

On the crossing of the energy levels of a parameter-dependent quantum-mechanical Hamiltonian

Francisco M. Fernández

Received: 3 June 2014 / Accepted: 6 July 2014 / Published online: 17 July 2014
© Springer International Publishing Switzerland 2014

Abstract The non-crossing rule for the energy levels of a parameter-dependent Hamiltonian is revisited and a flaw in a commonly accepted proof is revealed. Some aspects of avoided crossings are illustrated by means of simple models. One of them shows the close relationship between avoided crossings and exceptional points.

Keywords Avoided crossings · Non-crossing rule · Parameter-dependent operators · Exceptional points · PT symmetry

1 Introduction

It is well known that the potential energy curves of diatomic molecules do not cross (in fact, they even avoid each other) when the states have the same symmetry. This property of the electronic energies, commonly known as the non-crossing rule, has proved useful for the interpretation of many experiments in molecular spectroscopy and photochemistry [1, 2]. The theoretical explanation outlined by Teller [3], and typically reproduced in most textbooks on quantum chemistry [4, 5], was criticized by Naqvi and Brown [6]. After arguing that such a proof is based on a *non sequitur* the authors proposed an alternative justification of the non-crossing rule. Their argument is closely related to the Hellmann–Feynman theorem [7] in its more general off-diagonal form [8–12].

As a result of a recent investigation on non-Hermitian Hamiltonians we were led to revise the proofs on the non-crossing rule and the purpose of this paper is to put forward our analysis and discussion of the arguments given by Naqvi and Brown [6]. In

F. M. Fernández (✉)
División Química Teórica, INIFTA (UNLP, CCT La Plata-CONICET), Blvd. 113 S/N, Sucursal 4,
Casilla de Correo 16, 1900 La Plata, Argentina
e-mail: fernande@quimica.unlp.edu.ar

Sect. 2 we derive similar equations by means of the off-diagonal Hellmann–Feynman theorem [8–12] (and references therein). In Sect. 3 we illustrate the main theoretical conclusions by means of two simple examples. Finally, in Sect. 4 we summarize the main results and draw conclusions.

2 The off-diagonal Hellmann–Feynman theorem

The starting point is the time-independent Schrödinger equation

$$H\psi_n = E_n\psi_n. \quad (1)$$

It follows from $\langle\psi_m|H|\psi_n\rangle = \langle\psi_n|H|\psi_m\rangle^*$ and $E_m^* = E_m$, where $*$ stands for complex conjugation, that

$$(E_m - E_n)\langle\psi_m|\psi_n\rangle = 0. \quad (2)$$

From this expression we conclude that $\langle\psi_m|\psi_n\rangle = 0$ when $E_m \neq E_n$. This textbook result is well known but we write it here because it will be useful later on.

If H depends on a parameter λ , then the eigenfunctions and eigenvalues will depend on this parameter too. If we differentiate equation (1) with respect to λ and then apply the bra $\langle\psi_m|$ from the left we obtain the well known off-diagonal Hellmann–Feynman relation [8–12]

$$\langle\psi_m|H'|\psi_n\rangle = E_n'\langle\psi_m|\psi_n\rangle + (E_n - E_m)\langle\psi_m|\psi_n'\rangle, \quad (3)$$

where the prime denotes differentiation with respect to λ .

Suppose that E_m and E_n approach each other and cross at λ_0 : $\lim_{\lambda \rightarrow \lambda_0} (E_m - E_n) = 0$. When $\lambda \neq 0$ $\langle\psi_m|\psi_n\rangle = 0$ by virtue of equation (2) and because of continuity we should also have

$$\lim_{\lambda \rightarrow \lambda_0} \langle\psi_m|\psi_n\rangle = 0. \quad (4)$$

It follows from this equation and (3) that

$$\langle\psi_m|H'|\psi_n\rangle(\lambda_0) = \lim_{\lambda \rightarrow \lambda_0} \langle\psi_m|H'|\psi_n\rangle = 0. \quad (5)$$

Without this condition the approaching energy levels will not cross giving rise to an avoided crossing (it looks like an energy-level repulsion). Such behaviour requires a change in the slope of the approaching curves so that there should exist λ_m such that

$$E_m'(\lambda_m) = \langle\psi_m|H'|\psi_m\rangle(\lambda_m) = 0, \quad (6)$$

or λ_n such that

$$E_n'(\lambda_n) = \langle\psi_n|H'|\psi_n\rangle(\lambda_n) = 0, \quad (7)$$

or both. If the symmetries of ψ_m and ψ_n are different, then equation (5) holds for all λ and nothing prevents the approaching energy levels from crossing.

Throughout the discussion above we have tacitly assumed that the symmetry of H is the same for all λ (at least in the neighbourhood of λ_0 under analysis). In other words, we have assumed that both H and H' have the same symmetry. Suppose that the point group [13, 14] that describes the symmetry of H is G when $\lambda \neq \lambda_0$ and G_0 when $\lambda = \lambda_0$ and that the order h of G is smaller than the order h_0 of G_0 . Under such conditions the dimension of the subspaces of $H(\lambda_0)$ may be greater than those for $H(\lambda \neq \lambda_0)$ and we therefore expect some level crossings at $\lambda = \lambda_0$. Obviously, equation (5) applies to those states that become degenerate at this point. Naqvi [15] took into account such symmetry changes in a discussion of the crossing of potential-energy surfaces of polyatomic molecules.

It is clear that no further discussion is necessary for proving equation (4) that was required for deriving equation (5) from (3). However, Naqvi and Brown [6] criticized the continuity argument implied by equation (4). In order to discuss the additional steps in their proof we first derive another equation. If we differentiate the eigenvalue equation for ψ_m with respect to λ and apply $\langle \psi_n |$ from the left we arrive at an equation similar to (3):

$$\langle \psi_n | H' | \psi_m \rangle = E'_m \langle \psi_n | \psi_m \rangle + (E_m - E_n) \langle \psi_n | \psi'_m \rangle. \quad (8)$$

Subtracting the complex conjugate of equation (8) from equation (3) we obtain

$$(E_n - E_m)' \langle \psi_m | \psi_n \rangle + (E_n - E_m) \langle \psi_m | \psi_n \rangle' = 0, \quad (9)$$

which is obviously the derivative of equation (2) with respect to λ . When $\lim_{\lambda \rightarrow \lambda_0} (E_m - E_n) = 0$ equation (9) reduces to

$$[E'_n(\lambda_0) - E'_m(\lambda_0)] \langle \psi_m | \psi_n \rangle(\lambda_0) = 0. \quad (10)$$

Naqvi and Brown [6] considered two electronic states ψ_1 and ψ_2 of a diatomic molecule such that the corresponding electronic energy levels $E_1(R)$ and $E_2(R)$, where R is the internuclear distance, cross at $R = R_0$. They derived an equation similar to (10) that reads:

$$[E'_1(R_0) - E'_2(R_0)] \langle \psi_1^0 | \psi_2^0 \rangle = 0, \quad (11)$$

where ψ_1^0 and ψ_2^0 are the electronic states at $R = R_0$. They invoked this equation to prove that

$$\langle \psi_1^0 | \psi_2^0 \rangle = 0 \quad (12)$$

if $E'_1(R_0) \neq E'_2(R_0)$. The reason of this *circumlocution* was their concern about the continuity argument expressed in the statement: "It will be well to pause here momentarily and discuss the implications of Equation (12). Our demand that the two potential curves intersect at R_0 , forces us, to conclude that the overlap integral must

vanish even when $E_1 = E_2$. It is tempting to argue that, since $\langle \psi_1 | \psi_2 \rangle = 0$ for all R in the vicinity of $R = R_0$, it seems likely, on account of continuity, that it would also be true at R_0 . However, this argument is not only unnecessary but misleading, for we know that degenerate eigenfunctions need not be orthogonal; indeed we can choose them at will and make them to be non-orthogonal, if we so desire.” The reader may convince himself that the argument leading to equation (4) clearly implies that we do not choose those functions “at will” because the states at $R = R_0$ are just the ones that result from the limit $R \rightarrow R_0$ and, therefore, should remain orthogonal.

In order to prove that equation (12) holds even when $E_1^{(j)}(R_0) = E_2^{(j)}(R_0)$, $j = 0, 1, \dots, n$, provided that $E_1^{(n+1)}(R_0) \neq E_2^{(n+1)}(R_0)$, the authors differentiate equation (11) with respect to R as many times as necessary [6]. However, it is obvious that equation (11) is valid only for $R = R_0$ because we have discarded a term from the general equation valid for all R (see (9)). In order to carry out this proof correctly we should differentiate an equation like (9) as many times as necessary which is equivalent to differentiating an equation similar to (2) with respect to R just one more time. More precisely, if we define $\Delta(R) = E_1(R) - E_2(R)$ and $S(R) = \langle \psi_1 | \psi_2 \rangle (R)$ then equation (2) becomes $\Delta(R)S(R) = 0$. Differentiating it $n + 1$ times with respect to R and substituting R_0 for R we obtain

$$\sum_{j=0}^{n+1} \Delta^{(j)}(R_0)S^{(n+1-j)}(R_0) = \Delta^{(n+1)}(R_0)S(R_0) = 0, \tag{13}$$

from which it follows that $S(R_0) = 0$ when $\Delta^{(n+1)}(R_0) \neq 0$. In addition to being simpler and clearer, this argument is free from the flaw in the additional steps of the proof attempted by Naqvi and Brown [6]. However, in our opinion this discussion is unnecessary because, as argued above, $\lim_{R \rightarrow R_0} S(R) = 0$ always applies when

$$\lim_{R \rightarrow R_0} \Delta(R) = 0.$$

3 Examples

In Sect. 2 we mentioned the possibility that the symmetry of the system may change at $\lambda = \lambda_0$. In order to illustrate this point here we choose an extremely simple model, the quantum-mechanical harmonic oscillator

$$H = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + kx^2 + \lambda y^2, \quad k, \lambda > 0. \tag{14}$$

The eigenvalues and eigenfunctions of this dimensionless Hamiltonian operator are given by

$$E_{mn} = \sqrt{k}(2m + 1) + \sqrt{\lambda}(2n + 1), \quad m, n = 0, 1, \dots, \\ \psi_{mn}(x, y) = \phi_m(x, k)\phi_n(y, \lambda), \tag{15}$$

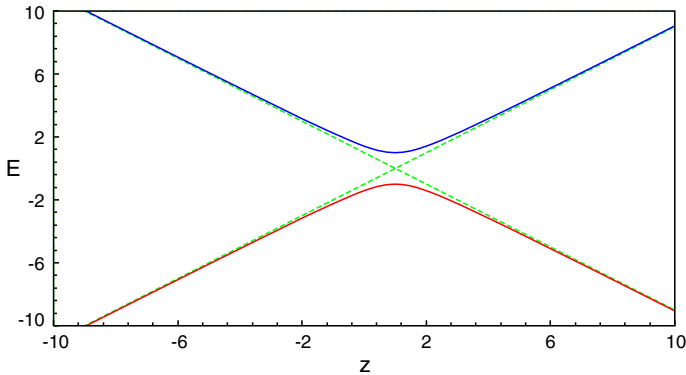


Fig. 1 Diagonal elements (dashed, green line) and eigenvalues (red, blue, continuous lines) for the two-level model (17) (Color figure online)

respectively, where $\phi_m(q, k)$ is an eigenfunction of the one-dimensional harmonic oscillator $H_{HO} = -\frac{\partial^2}{\partial q^2} + kq^2$.

When $\lambda \neq \lambda_0 = k$ the symmetry of the system is described by the Abelian point group C_{2v} that exhibits only one-dimensional irreducible representations [13, 14]. Therefore, its states are expected to be nondegenerate, except for accidental degeneracies that may occur when $\sqrt{\lambda/k}$ is rational. On the other hand, when $\lambda = \lambda_0$ we have an isotropic two-dimensional oscillator so that its symmetry is described by the full two-dimensional rotation group. Since all its eigenstates $\psi_{m+j}n-j$, $j = -m, -m+1, \dots, n$ are degenerate we expect an infinite number of crossings at $\lambda = \lambda_0$. Obviously, the off-diagonal matrix elements

$$\langle \psi_{mn} | H' | \psi_{m+j}n-j \rangle = \langle \phi_n | y^2 | \phi_{n-j} \rangle \delta_{m+m+j}, \quad (16)$$

vanish when $\lambda = \lambda_0$ in agreement with the argument given in Sect. 2.

The second example is even simpler but most interesting in some respects. In this case we choose a two-level system given by the matrix representation

$$\mathbf{H} = \begin{pmatrix} -1+z & -1 \\ -1 & 1-z \end{pmatrix}. \quad (17)$$

The diagonal elements intersect at $z = 1$ but the eigenvalues

$$E_1 = -\sqrt{z^2 - 2z + 2}, \quad E_2 = \sqrt{z^2 - 2z + 2}, \quad (18)$$

exhibit an avoided crossing as shown in Fig. 1. Note that $E'_m(z=1) = 0$, $m = 1, 2$, in agreement with equations (6) and (7). Figure 2 shows that the off-diagonal matrix element $\psi_1^t \cdot \mathbf{H}' \cdot \psi_2$, where ψ_1 and ψ_2 are the two column eigenvectors of \mathbf{H} , not only does not vanish but even exhibits a maximum precisely at $z = 1$.

It is well known that avoided crossings are associated to exceptional points in the complex plane [16–19]. Present case is not an exception as the eigenvalues (18)

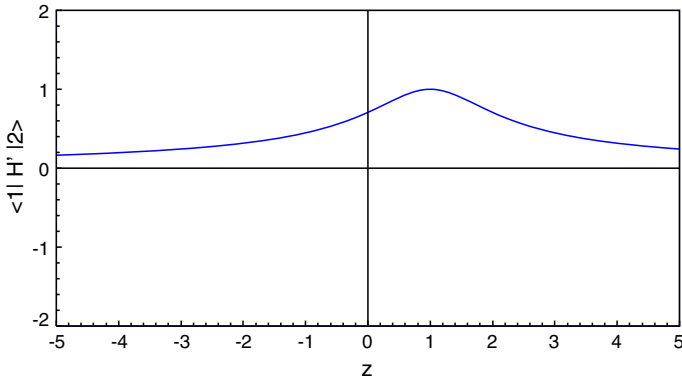


Fig. 2 Matrix element $\langle \psi_1 | H' | \psi_2 \rangle$ for the Hamiltonian (17)

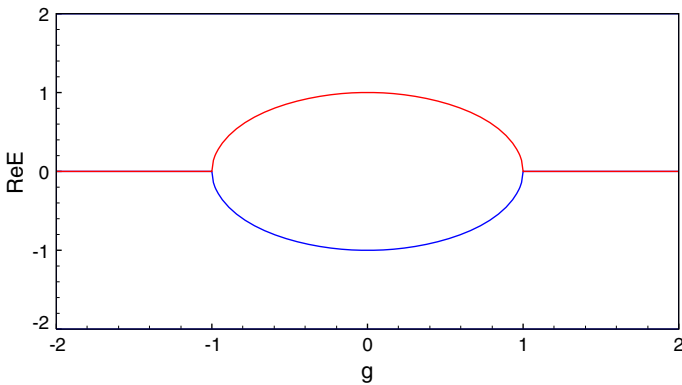


Fig. 3 Real parts of the two eigenvalues of the two-level model (19)

obviously cross in the complex z -plane at $z = 1 \pm i$. By means of the change of variables $z = 1 + ig$ we obtain a parity-time-symmetric non-Hermitian Hamiltonian [20]:

$$\mathbf{K} = \begin{pmatrix} ig & -1 \\ -1 & -ig \end{pmatrix}, \tag{19}$$

with eigenvalues

$$E_1 = -\sqrt{1 - g^2}, \quad E_2 = \sqrt{1 - g^2}. \tag{20}$$

In this case the eigenvalues are real for all $|g| < 1$ (unbroken parity-time (PT) symmetry [20]), approach each other as $g \rightarrow \pm 1$, coalesce at the exceptional points $g = \pm 1$ and become a pair of complex conjugate numbers for $|g| > 1$ (broken PT symmetry). This behaviour is shown in Fig. 3. At the exceptional points the two eigenvectors are linearly dependent [16–19].

It is most interesting to consider the more general case in which $z = x + iy$ that leads to an Hermitian Hamiltonian when $y = 0$ and a PT-symmetric one when $x = 1$. Figure 4 shows that $\Re E(x, y)$ is given by two intersecting surfaces that leave a hole

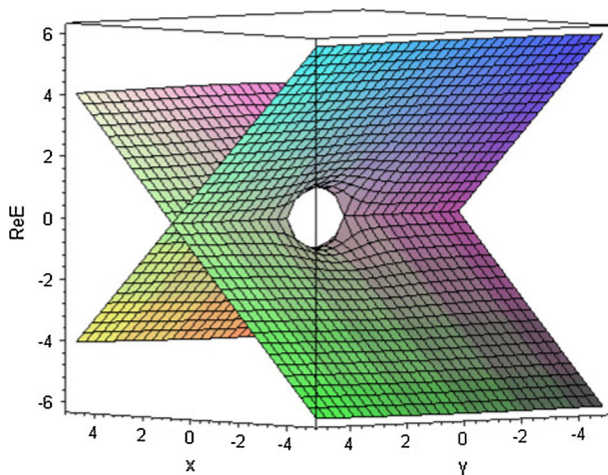


Fig. 4 Real parts of the eigenvalues of the Hamiltonian (17) when $z = x + iy$

where they do not touch. The intersection of the whole composite surface with the plane $(x, 0, z)$ yields the curves shown in Fig. 1 for the Hermitian Hamiltonian (17). On the other hand, the intersection with the plane $(1, y, z)$ yields the curve in Fig. 3 for the eigenvalues of the PT-symmetric Hamiltonian (19), where $y = g$.

4 Conclusions

The arguments put forward by Naqvi and Brown [6] are basically correct, except for the discussion of the orthogonality of the states at the crossing point $R = R_0$. In the first place, there is no problem with the orthogonality of the states at this point if one chooses them to be the result of the limit $R \rightarrow R_0$. Such states are not at all arbitrary and conserve their orthogonality even at the point of degeneracy. If one had any doubt about the orthogonality of the states at the crossing point one could in fact prove it as shown in equation (13) that is an improvement on the argument given by those authors that leads to the correct answer but is based on an inadequate equation.

Acknowledgments This report has been financially supported by PIP No. 11420110100062 (Consejo Nacional de Investigaciones Científicas y Técnicas, República Argentina).

References

1. A. Devaquet, Avoided crossings in photochemistry, *Presented at the Fifth International Symposium on Photochemistry* (Enschede, The Netherlands, 1974)
2. G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950)
3. M. Teller, *J. Phys. Chem.* **41**, 109 (1937)
4. H. Eyring, J. Walter, G.E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944)
5. F.L. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968)
6. K. Razi Naqvi, W. Byers Brown, *Int. J. Quantum Chem.* **6**, 271 (1972)

7. R.P. Feynman, Phys. Rev. **56**, 340 (1939)
8. D.J. Klein, P.L. DeVries, J. Chem. Phys. **68**, 160 (1978)
9. E.A. Castro, F.M. Fernández, J. Chem. Phys. **73**, 4711 (1980)
10. F.M. Fernández, Phys. Rev. B **69**, 037101 (2004)
11. R. Balawender, A. Holas, N.H. March, Phys. Rev. B **69**, 037103 (2004)
12. S.R. Vatsya, Phys. Rev. B **69**, 037102 (2004)
13. F.A. Cotton, *Chemical Applications of Group Theory* (Wiley, New York, 1990)
14. M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964)
15. K. Razi Naqvi, Chem. Phys. Lett. **15**, 634 (1972)
16. W.D. Heiss, A.L. Sannino, J. Phys. A **23**, 1167 (1990)
17. W.D. Heiss, Phys. Rev. E **61**, 929 (2000)
18. W.D. Heiss, H.L. Harney, Eur. Phys. J. D **17**, 149 (2001)
19. W.D. Heiss, Czech. J. Phys. **54**, 1091 (2004)
20. C.M. Bender, Rep. Prog. Phys. **70**, 947 (2007)