Detecting level crossings without solving the Hamiltonian. II. Applications to atoms and molecules

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A number of interesting phenomena occur at points where the energy levels of an atom or a molecule (anti) cross as a function of some parameter such as an external field. In a previous paper [M. Bhattacharya and C. Raman, Phys. Rev. Lett. 97, 140405 (2006)] we have outlined powerful mathematical techniques useful in identifying the parameter values at which such (avoided) crossings occur. In the accompanying article [M. Bhattacharya and C. Raman, Phys. Rev A 75, 033405 (2007)] we have developed the mathematical basis of these algebraic techniques in some detail. In this article we apply these level-crossing methods to the spectra of atoms and molecules in a magnetic field. In the case of atoms the final result is the derivation of a class of invariants of the Breit-Rabi Hamiltonian of magnetic resonance. These invariants completely describe the parametric symmetries of the Hamiltonian. In the case of molecules we present an indicator which can tell when the Born-Oppenheimer approximation breaks down without using any information about the molecular potentials other than the fact that they are real. We frame our discussion in the context of Feshbach resonances in the atom-pair $^{23}$Na–$^{85}$Rb which are of current interest.

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I. INTRODUCTION

Eigenvalues in the spectra of atoms and molecules often display (avoided) crossings when they are evaluated as a function of some parameter. The parameter can be an external field [1], an internal molecular coordinate [2], a ‘‘running’’ constant of coupling between submolecular constituents [3], a good quantum number [4], and so on. Important physical phenomena have been associated with such (avoided) crossings in the spectrum.

In atomic physics examples of such phenomena include Berry’s phase [5], Fermi resonances [4], the Hanle effect [1], and charge-exchanging ion-atom collisions [6]. Other effects occurring at level crossings include the vanishing of magnetic dipole transitions [7,8], the relativistic enhancement of ionization in Rydbergs [9], and optical shielding of collisions in ultracold ensembles [10]. More general examples can be culled from quantum physics: The tendency of eigenvalues to avoid each other is considered a signature of quantum chaos [11]; level crossing in a quantum system implies integrability of the corresponding classical system [12]; avoided crossings can be used to produce entanglement in adiabatic quantum information [13].

In molecular physics classic examples of level crossing phenomena are the Jahn-Teller [14] and molecular Aharonov-Bohm effects [15] which are crucial in relating molecular degeneracy to structure [2]. The celebrated work of Wigner and von Neumann [16] relating curve crossing to symmetry was formulated in the context of atomic and molecular physics, after a conjecture by Hund [17]. The use of the noncrossing rule formulated by Wigner and von Neumann (WvN) turns out to be crucial in molecular and chemical physics. In conjunction with correlation diagrams it is an indispensable aid to deciphering molecular reaction pathways [18]. The analysis of avoided crossings was pioneered by Landau [19] and Zener [20], and elaborated on by others ([21] and references therein).

On a fundamental level the Born-Oppenheimer approximation (BOA) [22], which forms the basis of almost all of molecular physics, breaks down at a crossing of the electronic curves in a molecule [23]. These crossings can either be symmetry-driven or occur in the absence of any symmetry considerations. In either case, it is being increasingly realized that the crossings which accompany the breakdown of the BOA provide pathways for many ultrafast reactions on the femtosecond time scale [2], particularly relevant to the photochemistry of polyatomic molecules [24]. The WvN rule forbids all but ‘‘accidental’’ level crossings in field-free diatomic molecules, but crossings can already be found in triatomic molecules [15], and are ubiquitous in polyatomic molecules [25]. It is suspected that in fact crossings are much more likely to occur than avoided crossings in polyatomic molecules [26].

In both atomic and molecular physics Stark and Zeeman level-crossing spectroscopies [1] have yielded important constants such as electric dipole moments [27] and polarizabilities [28], magnetic fine [29], and hyperfine [30] splittings, and excited state lifetimes [1]. In molecular physics level-crossing spectroscopy can probe otherwise inaccessible processes such as internal rotation [31]. A new type of trap for cold atoms has been devised exploiting the minimum that occurs in the upper atomic state during an avoided crossing as the magnetic field is tuned [32]. An avoided crossing that has come into intense focus in contemporary atomic and molecular physics is the Feshbach resonance [33,34]. Such a resonance has provided unique experimental control of the interactions in an ultracold atomic gas. For example, it has been used to tune free atom pairs into weakly bound molecules either cold or Bose-condensed [35], to vary the interactions in a Bose Einstein condensate (BEC) and make it implode or explode [36], and to explore the crossover in a degenerate fermionic gas from the BCS or the BEC side [37].

It is appropriate to remark here that (avoided) crossings are markers of quantum phase transitions [38]. If the Hamil-
tonian of a system depends on a parameter $P$ and its ground state approaches an (avoided) crossing at $P = P_c$ then $P_c$ is a point of nonanalyticity of the ground state energy. $P_c$ is called a critical point and indicates a phase transition which is usually accompanied by a qualitative change in the nature of correlations in the ground state of the system.

In an accompanying article [39] we have provided the operational details of algebraic technique useful for locating level (avoided) crossings in physical systems. In this paper we explicitly demonstrate the techniques on atoms and molecules in a magnetic field. We present specific results for the atom $^{23}\text{Na}$ whose spectrum has been well studied [40], and the molecule $^{23}\text{Na}^{85}\text{Rb}$ which is of current interest as a candidate for Feshbach resonances [41–43], but our analysis can be readily extended to other atoms and molecules.

The main results of this paper are the derivation of a class of invariants for the Breit-Rabi equation of magnetic resonance, and a way to indicate the breakdown of the Born-Oppenheimer approximation for a diatomic molecule. The atomic invariants turn out to contain much information about the degeneracies, crossings, and avoided crossings in the corresponding spectrum. We also show that the breakdown of the Born-Oppenheimer approximation can be detected assuming only that the corresponding molecular potentials are real, i.e., without relevance to their functional form or numerical values. Practically this proves to be of much convenience as the potentials are quite complicated.

The rest of the paper is organized as follows. In Sec. II we demonstrate the application of level crossing techniques to $^{23}\text{Na}$ in a magnetic field. In Sec. III we consider the non-interacting atom pair $^{23}\text{Na}^{85}\text{Rb}$ as a nontrivial prelude to the treatment in Sec. IV of the molecule $^{23}\text{Na}^{85}\text{Rb}$. Section V discusses limitations of the work and considers applications of algebraic technique to other systems, and Sec. VI contains the conclusions.

II. ATOMS

We will now apply algebraic technique to an atom in a uniform magnetic field. As a preface we describe the relevant Hamiltonian generally and mention some work already done with reference to level crossing in its spectrum.

A. The Breit-Rabi Hamiltonian

We assume that the atom has a single valence electron and possesses hyperfine structure (i.e., nonzero nuclear spin $I$, which couples to the electronic spin $S$) and is described by the Breit-Rabi Hamiltonian [44]

$$H_{BR} = AI \cdot S + B(aS_z + bI_z),$$

(1)

where $A$ measures the strength of the hyperfine coupling, and the direction along the uniform $B$ field is chosen to be the $z$ axis. $a$ and $b$ may be easily related to the electronic and nuclear gyromagnetic ratios and the Bohr magneton. We consider an atom in its internal ground state, so that its electronic orbital angular momentum $L=0$. We note that the operator $H_{BR}$ is linear in the parameters $A$, $B$, $a$, and $b$.

![FIG. 1. The parameters chosen for this plot were $A=1$ cm$^{-1}$, $a=0.1$ cm$^{-1}$ G$^{-1}$, and $b=-0.01$ cm$^{-1}$ G$^{-1}$. The plot shows the spectrum of $H_{BR}$ [Eq. (1)] for $S=1$ and $I=3/2$, exhibiting a “hidden symmetry” at the $B \neq 0$ crossings. The spectrum was calculated by analytically diagonalizing the matrix corresponding to the Breit-Rabi Hamiltonian [Eq. (1)], and then plotting the eigenvalues numerically. Two $(2I+1)=$ fourfold crossings can be seen at $B_h = \pm 20$ G [Eq. (3)]. At these points the lowest state from the $F=5/2$ manifold crosses the three highest states in the $F=3/2$ manifold. A similar spectrum exists for $I=2$ which is relevant to spin-relaxation processes in $^{87}\text{Rb}$ vapor [48].](033406-2)

$H_{BR}$ is the workhorse of magnetic resonance [45]; with a few redefinitions it can also describe fine structure [46]. More generally, it describes the coupling of any two quantum mechanical spins to each other as well as to an external field. With regard to level crossing phenomena $H_{BR}$ has been known to exhibit some interesting behavior. In zero magnetic field $H_{BR}$ exhibits an SU(2) symmetry, the generators of which are the three components of the total angular momentum

$$F = I + S.$$

(2)

The presence of a homogeneous magnetic field ($B \neq 0$) destroys this symmetry; the only obvious symmetry left is rotational invariance about the direction of the magnetic field. However, for $b=0$, $S=1$, $I \neq 0$, and the special magnetic field values of

$$B_h = \pm \left( I + \frac{1}{2} \right) \frac{A}{2a},$$

(3)

the Breit-Rabi Hamiltonian exhibits a $(2I+1)$fold “hidden” symmetry [47]. That is, at $B=B_h$, $2I+1$ levels in the spectrum cross at the same point as shown in Fig. 1 for $I=3/2$. It has been established that an SU(2) symmetry can be recovered for $H_{BR}$ at these points [47], although its generators are much more nontrivial than those in the field-free case (2), and the origin of the symmetry is not well understood [49]. The hidden symmetries in the $I=2$ case are experimentally relevant to the description of spin-relaxation in $^{87}\text{Rb}$ vapor [48]. Such a case is an example where level crossings have interesting physical consequences for an atom described by $H_{BR}$.

B. $^{23}\text{Na}$

Our motivation for inspecting the spectrum of an atom in a magnetic field for level crossings arose in the context of
TABLE I. The values of parameters used in the text, except where defined otherwise. Where confusion with the $^{87}$Rb parameters is not possible, $A_{Na}, aNa$, and $bNa$ have been referred to as $A$, $a$, and $b$ respectively. The numerical values presented in the table can be derived from [55].

\[
\begin{array}{|c|c|c|}
\hline
\text{No.} & \text{Parameter} & \text{Value} \text{ (units)} \\
\hline
1 & A_{Na} (A) & 0.029 547 6 \text{ cm}^{-1} \\
2 & aRb & 0.113 99 \text{ cm}^{-1} \\
3 & aNa (a) & 9.3482 \times 10^{-5} \text{ cm}^{-1} \text{ G}^{-1} \\
4 & aRb & 9.3482 \times 10^{-5} \text{ cm}^{-1} \text{ G}^{-1} \\
5 & bNa (b) & -3.755 12 \times 10^{-8} \text{ cm}^{-1} \text{ G}^{-1} \\
6 & bRb & -4.647 31 \times 10^{-8} \text{ cm}^{-1} \text{ G}^{-1} \\
\hline
\end{array}
\]

Feshbach resonances (\cite{34} and references therein). The experimental search for a Feshbach resonance characteristically begins with a spin-polarized sample of atoms and includes a broad sweep of the magnetic field. The Feshbach resonance occurs in the \textit{diatomic} spectrum and can be experimentally identified by examining inelastic loss [33], photoassociation [50] or rethermalization [51,52], for example. However if a crossing or a fine anticrossing is encountered in the \textit{atomic} spectrum while the magnetic field is being tuned, some of the atoms can be transferred to a different spin state, introducing an impurity into the sample [13] and possibly causing loss [53]. Also, for the purpose of theoretical bookkeeping it is useful to know if the low- and high-field states correlate adiabatically [54]. Such a correlation breaks down at a crossing. Lastly, eigenstates exchange character at an avoided crossing, which indicates a change in the good quantum numbers [34]. For these reasons, it is essential to be aware of (avoided) crossings in the atomic spectrum. The magnetic fields typically used in laboratory searches of Feshbach resonances are less than a kilogauss. Hence the parameter regime of our interest will be

\[
B_{\text{Fesh}} \in [0,1 \text{ kG}].
\]

We consider the specific case of an $^{23}$Na atom in its $3S_{1/2}$ ground state split by the hyperfine interaction into two levels labeled by the angular momentum $F=1+S$ [Eq. (2)] where $I=3/2$ and $S=1/2$ are the nuclear and electronic spins, respectively. We will refer to the atomic eigenstates in the $|F,M_F\rangle$ basis where $M_F$ is the component of $F$ along the magnetic field. In keeping with the discussion in Sec. V B [39] it is preferable to retain a polynomial form for the matrix elements. All representations will therefore be made in the uncoupled or “direct product” basis $|M_S,M_I\rangle$, where $M_{S,I}$ are the components of the electronic and nuclear spins along the magnetic field. Using the ordered basis

\[
|\frac{-1}{2},\frac{-3}{2}\rangle, |\frac{1}{2},\frac{3}{2}\rangle, |\frac{-1}{2},\frac{3}{2}\rangle, |\frac{1}{2},\frac{-3}{2}\rangle,
\]

we arrive at the matrix representation of Eq. (1):

\[
H_{bb} = \frac{1}{4} \begin{pmatrix}
3A - 2(a + 3b)B & -A + 2(a - b)B & 2\sqrt{3}A & -A + 2(a - b)B \\
-A + 2(a - b)B & 4A & 2\sqrt{3}A & -A + 2(a - b)B \\
2\sqrt{3}A & -2\sqrt{3}A & 3A + 2(a + 3b)B & 2\sqrt{3}A \\
2\sqrt{3}A & -2\sqrt{3}A & 3A + 2(a + 3b)B & 3A + 2(a + 3b)B
\end{pmatrix}.
\]

(6)

We note that every element in the matrix (6) is linear in the parameters $A$, $B$, $a$, and $b$. Further, only the diagonal elements contain all the parameters. The off-diagonal elements depend only on $A$. The numerical values of the parameters are given in Table I.

\[
I. \ b=0
\]

To begin our study of level crossings in the spectrum of Eq. (6) with a simplification we consider the fact that

\[
|b| \ll |a|
\]

(7)

in Eq. (1) [40]. This happens to be the case since the nuclear magneton is smaller than the Bohr magneton by the ratio of the electron-to-proton masses, which is $\sim 1000$. “Switching off” the interaction of the nuclear spin with the magnetic field, we set $b = 0$ in Eq. (6). We proceed to calculate the discriminant of $H_{bb}^{\text{field}}$ using built-in functions in Mathematica.
\[ D[H_{BR}^{\text{det}}] = \frac{81A^2a^6B^6(64A^6 + 32A^4a^2B^2 + 8A^2a^4B^4 + a^6B^6)}{65536}. \]

In order to find the crossings in the spectrum of \( H_{BR}^{\text{det}} \) we look for the real roots of Eq. (8) (as per Sec. III [39]). By inspecting Eq. (8) we detect a 26-fold real root at \( B=0 \). This root corresponds to “zero-field” crossings conventionally known as degeneracies rather than as crossings, and to which we will return presently. The remaining part of Eq. (8) is the factor in parentheses. It is even in \( B \) and exhibits no sign changes in its coefficients; by Descartes’ rule it has no real roots (Sec. VI B 4 [39]). Hence there are no level crossings in the spectrum for \( B \neq 0 \), a fact we have established without looking at the spectrum itself. That this can be done is of course well known.

The factor in parentheses in Eq. (8) is a sextic with no real roots, hence all its roots must be complex. The roots can be obtained analytically:

\[ B = \pm \frac{2A}{a}i, \quad \frac{(\pm 1 \pm i\sqrt{3})A}{a}. \]

It must be mentioned that the case of the discriminant (8) is exceptional since for any general physical system the roots cannot be obtained analytically and have to be solved for numerically. The real parts of the complex roots are expected to correspond to avoided crossings (Sec. VI B 3 [39]). From Eq. (9) these occur at

\[ B = 0, \quad \pm \frac{A}{a}. \]

For \(^{23}\text{Na} \), \( A/a = 316 \text{ G} \) [40]. We can verify the presence of the avoided crossings by allowing ourselves to look at the spectrum (Fig. 2). Physically the field \( B = |A/a| \) corresponds to the crossover into the Paschen-Back regime. It is the point at which the Zeeman energy becomes comparable to the hyperfine splitting [34].

We now make some detailed comments on the structure of Eq. (8). We note that in keeping with the arguments of Sec. VI B 1 [39] the degree of the discriminant is even in every parameter. This is one check of the correctness of Eq. (8). Also using Eq. (16) Sec. VI B 1 [39] we expect the degree of the discriminant to be 56 mod 2 in any parameter. Equation (8) is actually of degree 32 in the parameter \( B \). This can be understood in the context of the discussion in Sec. VI B 1 [39], since all the off-diagonal elements of the matrix (6) are independent of \( B \), and many of them are identically zero.

Let us now reconsider the 26-fold real root of Eq. (8) at \( B=0 \). The exponent (26) of this root may be traced to the hyperfine degeneracies of the Hamiltonian [Eq. (1)] in the absence of a magnetic field, which were found by solving for the spectrum (Fig. 2). From the spectrum we know that there are \( 3(F=1) \) and \( 5(F=2) \) hyperfine states in each degenerate manifold. Since a crossing is defined to be the intersection of exactly two curves [Sec. VI B 7 (a) [39]] the \( 3(F=1) \) curves meeting at \( B=0 \) in the spectrum give rise to \( \binom{3}{2} = 3 \) crossings.

![FIG. 2. The parameters used for both plots are given in Table I.](image)

(a) The spectrum of \( H_{BR}^{\text{det}} \) for \(^{23}\text{Na} \) \((S=1/2, I=3/2)\). The spectrum was calculated by analytically diagonalizing the matrix in Eq. (6), and plotting the eigenvalues numerically. The only crossings are at \( B=0 \). There are three avoided crossings, of which two have been highlighted: The avoided crossing at \( B=0 \) occurs between the states shown with dashed lines; the avoided crossing at \( B=316 \text{ G} \) occurs between the states shown with dotted lines. (b) \( \log[D[H_{BR}^{\text{det}}]+1] \), the logarithmic representation of the discriminant of \( H_{BR}^{\text{det}} \). There is a single dip at \( B=0 \) corresponding to degeneracies in the spectrum. The overall trend of the curve is evidently logarithmic. Note that (a) the spectrum as well as (b) the discriminant are both symmetric in \( B \) but some individual eigenvalues, such as the dotted ones in (a), are not.

Likewise the \( 5(F=2) \) curves give rise to \( \binom{5}{2} = 10 \) crossings. Each crossing contributes a factor quadratic in \( B \) (Sec. VI B 1, [39]) to the discriminant. Since

\[ 2 \left[ \binom{3}{2} + \binom{5}{2} \right] = 26, \]

the exponent of the root at \( B=0 \) in Eq. (8) is accounted for. The 24-fold root of Eq. (8) at \( A=0 \) may be explained in a similar way. For \( A=0 \) the spectrum consists of \( 4(M_S=-1/2) \) states all degenerate and \( 4(M_S=1/2) \) states also degenerate amongst themselves but not with the \( (M_S=1/2) \) states. The number of crossings in either manifold is \( \binom{4}{2} = 6 \), and the total is 12. Thus the exponent of \( A \) in the discriminant (8) should be —and is—24. We see that the strengths of the zeros of the discriminant faithfully encode the degeneracies due to the physical symmetries of the corresponding Hamiltonian. As remarked in Sec. VI B 7 (a) [39] this fact is a useful check on the correctness of the discriminant. Conversely, the presence of manifold roots in the discriminant alerts us to the
existence of a symmetry in the corresponding physical system.

As a last check we can verify that the bound of Eq. (23) Sec. VI B 1 [39] on the total number of (avoided) crossings is exactly satisfied at both $A=0$ and $B=0$. The degree of the discriminant [Eq. (8)] in the parameters $A(B)$ is $k^{A(B)} = 30(32)$. The number of crossings is $n_{c}^{A(B)} = 12(13)$ and the number of avoided crossings $n_{ac}^{A(B)} = 3(3)$. The bound of Eq. (23) Sec. VI B 1 [39] holds exactly since

$$n_{c}^{A(B)} + n_{ac}^{A(B)} = k^{A(B)}/2.$$  \hspace{1cm} (12)

2. $b \neq 0$

What happens if $b \neq 0$, i.e., if we switch back on the interaction between the nuclear spin and the magnetic field? To find out we calculate the discriminant $D[H_{BR}]$ for $b \neq 0$,

$$D[H_{BR}]= \frac{81}{65536}B^{26}(a + 3b)^{2}[64A^{6} + 32A^{4}(a - b)^{2}B^{2}$$

$$+ 8A^{2}(a - b)^{2}B^{4} + (a - b)^{6}]B^{2}[(a + 3b)A \pm 2abB]$$

$$\times[(a + 3b)A \pm (a + b)2bB]$$

$$\times[(a + 3b)A \pm (a + b)2bB]$$

$$\times[(a - 5b)(a + 3b)A^{2} - 4b^{2}(a + 2ab + 3b^{2})B^{2}]$$

$$\times[(a - 5b)(a + 3b)A^{2} + 4b^{2}B(a - b)]$$

$$\times B - 4ab^{2}(a - 2b)B^{2}]^{2}. \hspace{1cm} (13)$$

The introduction of $b$ brings about several changes in the discriminant as may be seen by comparing Eqs. (8) and (13). First, the $A^{24}$ degeneracy in Eq. (8) is removed: Even in the absence of hyperfine interaction ($A=0$) the coupling of the nuclear spin to a nonzero magnetic field ($B \neq 0$) prevents the occurrence of degeneracy in the spectrum.

Further, the avoided crossings now correspond to the roots of the sextic in the first line of the right-hand side of Eq. (13), which is the same as the sextic in braces in Eq. (8), but with $a$ replaced by $a-b$. Not surprisingly then, the roots can be found analytically as for Eq. (8) and are

$$B = \pm \frac{2A}{a-b}, \hspace{1cm} (14)$$

Hence the avoided crossings are now located at

$$B = 0, \pm \frac{A}{a-b}. \hspace{1cm} (15)$$

The avoided crossings located at $\pm A/(a-b)$ have moved slightly closer to the origin ($B=0$) since $b/a \approx -10^{-3}$ for $^{23}$Na (Table I).

More importantly, there now appear crossings in the spectrum for $B \neq 0$, as can be seen from the roots of the squared factor in curly braces in Eq. (13), which are all real. The magnetic fields corresponding to the crossing points can be obtained analytically in terms of the remaining parameters:

$$B = \pm \frac{(a + 3b)A}{2ab}, \pm \frac{(a + 3b)A}{(a + b)2b}, \pm \frac{(a + 3b)A}{(a + 2b)2b},$$

$$\pm \frac{A}{2b} \left[ (a - 5b)(a + 3b)A^{2} - 4b^{2}(a + 2ab + 3b^{2})B^{2} \right]^{1/2},$$

$$\pm \frac{A}{2b} \left[ (a - 5b)(a + 3b)A^{2} + 4b^{2}B(a - b) \right]^{1/2}, \hspace{1cm} (16)$$

It should be noted that the last four roots in Eq. (16) are real only if $(a-b)^{4} \geq 16ab^{2}(a-2b)$, which is the case for $^{23}$Na as may be verified from Table I. If this condition is not satisfied the four roots are complex and correspond to two avoided crossings.

For $B > 0$ there are six crossings clustered around 400 kG, a rather high value compared to $B_{	ext{Fosh}}$ defined in Eq. (4). These crossings were introduced due to the turn-on of $b$, the coupling of the nuclear spin to the magnetic field. The discriminant thus indicates in a clear way the physical mechanism responsible for crossings in the Breit-Rabi spectrum of the ground state of $^{23}$Na. A similar calculation reveals this to be true also of the excited $3^{2}P_{1/2}$ hyperfine manifold in $^{23}$Na but not of the $3^{2}P_{3/2}$ manifold, where crossings survive as long as $a \neq 0$.

In the regime $B_{	ext{Fosh}} \in [0, 1 \text{ kG}]$ therefore the discriminant alerts us to the absence of any crossings as well as to the presence of two avoided crossings for $^{23}$Na. Plots of the spectrum and the discriminant, using parameters optimized for visibility are shown in Fig. 3. Since the spectrum of $H_{BR}$ has no crossings in our region of interest, each curve extrapolates uniquely to a low-field state and can therefore be labeled using $[FM]$, although strictly speaking $F$ is not conserved in the presence of a magnetic field. Also the avoided crossings correspond to large gaps as can be seen from the spectrum and will not lead to impurities in the atomic sample while the magnetic field is being tuned across them.

We would like to note at this point that the exercise conducted so far in this section demonstrates the typical use of algebraic technique. The discriminant is first calculated and used to locate the (avoided) crossings. The spectrum is then consulted and more detailed information obtained.

To the best of our knowledge invariants of the Breit-Rabi Hamiltonian such as Eqs. (8) and (13), 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 $H_{BR}$. Examination of these invariants yields interesting information about the corresponding physical systems.

For example, from the analytic form of the roots in Eq. (16) we find that though they can cluster close to each other for some values of the parameters $A$, $B$, $a$, and $b$, they cannot all be made to coincide exactly for any combination. This implies the presence of an approximate symmetry of the Hamiltonian $H_{BR}$, which becomes exact when $S=1$ [49]. The discriminant for the corresponding $(S=1)$ Hamiltonian (whose scaled spectrum is shown in Fig. 1) explicitly points to the presence of the hidden symmetry at $B=\pm 20\text{ G}$, in the units of Fig. 1. It contains the factors $(B \pm 20)^{12}$ which correctly account for the location of the crossings as well as the
sponding to the crossings are found to reach down to zero, and number as well as magnetic field locations are therefore easier to

symmetric in has not been included here.

cumbersome the complete expression for the discriminant ing the 12-fold root in the discriminant. Since it is rather

degeneracy of the four intersecting curves as $2^4 = 12$. Also using the techniques in Sec. VI B 7 (b) [39] it can be verified that the first 11 subdiscriminants vanish at $B = \pm 20$, indicating the 12-fold root in the discriminant. Since it is rather

different $M_F$, i.e., different symmetry. Thus there are no accidental crossings in the Breit-Rabi spectrum, and all the (avoided) crossings obey the WvN noncrossing rule.

III. NONINTERACTING ATOM PAIRS

Before we consider the case of a molecule in a magnetic field, we examine the corresponding noninteracting atom pair. In the context of Feshbach resonances, this corresponds to the asymptotic part of an s-wave collision between the two atoms, i.e., when they are far apart [34].

For our example we pick the $^{23}$Na atom considered in Sec. II B above, and an $^8$Rb atom. The entrance channel to the collision is labeled by the $|F, M_F\rangle$ states in which we prepare the atoms: $|2, 2\rangle_{Na}$, $|2, 2\rangle_{Rb}$. The presence of the magnetic field preserves only the component of the total angular momentum ($M_{\text{Total}} = 4$) along its direction. This implies a coupling to three other states with the same $M_{\text{Total}}$:

$$ |2, 2\rangle, |3, 2\rangle, |2, 1\rangle, |3, 3\rangle, |1, 1\rangle, |3, 3\rangle. $$

Here we have retained the ordering with respect to the atomic species and dropped the subscripts. Following the discussion of Sec. V B [39] we work in the “direct product” basis $|M_F, M_S\rangle_{Na}|M_F, M_S\rangle_{Rb}$. The states in this basis which give rise to the states in [Eq. (17)] are
where we have again retained the ordering with respect to the atomic species and dropped the subscripts.

Since we are considering atoms which are yet too far apart to interact, the Hamiltonian of the system, $H_{BR}^{Na-Rb}$, is just the sum of the individual energies $H_{BR}$ [Eq. (1)] of each atom. In the ordered basis presented in Eq. (18) we obtain the representation

$$
H_{BR}^{Na-Rb} = \begin{pmatrix}
\frac{3ANa}{4} + \frac{3ARb}{4} & \frac{(aNa + 3bNa)B}{2} & \frac{\sqrt{3}ARb}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}ANa}{2} & \frac{(aNa + 3bNa)B}{2} & \frac{\sqrt{3}ANa}{2} & \frac{ANa}{4} + \frac{5ARb}{4} \\
0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}ANa}{2} & \frac{(aNa + 3bNa)B}{2} & \frac{\sqrt{3}ANa}{2} & \frac{ANa}{4} + \frac{5ARb}{4} & \frac{(aNa + 3bNa)B}{2} \\
\end{pmatrix},
$$

where $ANa, ARb$ are the hyperfine splittings and $aNa(bNa), aRb(bNa)$ are the electronic (nuclear) couplings to the magnetic field for the $^{23}Na$ and $^{85}Rb$ atoms, respectively. The numerical values of these parameters are given in Table I.

The two-atom internal energies corresponding to $H_{BR}^{Na-Rb}$ are shown in the spectrum in Fig. 4(a). They define the thresholds of the collision for the various internal states (17) of the two atoms for a given value of $B$. It is of both experimental and theoretical interest to inspect this spectrum for crossings in the regime $B_{red} \in [0, 1 \text{ kG}]$. This is because for a given collision entrance channel, bound states for a Feshbach resonance are only available from channels higher in energy [33]. Hence it is important to track the energy hierarchy of the levels, which changes at a crossing. We substitute numbers for all the atomic constants (given in Table I) and present the discriminant of $H_{BR}^{Na-Rb}$ as a polynomial in $B$ only:

$$
D[H_{BR}^{Na-Rb}] = NB^2 \prod_{j=1}^{2} (B - c_{j})^2 \prod_{j=1}^{2} (B - a_{j})(B - \tilde{a}_{j}),
$$

where $c_1 = 502.2 \text{ G}$ and $c_2 = 4.73 \text{ MG}$ denote the non-zero-field crossings (there is one at $B=0$ also). The avoided crossings correspond to the complex roots $a_1 = (-316+547.2i) \text{ G}$ and $a_2 = (-2437.6+2725.3i) \text{ G}$. $N$ is an overall numerical factor. A smooth representation of the quite nonlinear Eq. (20) is provided by plotting $\log[D[H_{BR}^{Na-Rb}] + 1]$ [Fig. 4(b)]. As a visual aid to locating crossings this is, as in the case of Fig. 4, superior to the spectrum.

We make some further observations about Fig. 4. We note first that the shallow avoided crossings in the spectrum [Fig. 4(a)] are not revealed in the plot of the discriminant [Fig. 4(b)].
FIG. 4. The parameters used for all three plots are given in Table I. (a) The spectrum of $H_{\text{BR}}^{23\text{Na}-23\text{Rb}}$ for the $M_{\text{total}}=4$ manifold. The spectrum was calculated by analytically diagonalizing the matrix in Eq. (19) and plotting the eigenvalues numerically. Note that the spectrum is not symmetric in $B$. The avoided crossings at $-316(-2437)$ G are between the states drawn using solid (dotted) lines. The crossings at 0 and 502.2 G between the states $[2,1]3,3$ and $[2,2]3,2$ are not well resolved, occur in the region circled by the dotted ellipse, and are shown in detail in (c). (b) Logarithmic representation of the discriminant of $H_{\text{BR}}^{23\text{Na}-23\text{Rb}}$, displaying the crossings clearly. Like the spectrum in (a) the representation of the discriminant is not symmetric in $B$. (c) Detail of the part of the spectrum in (a) circled by the dotted ellipse shows crossings at $B=0,502.2$ G (indicated by the vertical dotted lines). It is still quite difficult to resolve the two crossings if we try to include them both on the same scale.

Actually sensitive to avoided crossings and goes through local minima (they do not touch zero) at those points. However for shallow avoided crossings the minima are not very pronounced and are even less visible on a logarithmic scale. Also, the presence of a crossing at or near the same parameter value introduces a strong feature (i.e., a dip to zero) in the discriminant, which further obscures the signature of the avoided crossing. Secondly, the spectrum in Fig. 4(a) is not symmetric in $B$. The symmetry due to Kramer’s theorem [46] which applied to the $^{23}\text{Na}$ atom (which has an odd number of electrons) in Sec. II B 2 no longer holds for the atom pair (which has an even number of electrons). This asymmetry is reflected in the discriminant [in Eq. (20) and in Fig. 4(b)], as the $a_{1,2}$ in Eq. (20) are not purely imaginary. This again raises the issue of whether there is a correlation between the (a) symmetries of the discriminant and the Hamiltonian for any particular parameter (Sec. VIII C [39]).

A detailed study of the crossings in the spectrum [Fig. 4(c)] indicates that Feshbach resonances may be expected in the [2,1]3,3 entrance channel for $B \in [0,502.2$ G] only. Only in that interval does the entrance channel cross below the state [2,2]3,2; elsewhere it is the most energetic state in the $M_{\text{total}}=4$ manifold. This is an example of how the identification of level crossings proves useful in guiding an experimental search for Feshbach resonances in the laboratory.

The use of Eq. (20) makes the study of the variation of the (avoided) crossings with the parameters of the problem quite easy. For example, if we neglect only the coupling $b_{\text{Na}}(b_{\text{Rb}})$ of the $^{23}\text{Na}(^{23}\text{Rb})$ nucleus to the magnetic field the crossing $c_2$ moves to 0.9(−1.1) MG. If we neglect both $b_{\text{Na}}$ as well as $b_{\text{Rb}}$, $c_2$ disappears from the spectrum and only the crossings at $B=0$ and $B=502.2$ G (shown in Fig. 4) remain. Further they are shifted, as are the avoided crossings, by about ±0.05% of their previous values. As a result of setting $b_{\text{Na}}$ and $b_{\text{Rb}}$ equal to zero the degree of the discriminant in $B$ also goes down, so the bound of Eq. (23) Sec. VI B 1 [39] on the total number of (avoided) crossings still holds.

IV. MOLECULES

Now we analyze the case of a heteronuclear diatomic molecule in a magnetic field. We consider the $^{23}\text{Na}^{23}\text{Rb}$ molecule, which we model by introducing interactions between the atoms of the $^{23}\text{Na}^{23}\text{Rb}$ pair of Sec. III. The molecular Hamiltonian is

$$H_{\text{mol}} = E_{\text{kin}} + U(B) + V(R).$$  \hspace{5cm} (21)

Here $E_{\text{kin}}$ denotes the kinetic energy of the nuclei, $U(B)$ the internal energies of the respective atoms in the magnetic field, and $V(R)$ the molecular potential energy at the internuclear distance $R$. Specifically,

$$V(R) = V_S P_S + V_T P_T,$$  \hspace{5cm} (22)

where $V_S(T)$ are the molecular (singlet, triplet) electrostatic potentials, and $P_{S,T}$ are projection operators on to the corresponding subspaces [54]. $V_{S,T}$ are usually complicated functions of the internuclear distance and are obtained most reliably from experimental spectroscopic data [43]. In writing the molecular potential (22) we have neglected the weak spin-spin potential energy [34].

In the standard Born-Oppenheimer approximation (BOA) of molecular physics the $E_{\text{kin}}$ in Eq. (21) is at first neglected and a set of adiabatic electronic potential curves obtained by diagonalizing the (in our case $4 \times 4$) interaction matrix
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 is 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 \[54\].

In the basis (18) as used in Sec. III the matrix representation of the operator $H_{BO}$ [Eq. (23)] is

\[
H_{BO} = U(B) + V(R),
\]  

\[
\begin{pmatrix}
\frac{3ANa}{4} + \frac{3ARb}{4} + \frac{V_T}{2} \\
\frac{(aNa + 3bNa)B}{2} + \frac{\sqrt{5}ARb}{2} + \frac{(aRb + 3bRb)B}{2} \\
\frac{\sqrt{5}ARb}{2} + \frac{(aNa + 3bNa)B}{2} + \frac{(aRb - 5bRb)B}{2} + \frac{V_S + V_T}{2}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{ANa}{4} + \frac{5ARb}{4} + \frac{(aNa + bNa)B}{2} + \frac{\sqrt{3}ANa}{2} + \frac{(aRb + 5bRb)B}{2} + \frac{V_T}{2}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{V_S - V_T}{2} \\
\frac{\sqrt{3}ANa}{2} - \frac{(aNa - 3bNa)B}{2} + \frac{(aRb + 5bRb)B}{2} + \frac{V_S + V_T}{2}
\end{pmatrix}
\]

\[
0
\]

We note that the two previously unconnected block diagonal submatrices in Eq. (19) are now connected by the matrix element $(V_S - V_T)/2$. Matrices similar to Eq. (24) were explicitly derived in [56] for the heteronuclear diatomics HD, TD in a magnetic field [57]. The eigenvalues of $H_{BO}$ correspond to the Born-Oppenheimer electronic potential-curves of the molecule $^{23}$Na$^{85}$Rb in the manifold where the projection of total angular momentum along the magnetic field is 4. Plots of the eigenvalues of $H_{BO}$ are shown in Fig. 5 as a function of the internuclear distance $R$ for different values of the magnetic field $B$. In order to improve the clarity of the spectra Lennard-Jones potentials [58] have been used instead of the experimentally obtained $^{23}$Na$^{85}$Rb [43] potentials. However, the parameters in the Lennard-Jones potentials—the depths and the locations of the singlet and triplet minima—have been assigned using actual experimental data [43]. Both the actual potentials and the Lennard-Jones model exhibit qualitatively similar spectra.
Zeeman energies are identically zero. Furthermore, crossings of the electronic curves in a diatomic molecule influence spin-flipping and hyperfine-induced predissociation, which are important processes for spin-polarized gases [36].

Since the BOA breaks down at the crossings in the spectrum of $H_{BO}$ we try to locate the real roots of $D[H_{BO}]$. But first we make a crucial transformation. We rewrite Eq. (22) as

$$V(R) = X(P_S - P_T) + D,$$  \hfill (25)

where

$$X = (V_S - V_T)/2$$ \hfill (26)

is the quantum mechanical exchange energy responsible for chemical bonding and

$$D = (V_S + V_T)/2.$$ \hfill (27)

The “direct product” basis states (18) used to evaluate the matrix elements of $V(R)$ [Eq. (25)] are not eigenstates of the singlet and triplet projection operators $P_{S,T}$. Thus the first term $X(P_S - P_T)$ of $V(R)$ will give rise to diagonal as well as off-diagonal terms in the matrix representation of $V(R)$. However, the second term $D$ does not depend on the spin operators $P_{S,T}$ and will only give rise to diagonal terms in the matrix representation of $V(R)$. This can be verified from the matrix representation of $H_{BO}$ [Eq. (24)]. The off-diagonal terms involve $X$ only, while the diagonal elements involve $(V_S + V_T)/2 = D$ as well as $V_T = D - X$.

The introduction of $X$ turns out to be crucial to the solution of the curve crossing problem, because of the following reason. The $V_{S,T}$ as mentioned above, are rather complicated functions of the internuclear distance $R$. For $^{23}{\text{Na}}^{85}{\text{Rb}}$ for instance, modeling of the latest experimental data requires 32(47) parameters to fit $V_{S(T)}$, respectively [43]. The parameters of this fit have to be varied within their uncertainties, in order to arrive at the bounds on the Feshbach resonance predictions as well as to establish their validity. Varying all the parameters entails a numerical exercise in $(32+47+1=)180$-dimensional parameter space, in order to inspect the spectrum for crossings for each set of $V_S, V_T, and B$. This is not a practical exercise. We show below how by introducing $X$, we can find crossings in the spectrum of $H_{BO}$ by just requiring $V_S - V_T$ to be real. The procedure used will bypass any need to know the details of the complicated functional dependence of $V_{S,T}$ on $R$.

We recall that $D[H_{BO}]$ does not change if we subtract the same function from all the diagonal elements of $H_{BO}$ (Sec. V C [39]). Making use of this general property of discriminants, we remove the second term ($D$) in Eq. (25). That is, in order to find the discriminant we calculate $D[H_{BO} - D] = D(H_{BO})$. In the matrix in Eq. (24) it can be seen that after subtraction of $(V_S + V_T)/2$ from the diagonal terms the potentials $V_{S,T}$ only appear in the combination $(V_S - V_T)/2 = X$. We emphasize that $H_{BO} - D$ is a different Hamiltonian from $H_{BO}$ and that the formulation we have proposed is not applicable to the case of spectral searches. That is, although subtraction of $D$ can isolate the pure spin effects in

It is important 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. These crossing points are also of interest from other points of view. For instance, it has been shown that diatomic molecular electronic states can interact through the nuclear motion in a magnetic field at these crossings [25]. These interactions can be essentially regarded as vibronic, and are usually found, in the field-free case only in polyatomic molecules. Thus their presence in a diatomic molecule in the presence of a field is an interesting phenomenon. Further, crossings of the electronic curves in a diatomic molecule influence spin-flipping and hyperfine-induced predissociation, which are important processes for spin-polarized gases.
the Hamiltonian [56] in terms of the single variable \( X \) we still have to assign \( X \) a numerical value and uncertainty if we insist on using the spectrum to search for crossings.

We now substitute numbers for all the atomic constants (from Table I) in \( D[H_{BO}] \) which gives us

\[
D[H_{BO}] = \sum_{n=0}^{6} a_n(B)X^n,
\]

a polynomial of degree 6 in \( X \), whose coefficients \( a_n \) are polynomials in \( B \). Specific information about numerical parameter values can be established readily from Eq. (28), such as the absence of any crossings for \( X \neq 0 \) at \( B = 0 \), i.e., for a field-free heteronuclear diatomic molecule. However the turn-on of the magnetic field does introduce real roots for \( X \), and possible crossings for the molecule, consistent with earlier studies of vibronic interactions [25] as well as spectral identifications of such crossings [56].

In order to make our physics question amenable to mathematics we now phrase our enquiry about curve crossings in the following way: Can electronic level crossings be produced in the molecule \( D[H_{BO}] = 0 \) by the fields available in the laboratory \( (B_{\text{Fesh}} \leq [0, 1 \, \text{kG}]) \) for any real value of the exchange energy \( X \in [-\infty, +\infty] \)? Note that we do not assign any numerical value or a corresponding uncertainty to \( X \). All that we demand is that it be a real number, which it is. The answer to the question posed above can be found by examining the number of sign variations in the Sturm-Habicht (SH) sequence of \( D[H_{BO}] \) at \( X = \pm \infty \) (Sec. VI B 5 [39,59]).

The elements of the SH sequence are polynomials in the coefficients (Sec. VI B 5 [39]) \( p_n(B) \) in Eq. (28) which are themselves polynomials in the magnetic field \( B \). The elements of the SH sequence are therefore polynomials in \( B \) and change sign on either side of their zeros. Therefore a systematic way of searching for the real roots of \( D[H_{BO}] \) in \( X \) is to examine the SH sequence elements to the left and right of each of their zeros for \( B_{\text{Fesh}} \in [0, 1 \, \text{kG}] \). Once an interval is found in which real roots exist, the interval can be narrowed to find the values of \( X \) for which crossings exist. The obtained values of \( X \) can then be substituted in Eq. (28) in order to solve for the corresponding values of \( B \). We started by looking at the interval \( X \in [-\infty, +\infty] \) as a first guess, which turned out to be adequate. A more physical guess might be the interval \( X \in [0, +\infty] \) as the singlet well is always deeper than the triplet [18]. Further, if a certain range of internuclear distances \( R \) is of interest, the interval for \( X \) can be modified appropriately. This will require some knowledge of the molecular potentials, but a safe guess can easily be made even if the information about the \( V_{S,T} \) is quite imprecise.

In our case we have the benefit of having analyzed Eq. (20) which is the same as Eq. (28) with \( X = 0 \). Equation (20) implied the presence of real roots at \( B = 0 \), 502.2 G, and 4.73 MG, of which only the first two are in the regime of our interest \( B_{\text{Fesh}} \in [0, 1 \, \text{kG}] \). The SH analysis on the other hand indicates the presence of two roots for \( D[H_{BO}] \) for \( B_{\text{Fesh}} \in [0, 1 \, \text{kG}] \) and \( X \in [-\infty, +\infty] \). Narrowing the interval to a small one around \( X = 0 \) (\( X \in [-\epsilon, +\epsilon] \), where \( \epsilon \ll 1 \)) still yields two real roots, and points to \( X = 0 \) as a double root. Substituting \( X = 0 \) in \( D[H_{BO}] \) then yields \( B = 0 \) G and 502.2 G, as expected. Other than these there do not exist crossings for any \( X \) and the BOA is valid everywhere else in the parameter regime of interest.

We have demonstrated above the ability to extract the location of crossings in the spectrum of a diatomic molecule in a magnetic field knowing only the difference of the Born-Oppenheimer potentials \( V_{S,T} \) to be a real number. The locations of the crossings are entirely determined by atomic constants (Table I), and certainly limited by their accuracy. However the atomic constants are known to much better accuracy than the molecular potentials. To find the specific values of the internuclear distance \( R \) at which the crossings actually occur the \( V_{S,T} \) have to be consulted. However, in the present case we are actually interested in staying away from crossings since they represent the breakdown of the BOA, which is a problem from a physical as well as computational point of view. Algebraic technique allows us to find every value of the magnetic field that could cause the BOA to break down. If the regimes of magnetic field that correspond to breakdown of the BOA can be avoided, we need not refer to the \( V_{S,T} \) at all. That is, we do not need to know the values of the internuclear distance \( R \) at which the crossings occur.

More generally speaking the example using molecules in this section demonstrates the power of algebraic technique in being able to locate crossings even for Hamiltonians where information regarding some parameters (X for instance) is incomplete or is too complex to be useful for spectral searches.

V. DISCUSSION

Here we discuss some of the analysis presented in the article above as well as offer some comments on other systems where algebraic technique can be applied.

A. Atom pairs and molecules in magnetic fields

It is important to realize that the conclusions in the case of molecules rest on the assumption that the electrostatic potentials \( V_{S,T} \) can be decomposed onto orthogonal subspaces of the corresponding Hamiltonian, as in Eq. (22). In fact the latest spectroscopic data shows that even in the absence of a magnetic field the potentials cannot be rigorously decomposed into orthogonal singlet and triplet spaces near dissociation [43] as there is mixing due to hyperfine energies; a full coupled channel calculation is the only way to fit the experimental data describing bound rovibrational energies in the potentials \( V_{S,T} \). However, the error in neglecting this correction has been calculated [43] and is not large for many states. Hence the single-channel approximation may still be used in a first pass to estimate the Feshbach resonance positions, and has been, in the past [41,54,56].

We would also like to make some comments in the context of the VwN noncrossing rule [16]. We have not pursued the analysis far enough to establish if the (avoided) crossings in the case of the noninteracting atom pair (Fig. 4) obey the noncrossing rule. The state pairs \( |21\rangle - |11\rangle \) seem to

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TABLE II. Some examples of physical systems described by the Hamiltonian (29) and amenable to algebraic level crossing techniques described in this and the (previous) accompanying paper [39]. Only the nonzero parameters and their relationship to each other, if any, have been mentioned. For polar molecules, for instance, \( C_{xy} = C_{yz} = C_{xz} = 0 \).

<table>
<thead>
<tr>
<th>No.</th>
<th>Physical system</th>
<th>Nonzero parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polar molecules</td>
<td>( C_{xx} \neq C_{yy} \neq C_{zz} )</td>
<td>[60]</td>
</tr>
<tr>
<td>2</td>
<td>Doubly even nuclei</td>
<td>( C_{xx} \neq C_{yy} \neq C_{zz} )</td>
<td>[61]</td>
</tr>
<tr>
<td>3</td>
<td>Massive spinors in an anisotropic universe</td>
<td>( C_{xx} \neq C_{yy} \neq C_{zz} )</td>
<td>[62]</td>
</tr>
<tr>
<td>4</td>
<td>Spin-1 BEC with dipolar interactions</td>
<td>( C_{xx} = C_{yy} = C_{zz} )</td>
<td>[63]</td>
</tr>
<tr>
<td>5</td>
<td>Two-mode BEC in an asymmetric potential</td>
<td>( C_{zz}, B_x \neq B_z )</td>
<td>[64]</td>
</tr>
<tr>
<td>6</td>
<td>Neutrons in a helical magnetic field</td>
<td>( C_{zz}, B_x \neq B_z )</td>
<td>[65, 66]</td>
</tr>
</tbody>
</table>

have the same symmetry since they avoid each other. Likewise the pair \([22]|32rangle-[22]|22rangle\) seems to possess like symmetry since they too avoid each other. However the symmetries are different in the two cases since the states \([21]|33rangle\) and \([22]|32rangle\) do intersect. An examination of the detailed symmetry properties of the eigenstates should reveal these extra symmetries (beyond that of rotation about the magnetic field), if they exist, or prove the crossings to be accidental.

The case of homonuclear molecules (such as Na\(_2\)) has not been broached above to keep the discussion cogent. However interest in such dimers is long-standing and a large amount of work has been done both theoretically and experimentally ([34] and references therein) especially with regard to Feshbach resonances. It would seem natural and straightforward to extend the work presented here to the case of the homonuclears. However, we found that the application of algebraic theory presents some interesting issues when applied to the case of homonuclear diatomic molecules. Due to the requirements of statistics (bosonic or fermionic) the atom-pair (or molecular) states have to be symmetrized. As a result of the indistinguishability of the atoms the number of available states decrease. This leads to a contraction of the Hamiltonian matrix—it is now of lower dimension than it was before the symmetrization was applied. Naively calculating the discriminants of such Hamiltonian matrices leads to incorrect answers. For example the number of zero-field crossings in the spectrum is not accurately reflected in the structure of the discriminant. A correct prescription for calculating the discriminant needs to be found before the rest of algebraic technique can be transferred to this important class of problems.

B. Other systems

So far we have demonstrated the application of curve-crossing methods to realistic atomic and molecular spectra. Below we discuss possible future extensions of our work. Our methods can readily be applied to other atoms and molecules in magnetic fields in a way algorithmically similar to the cases discussed above. It is not difficult to extend the list of applications to atoms, molecules or other units of matter in a variety of circumstances. For example we note that the Breit-Rabi Hamiltonian [Eq. (1)] is a specific instance of a generic “spin-Hamiltonian”

\[
H_{\text{spin}} = \sum_{i,j} C_{ij} J_i J_j + \sum_i B_i J_i. \tag{29}
\]

Here the \( J_i \) are angular momentum operators and the indices \( i,j \) run over the spatial coordinates \( x,y,z \). By choosing the “coupling” \( (C_{ij}) \) and “field” \( (B_i) \) parameters appropriately Hamiltonians that can model real physical systems can be constructed from Eq. (29). Such Hamiltonians can then be subjected to level crossing analysis in the manner shown in this article. We have provided some specific examples of the possible physical systems in Table II.

Of course algebraic methods are not limited to Hamiltonian matrices describing quantum objects, nor for that matter to matrices arising in physics. Any system which contains parameters and can be modeled using a matrix is amenable to algebraic technique.

VI. CONCLUSIONS

In conclusion, we have applied powerful algebraic techniques to the spectra of atoms and molecules in order to find information about the number and location of (avoided) crossings, their degeneracy and behavior as a function of the atomic and molecular parameters, and their relation to the symmetries of the corresponding Hamiltonian. We have also found another way of visualizing them. As our main results, we have derived a class of invariants of the Breit-Rabi equation of magnetic resonance and devised a rigorous test for the breakdown of the Born-Oppenheimer approximation for molecules, assuming only that the molecular potentials are real.

ACKNOWLEDGMENTS

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[57] It should be mentioned that curve crossings were examined in this study albeit for the single magnetic field value of 100 kG.
[58] The Lennard-Jones potentials \( V_{LJ} = -D \Sigma + D_d \left[ 1 - R_{ST} / R \right]^6 \) were used with the singlet (triplet) well depths \( D_{ST} = -503.0 \) and the bond lengths \( R_{B} = 3.64(5.74) \) Å all taken from [43]. \( R \) is the internuclear distance.