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 $^{23}\text{Na} - \text{Rb}$, which is of current interest as a candidate for Feshbach resonances [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 $2 \times 2$ matrix,

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

(1)

which may represent the Hamiltonian of a two-state system. The notation implies that every matrix element is a polynomial in that parameter. We demonstrate our method on atoms and molecules in a magnetic field, when eigenvalues of a physical observable are varied using an external parameter. We have discovered 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.

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

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Letter by analogy to the example stated above. We consider a matrix $H(P)$, not trivially diagonal, of dimension $n$ and depending polynomially on the set of parameters $P = \{P_1, \ldots, P_N\}$. The characteristic polynomial of $H(P)$ is of degree $n$ in the eigenvalue $E$. The roots $\lambda_{1,2,\ldots,n}$ of this polynomial are used to define its discriminant

$$D[H(P)] = \prod_{i<j}^n (\lambda_i - \lambda_j)^2,$$

which is an invariant of $H(P)$. It follows from Eq. (2) that $D[H(P)]$ does not change if the same quantity is added to every eigenvalue $\lambda_i$; in fact it does not even change if the same quantity is added to each diagonal term of $H(P)$, since this corresponds to a shift of the entire spectrum.

Now, as in the case of $\Delta$ above, $D[H(P)]$ can also be calculated from the coefficients $C_i$ of the characteristic polynomial without recourse to the roots. In the general case this can be done since $D[H(P)]$ can be written in terms of the determinant of the $(2n-1) \times (2n-1)$ Sylvester matrix of the characteristic polynomial [4]:

$$D[H(P)] = \frac{(-1)^{n(n-1)/2}}{C_n} \begin{vmatrix} C_n & C_{n-1} & \cdots & C_0 \\ C_n & \cdots & \cdots & \cdots \\ \vdots & \ddots & \ddots & \vdots \\ nC_n & \cdots & \cdots & 0 \\ n^2C_n & \cdots & 2C_1 & 2C_2 \end{vmatrix} \quad (3)$$

Equation (3) has two important implications. First, even if the roots cannot be calculated analytically, which is true in general for $n \geq 5$, $D[H(P)]$ always can be. This means that the analytical mapping—supplied by the discriminant—between the level-crossing and polynomial root-finding problems is preserved for all $n$. Second, one can detect level crossings without solving for the spectrum. This implies, as will be shown, the existence of powerful algebraic alternatives to numerically intensive spectral searches for crossings.

As in the case of $\Delta$ the real roots of Eq. (2) correspond to crossings in the spectrum of $H(P)$; as well, the real parts of the complex roots of Eq. (2) indicate avoided crossings [17]. Further, in our simple example, $\Delta$ turned out to be quadratic in a single parameter $T$; in general $D[H(P)]$ will be a high order polynomial in $N$ variables. Typically, in order to locate the roots of this polynomial we will examine its coefficients. For example a simple method we will use is Descartes’ Rule of Signs from elementary algebra which equates the number of real roots of a polynomial to the number of sign changes in its coefficients, modulo 2. A more sophisticated concept we will use is that of a Sturm-Habicht sequence [4] of a polynomial, say in the variable $Y$. The difference in the number of sign variations in this sequence at $Y = l$ and $Y = r$ equals the number of real zeros of the polynomial in the interval $[l, r]$ exactly.

Let us now apply the methods outlined above to an atom in a uniform magnetic field. Such a system is relevant to the search for a Feshbach resonance, which typically begins with a spin-polarized sample of atoms and requires a broad sweep of the magnetic field. Experimentally, if a crossing or a fine anticrossing is encountered in the atomic spectrum while the magnetic field is tuned, some of the atoms can be transferred to a different spin state, introducing an impurity [18]. For theoretical bookkeeping, it is useful to know if the low- and high-field states correlate adiabatically [19]. Such a correlation breaks down at a crossing. For these reasons, it is essential to be aware of crossing phenomena in the atomic spectrum. The magnetic fields used in Feshbach resonance searches are typically less than a kilogauss. Hence the parameter regime of our interest will be $B_{\text{Fesh}} \in [0, 1 \text{ kG}]$.

To work with a concrete example we consider an $^{23}\text{Na}$ atom in its $3S_{1/2}$ ground state split by the hyperfine interaction into two levels labeled by the angular momentum $F = I + S$ where $I = 3/2$ and $S = 1/2$ are the nuclear and electronic spins, respectively. In the presence of a uniform magnetic field $B$ along the $z$ axis the atomic spectrum is described by the Breit-Rabi (BR) Hamiltonian [20]

$$H_{BR} = A \mathbf{I} \cdot \mathbf{S} + B(aS_z + bI_z), \quad (4)$$

where $A$ measures the strength of the hyperfine coupling and $a$ and $b$ may be easily related to the electronic and nuclear gyromagnetic ratios and the Bohr magneton. Throughout this Letter we will refer to the atomic eigenstates in the $(F, M_F)$ basis where $M_F$ is the component of $F$ along the $z$ axis. In order to retain the polynomial form of the matrix elements, however, all representations will be made in the uncoupled basis $|M_s, M_j\rangle$, where $M_s$ and $M_j$ are the components of the respective spins along the $z$ axis. Such a representation in the ordered basis $|\frac{1}{2}, -\frac{3}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{3}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{3}{2}\rangle$, and $|\frac{1}{2}, \frac{3}{2}\rangle$ yields for Eq. (4)

$$H_{BR} = \frac{1}{4} \begin{pmatrix} 3A - 2(a + 3b)B & -3A + 2(a - 3b)B & 2\sqrt{3}A \\ -3A + 2(a - 3b)B & 2\sqrt{3}A & A - 2(a + b)B \\ 2\sqrt{3}A & A - 2(a + b)B & -A + 2(a - b)B \end{pmatrix} \begin{pmatrix} 4A \\ -A - 2(a - b)B \\ A + 2(a + b)B \end{pmatrix}. \quad (5)$$

To begin with a simplification we consider the fact that $| b | \ll | a |$ in Eq. (4) [21]. Setting $b = 0$ in Eq. (5) we calculate the
discriminant of $H_{BR}^{b=0}$ using built-in functions in MATHEMATICA:

$$D[H_{BR}^{b=0}] = \frac{81A^2a^2B^6(64A^6 + 32A^4a^2B^2 + 8A^2a^4B^4 + a^6B^6)}{65536}.$$  

Considered as a polynomial in $B$, $D[H_{BR}^{b=0}]$ 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 $D[H_{BR}^{b=0}]$ 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 $D[H_{BR}]$ for $b \neq 0$, the expression for which will be presented elsewhere on account of its length [16]. From the roots of $D[H_{BR}]$ 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 $B_{Fesh} \in [0, 1]$ 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

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

(7)

Here $E_{\text{kin}}$ 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

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

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 ($M_{\text{Total}} = 4$) along the magnetic field is preserved by the interaction $V(R)$, we need to consider in addition only the states which have the same $M_{\text{Total}}$: $|2, 2\rangle, |2, 1\rangle, |3, 3\rangle$, and $|1, 1\rangle$. 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 $E_{\text{kin}}$ in Eq. (7) is at first neglected and a set of adiabatic electronic potential curves obtained by diagonalizing the (in our case 4 x 4) interaction matrix

$$H_{BO} = U(B) + V(R),$$

(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 $D[H_{BO}]$. But first we make a crucial transformation. We rewrite Eq. (8) as

$$V(R) = X(p_S - p_T) + (V_S + V_T)/2,$$

(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 $^{23}$Na$^{85}$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 $32 + 47 + 1 \approx 80$-dimensional parameter space, always limited by resolution, to inspect the spectrum for crossings for each $V_S, V_T, B$. 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 $D[H_{BO}]$ 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 $D[H_{BO} - (V_S + V_T)/2] = D[H_{BO}]$. We then substitute numbers for all the atomic constants in $D[H_{BO}]$ which gives us $D[H_{BO}] = \sum_{n=0}^6 \alpha_n \langle B \rangle X^n$, 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 ($D[H_{BO}] = 0$) by the fields available in the laboratory ($B_{Fesh} \in [0, 1 \text{ kG}]$)? The answer can be found by examining the number of sign variations in the Sturm-Habicht sequence of $D[H_{BO}]$ at $X = \pm \infty$ [4]. Only two real roots are found in the interval $B_{Fesh} \in [0, 1 \text{ kG}]$, at $B = 0 \text{ G}$ and $502.2 \text{ G}$, 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”

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

(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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