings to one of locating polynomial roots and bypasses the need to find eigenvalues.

An extension of this simple example to larger matrices and more than one parameter leads to the study of multivariate polynomials, a topic in algebraic geometry [4]. Assigning the task of a rigorous exposition to a separate publication [16], we motivate the technique used in this

discriminant of $H_{\text{BR}}^{b=0}$ using built-in functions in MATHEMATICA:

$$D[H_{\text{BR}}^{b=0}] = \frac{81A^{24}a^{26}B^{26}(64A^6 + 32A^4a^2B^2 + 8A^2a^4B^4 + a^6B^6)}{65\,536}. \quad (6)$$

Considered as a polynomial in B , $D[H_{\text{BR}}^{b=0}]$ is even and exhibits no sign changes in its coefficients; by Descartes' rule it has no real roots for $B \neq 0$ [4]. Hence there are no level crossings in the spectrum. The real parts of the complex roots of $D[H_{\text{BR}}^{b=0}]$ imply well-documented, widely avoided crossings at $B = 0$ and A/a ($= 316$ G for ^{23}Na) [21]. Physically, the latter corresponds to the crossover into the Paschen-Back regime.

We now calculate the discriminant $D[H_{\text{BR}}]$ for $b \neq 0$, the expression for which will be presented elsewhere on account of its length [16]. From the roots of $D[H_{\text{BR}}]$ we infer the following changes introduced by the presence of b . The avoided crossings are now located at $B = 0$ and $A/(a - b)$ and have moved closer since $b/a \sim -10^{-3}$ for ^{23}Na . More importantly there now appear crossings in the spectrum for $B \neq 0$. Evidently the coupling, b , of the nuclear spin to the magnetic field is the mechanism responsible for crossings in the Breit-Rabi spectrum. For $B > 0$ there are 6 crossings clustered around 400 kG. In the regime $B_{\text{Fesh}} \in [0, 1 \text{ kG}]$ therefore the discriminant alerts us to the absence of any crossings as well as to the presence of two avoided crossings.

To the best of our knowledge invariants of the Breit-Rabi Hamiltonian such as Eq. (6), which can be calculated once the spins I and S are specified, have not been pointed out previously. They are complete catalogs of the parametric symmetries of H_{BR} . More generally, although we have picked an example from atomic physics, it should be clear that for any system represented by a parameter-dependent matrix, the discriminant is a powerful tool for investigating the location of crossings, their behavior as a function of the parameters as well as the physical mechanisms responsible for their occurrence.

We now show how this method yields quite remarkable results in the more involved case of a diatomic molecule in a magnetic field. We consider a molecule made up of the previously considered ^{23}Na atom and an ^{85}Rb atom. The molecular Hamiltonian is

$$H_{\text{Mol}} = E_{\text{kin}} + U(B) + V(R). \quad (7)$$

Here E_{kin} denotes the kinetic energy of the nuclei, $U(B)$ the internal energies of the atoms in the magnetic field, and $V(R)$ the molecular potential energy at the internuclear distance R . Specifically, $U(B)$ can be obtained from Eq. (4), and

$$V(R) = V_S P_S + V_T P_T, \quad (8)$$

where $V_{S,T}$ are the molecular (singlet, triplet) electrostatic potentials, and $P_{S,T}$ are projection operators on to the corresponding subspaces [19].

To work with a concrete example we prepare the Na-Rb atom pair in the state $|2, 2\rangle_{\text{Na}}|2, 2\rangle_{\text{Rb}}$, the ‘‘open’’ channel

for their collision. Since the component of the total angular momentum ($M_{F\text{total}} = 4$) along the magnetic field is preserved by the interaction $V(R)$, we need to consider in addition only the states which have the same $M_{F\text{total}}$: $|2, 2\rangle|3, 2\rangle$, $|2, 1\rangle|3, 3\rangle$, and $|1, 1\rangle|3, 3\rangle$. Here we have retained the ordering of the atoms and dropped the subscripts. The four states mentioned above make up the electronic Hilbert space of the molecule.

In the standard Born-Oppenheimer approximation (BOA) of molecular physics the E_{kin} in Eq. (7) is at first neglected and a set of adiabatic electronic potential curves obtained by diagonalizing the (in our case 4×4) interaction matrix

$$H_{\text{BO}} = U(B) + V(R), \quad (9)$$

for a given B and for a large enough range of R . In order to find the bound rovibrational levels one must then solve for the nuclear motion on these curves. The calculation has to be repeated for different values of B until a bound state equals the open channel in energy: this yields the simplest estimate of a Feshbach resonance location [19].

It is imperative to know if there are crossings among the electronic potentials generated by H_{BO} , because the BOA breaks down precisely at such points, and invalidates the Feshbach resonance estimate. For this reason we investigate the discriminant $D[H_{\text{BO}}]$. But first we make a crucial transformation. We rewrite Eq. (8) as

$$V(R) = X(P_S - P_T) + (V_S + V_T)/2, \quad (10)$$

where $X(R) = (V_S - V_T)/2$, signifies the quantum mechanical exchange energy responsible for chemical bonding and plays a critical role in the curve-crossing problem by allowing us to avoid the following difficulty. The $V_{S,T}$ depend very sensitively on R . For $^{23}\text{Na}^{85}\text{Rb}$ for instance, the latest data requires 32(47) parameters to fit $V_{S(T)}$, respectively [15]. These parameters are usually varied within their uncertainties, for instance to yield bounds on the Feshbach resonance predictions. It would require a numerical effort in $(32 + 47 + 1) = 80$ -dimensional parameter space, always limited by resolution, to inspect the spectrum for crossings for each V_S , V_T , and B . We demonstrate below how the introduction of X renders the determination of curve crossings for H_{BO} completely insensitive to the complicated functional form of the Born-Oppenheimer potentials.

Since $D[H_{\text{BO}}]$ does not change if we subtract the same quantity from all the diagonal elements of H_{BO} , we drop the second term in Eq. (10), i.e., we calculate $D[H_{\text{BO}} - (V_S + V_T)/2] (= D[H_{\text{BO}}])$. We then substitute numbers for all the atomic constants in $D[H_{\text{BO}}]$ which gives us $D[H_{\text{BO}}] = \sum_{n=0}^6 p_n(B)X^n$, i.e., a polynomial of degree 6 in X , whose coefficients depend on B . We now phrase our

inquiry about curve crossings in the following way: is there *any* real value of the exchange energy ($X \in [-\infty, +\infty]$) for which molecular curve crossings can be produced ($D[H_{\text{BO}}] = 0$) by the fields available in the laboratory ($B_{\text{Fesh}} \in [0, 1 \text{ kG}]$)? The answer can be found by examining the number of sign variations in the Sturm-Habicht sequence of $D[H_{\text{BO}}]$ at $X = \pm\infty$ [4]. Only two real roots are found in the interval $B_{\text{Fesh}} \in [0, 1 \text{ kG}]$, at $B = 0 \text{ G}$ and 502.2 G , both for $X = 0$. Other than these we locate no crossings for any X and the BOA is valid everywhere else in the parameter regime of interest.

We think it is quite remarkable, and points to the power of the algebraic approach, that in order to extract information about crossings in the spectrum of a diatomic molecule in a magnetic field we did not avail of any knowledge about the Born-Oppenheimer potentials ($V_{S,T}$) except that their difference is a real number. The curve crossings are entirely determined by atomic constants. Of course whether and at what R the crossings actually occur will depend on the specific form of the $V_{S,T}$. The algebraic method allows us to locate the complete set of magnetic fields that could cause the BOA to break down. If this set is not too restrictive, or is not in the neighborhood of a Feshbach resonance, one need not refer to the $V_{S,T}$ at all.

Having demonstrated the application of curve-crossing methods to atomic and molecular spectra we now discuss possible extensions of our work. Our methods can readily be applied to other atoms and molecules. More generally we note that Eq. (4) is just a single example from an entire class of “spin Hamiltonians”

$$H_{\text{spin}} = \sum_{i,j} C_{ij} J_i J_j + \sum_i B_i J_i. \quad (11)$$

Here the J_i are angular momentum operators and the indices i, j run over the spatial coordinates x, y, z . With the appropriate choices for the “coupling” (C_{ij}) and “field” (B_i) parameters, effective Hamiltonians for many physical systems can be set up and analyzed for level crossings. Specific examples of such systems are polar molecules in an electric field [22], a spin-1 BEC with magnetic dipole interaction [23], doubly-even nuclei described by the triaxial rotor model [24], massive spinors in an anisotropic universe [25], and so on. Of course our methods are not limited to Hamiltonian matrices. They can be applied to matrices that describe the stability of gyroscopes [2], the polarization of light [26], or the payoff in a game [3], for instance. In sum, a large number of mathematical models contain parameters, and many of them involve matrices. We have shown how to extract curve-crossing information from cases with effectively one and two tunable parameters. Application to other systems as well as to a larger number of parameters are among the natural extensions of our work.

In conclusion, we have demonstrated a powerful and rigorous algebraic method for locating curve crossings in

the spectra of physical systems. Along the way we have pointed out a new class of invariants of the Breit-Rabi equation of magnetic resonance and placed the Born-Oppenheimer approximation for calculating Feshbach resonances on a rigorous basis, using very little information about molecular potentials.

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