

# The Non-Crossing Rule in Molecular Quantum Mechanics

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## Abstracts

Previous mathematical proofs of the non-crossing rule concerning the potential energy curves of a diatomic molecule are examined and criticised. A new treatment is presented which is simple and mathematically rigorous.

Un traitement à la fois simple et avec rigueur mathématique est donné pour la "non-crossing rule" concernant les courbes de potentiel dans les molécules diatomiques. Un examen minutieux et critique des preuves que jusqu'à présent ont été données de cette règle précède notre déduction et en justifie sa nécessité.

Hier werden bisherige mathematische Beweise der "non-crossing" Regel in Verbindung mit Potentialenergiekurven eines zwei-atomigen Moleküls untersucht und kritisiert. Es wird eine neue Behandlung vorgeschlagen, die einfach und mathematisch rigoros ist.

The non-crossing rule, which is continually invoked in constructing the correlation diagrams for the electronic states of diatomic molecules, asserts that potential energy curves of the electronic states of the same symmetry species cannot cross as the internuclear distance is varied [1]. The rule is of immense importance in quantum mechanics and applies, in fact, to any system whose energy depends on a variable parameter which occurs in the Hamiltonian of the system. There is massive experimental evidence in spectroscopic literature for the validity of the non-crossing rule; the doubt which some earlier experiments cast on its ubiquity has now been dispelled, and in no instance does the rule seem to be violated [2].

It is our intention to point out in this paper that, of the two attempts that have been made at proving this indispensable rule, one is based on a *non-sequitur*, while the other incurs a defect by considering only two wave functions in a variational discussion; and to present a new derivation which seems to lack these deficiencies.

The most frequently cited proof, due originally to Teller [3] and quoted with or without some minor alterations by a number of other authors [4-9], is reproduced below for the sake of completeness. We assume that we already know all the correct

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eigenfunctions of the molecule except those corresponding to the two potential curves whose intersection we wish to investigate. Further, let us have two wave functions  $\phi_1$  and  $\phi_2$  which are orthogonal to all the *known* wave functions and to each other; the two unknown wave functions may be written as linear combinations of  $\phi_1$  and  $\phi_2$ . Let  $H(R)$  be the electronic Hamiltonian of the molecule, where  $R$  denotes the internuclear distance. The energy levels can be determined by solving the secular equation

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle = H_{ji}^*$$

Thus

$$E_{1,2} = \frac{1}{2}(H_{11} + H_{22}) \pm [(H_{11} - H_{22})^2 + 4 |H_{12}|^2]^{1/2}$$

The two values of  $E$  will be equal only if the two conditions

$$H_{11} = H_{22}$$

and

$$H_{12} = 0$$

are satisfied simultaneously. If at some value of  $R$  ( $= R_0$ , say)  $H_{11}(R_0) = H_{22}(R_0)$ , it will be a mere accident if  $H_{12}(R_0)$  is also zero. Thus it is almost impossible that by varying one parameter,  $R$ , we will achieve the condition  $E_1 = E_2$ ; hence the non-crossing of the two curves. However, if  $\phi_1$  and  $\phi_2$  belong to two different irreducible representations of the symmetry group of  $H$ ,  $H_{12}$  will be identically zero (at all  $R$ ) and crossing is possible.

We will now demonstrate that the foregoing argument proves the non-crossing rule only by begging the question at issue, and that it is logically deficient. As this fallacy seems to have been overlooked so far, a detailed discussion may not be amiss.

Since  $\phi_1$  and  $\phi_2$  belong to the same function space as that spanned by the two unknown eigenfunctions  $\psi_1$  and  $\psi_2$ , we can relate the two pairs of functions by the following orthogonal transformation matrices:

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$$

where  $\theta$  is some angle which will depend on  $R$ ; conversely,

$$\begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

We now calculate the relevant matrix elements:

$$H_{12} = \frac{1}{2}(E_1 - E_2) \sin 2\theta$$

$$H_{11} = E_1 \cos^2 \theta + E_2 \sin^2 \theta$$

$$H_{22} = E_1 \sin^2 \theta + E_2 \cos^2 \theta$$

whence

$$H_{11} - H_{22} = (E_1 - E_2) \cos 2\theta$$

It can now easily be seen that when  $H_{11} = H_{22}$ ,  $H_{12}$  must either be zero or  $\frac{1}{2}(E_1 - E_2)$ . But the former possibility can be ruled out only if we know that  $E_1 \neq E_2$ ; thus, the argument that the two conditions

$$H_{11} = H_{22} \quad \text{and} \quad H_{12} = 0$$

will not be satisfied simultaneously, does not follow unless it is shown that  $E_1$  cannot equal  $E_2$ , which is to be proved.

As  $\phi_1$  and  $\phi_2$  must vary with  $R$ , they cannot be constructed without a knowledge of the eigenfunctions  $\psi_{1,2}$  and the eigenvalues  $E_{1,2}$ , and it seems extremely artificial that one does not start with the correct wave functions themselves. Further, since any discussion of the eigenvalues is inherently restricted to the particular value of  $R$  for which  $\phi_1$  and  $\phi_2$  have been defined, it is impossible to examine the intersection of two potential curves. It will be seen later that only by considering two suitably chosen neighbouring points is it possible to derive two *independent* conditions and prove the theorem stated in the non-crossing rule.

The earliest discussion due to von Neumann and Wigner [10] was based on a somewhat different proof, which has also been given in slightly modified forms by Landau and Lifshitz [11] and by Heine [12]. It proceeds as follows. If two energy curves  $E_1(R)$  and  $E_2(R)$  are to intersect at some point, they must have values which are very nearly equal in the vicinity of the crossing point. Let us consider a point  $R^{(0)}$  where the electronic Hamiltonian is  $H^{(0)}$  and the two functions  $E_1$  and  $E_2$  have values  $E_1^{(0)}$  and  $E_2^{(0)}$  which are very close but not equal to each other. Let  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  be the corresponding wave functions. We now change the internuclear distance to  $R^{(0)} + \delta R$  and see whether  $E_1$  and  $E_2$  become equal. Increasing the internuclear distance by an amount  $\delta R$  changes the Hamiltonian to  $H^{(0)} + V$ , where  $V$ , given by

$$V = H(R^{(0)} + \delta R) - H^{(0)} = \frac{\partial H^{(0)}}{\partial R} \delta R + \dots$$

is a small correction term.  $E_1(R^{(0)} + \delta R)$  and  $E_2(R^{(0)} + \delta R)$  can be regarded as eigenvalues of the new Hamiltonian;  $V$ , as a perturbation to the operator  $H^{(0)}$ .

We look in the zeroth approximation for a solution of the form\*

$$(1) \quad \psi = a\psi_1^{(0)} + b\psi_2^{(0)}$$

and evaluate  $E_1(R^{(0)} + \delta R)$  and  $E_2(R^{(0)} + \delta R)$  by applying perturbation theory. It is easy to arrive at the secular equation

$$\begin{vmatrix} E_1^{(0)} + V_{11} - E & V_{12} \\ V_{21} & E_2^{(0)} + V_{22} - E \end{vmatrix} = 0$$

We see then that the conditions for crossing to occur are:

$$(2) \quad E_1^{(0)} - E_2^{(0)} + V_{11} - V_{22} = 0$$

$$(3) \quad V_{12} = 0$$

It should be noted that these conditions, unlike those derived by Teller, are not interdependent, and the lefthand sides of Equations (2) and (3) are not explicit functions of  $(E_1 - E_2)$ . The rest of the argument is identical with the concluding part of Teller's proof and will not be repeated.

At first sight it might seem that writing the zero-order wave function at  $(R^{(0)} + \delta R)$  as a linear combination of  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$ , rather than as a linear combination of the complete set of functions  $\psi^{(0)}$ , is a legitimate use of perturbation theory. However, the contribution due to the states not included in the truncated expansion of Equation (1) will vanish in the limit  $\delta R \rightarrow 0$  only if  $E_1^{(0)} = E_2^{(0)}$  at  $R = R^{(0)}$ . But then the two curves will intersect by definition and the degeneracy will persist as  $V$  will also vanish at  $R^{(0)}$  and there will no longer be a perturbation. The wave function of Equation (1) is admissible if the molecule has only two potential curves, for  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  will then form a complete set by themselves; or if the operator  $H^{(0)}$  has two close eigenvalues  $E_1^{(0)}$  and  $E_2^{(0)}$  and all other eigenvalues lie far from these two. However, in the absence of any knowledge about the other eigenstates of the molecule, employment of Equation (1) is difficult to accept, and a proof which hinges on the veracity of Equation (1) loses its rigour when applied to a diatomic molecule with a plethora of energy curves many of which *may* have close values at a particular internuclear distance.

It is often remarked [1, 11, 13] that if, in a certain approximation, two energy curves belonging to the same symmetry species intersect, then taking into account the small terms in the Hamiltonian that were originally ignored would obviate the seeming crossing and the curves would "repel" each other. The inclusion of the previously neglected terms in the Hamiltonian is tantamount to the introduction of a perturbation in the system and would, of course, lift the degeneracy which was initially present. But this argument, though correct in its logical form

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\* Von Neumann and Wigner start by expressing the wave function in terms of a complete set, but drop, in the later stages, all other functions except the two shown in Equation (1).

and physical contents, is not altogether conclusive; what, one may ask, would happen if one knew the exact eigenfunctions and a Hamiltonian which takes account of all the terms?

We now proceed to derive an alternative proof of the non-crossing rule by considering the exact eigenfunctions and the complete Hamiltonian for a diatomic molecule. Consider the crossing of two energy eigenvalues  $E_1(R)$  and  $E_2(R)$  at  $R = R_0$ ; so that

$$(4) \quad E_1(R_0) = E_2(R_0) = E_0$$

Note that this condition does not by itself guarantee crossing, as the states may be degenerate for all values of  $R$ . The crossing of two eigenvalues as functions of  $R$  means that for  $R = R_0 + \delta R$  the energies

$$E_1(R_0 + \delta R) = E_0 + \delta E_1 \quad \text{and} \quad E_2(R_0 + \delta R) = E_0 + \delta E_2$$

are *different*, so that

$$(5) \quad \delta E_1 \neq \delta E_2$$

This inequality will now be used to derive an additional requirement for crossing.

Let the Schrödinger equation for the first state be

$$(H - E_1)\psi_1 = 0$$

Consider a small change from  $R_0$  to  $R_0 + \delta R$  and let the perturbed Schrödinger equation be

$$(H_0 - E_0) \delta\psi_1 + (\delta H - \delta E_1)\psi_1^0 = 0$$

Should one choose to argue that, in order to obtain the above equation, we have immolated mathematical rigour by discarding the terms which are quadratic in  $\delta$ , it will be enough to mention that a completely rigorous treatment, presented in the Appendix, vindicates the analysis which follows.

Multiply the complex conjugate of the last equation by the second eigenfunction  $\psi_2^0$  for  $R = R_0$  and integrate to get

$$(6) \quad \langle \psi_1^0 | \delta H | \psi_2^0 \rangle = \delta E_1 \langle \psi_1^0 | \psi_2^0 \rangle$$

By repeating the above analysis with the Schrödinger equation for the second state and multiplying by the complex conjugate of  $\psi_1^0$  it follows that

$$\langle \psi_1^0 | \delta H | \psi_2^0 \rangle = \delta E_2 \langle \psi_1^0 | \psi_2^0 \rangle$$

Therefore by subtraction

$$(7) \quad (\delta E_1 - \delta E_2) \langle \psi_1^0 | \psi_2^0 \rangle = 0$$

and, knowing that  $\delta E_1 \neq \delta E_2$ , we deduce

$$(8) \quad \langle \psi_1^0 | \psi_2^0 \rangle = 0$$

It will be well to pause here momentarily and discuss the implications of Equation (8). 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 only exception occurs when the two functions belong to different irreducible representations of the symmetry group of  $H$ , in which case  $\langle \psi_1 | \psi_2 \rangle$  will be identically zero at all  $R$  because of the different symmetries of the two functions, and there is no way of making the overlap integral different from zero at any  $R$ .

Returning to Equation (6), it can now be seen that the inequality (5) implies the further condition:

$$(9) \quad \langle \psi_1^0 | \delta H | \psi_2^0 \rangle = 0$$

Let us suppose that  $\delta H$  can be expanded as a power series in  $\delta R$ ,

$$\delta H = -F\delta R + \dots$$

Then, retaining only the first-order term for simplicity, Equation (6) requires that  $F_{12}(R_0) = 0$ , where

$$F_{12} = \langle \psi_1 | F | \psi_2 \rangle \equiv -\langle \psi_1 | \partial H / \partial R | \psi_2 \rangle$$

Thus for crossing, two conditions\* are required:

$$(10) \quad \begin{aligned} E_1(R_0) &= E_2(R_0) && \text{(degeneracy)} \\ F_{12}(R_0) &= 0 && \text{(crossing)} \end{aligned}$$

The usual argument now applies: there is no reason why these should be satisfied simultaneously,† *unless* one of them vanishes automatically for all  $R$ ; that is, either the degenerate case  $E_1(R) = E_2(R)$ , or  $F_{12}(R) = 0$  for all  $R$  due to symmetry ( $F = -\partial H / \partial R$  will have the symmetry of the Hamiltonian).

We emphasize, in conclusion, that Teller's simplified formulation fails to arrive at the essential condition for crossing because it gives no special consideration to a value of  $R$  distinct from the crossing point,  $R_0$ . This is the underlying

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\* If the eigenfunctions  $\psi_1$  and  $\psi_2$  cannot be chosen to be real (which is unlikely), then the equation  $F_{12}(R_0) = 0$  is equivalent to *two* real conditions, and crossing is even less likely.

† It is, however, not strictly impossible that both are fulfilled for just one value of  $R$  (accidental crossing).

difference between Teller's approach and that adopted by von Neumann and Wigner and by us. Our treatment seems more satisfactory than the pioneering discussion due to von Neumann and Wigner, for the analysis is obviously rigorous and does not require the use of an approximate form of degenerate perturbation theory.

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### Appendix

#### A. Further discussion of crossing

Two curves  $f(x)$  and  $g(x)$  which touch each other at a point for which  $x = a$  are said, in the parlance of differential calculus, to *cross* at the point of contact, if the difference  $f(a + h) - g(a + h)$  has opposite signs for small positive values of  $h$  and for *numerically* small negative values of  $h$  [14]. We will reserve, in the Appendix, the terms "crossing" and "intersection" for the behaviour specified in the preceding sentence, and use the more general words "contact" and "touch" to describe what we have been indiscriminately calling crossing of curves. In other words, we will now discuss the "no-contact" rule and explore the conditions under which energy levels of like symmetry can touch each other when the parameter  $R$  is allowed to vary.

Consider two curves  $E_1(R)$  and  $E_2(R)$  which have a contact at  $R = R_0$ , i.e.

$$(4') \quad E_1(R_0) = E_2(R_0) = E_0$$

Now, for a contact of  $n$ th order to occur at  $R = R_0$ , we must also have

$$(11) \quad E_1'(R_0) = E_2'(R_0), E_1''(R_0) = E_2''(R_0), \dots, E_1^{(n)}(R_0) = E_2^{(n)}(R_0)$$

and

$$(12) \quad E_1^{(n+1)}(R_0) \neq E_2^{(n+1)}(R_0)$$

where the superscripts denote differentiation with respect to  $R$ .

We begin by writing the Schrödinger equation for the first state

$$(H - E_1)\psi_1 = 0$$

Differentiation with respect to  $R$ , at the point  $R = R_0$ , yields

$$(H_0 - E_0)\psi_1'(R_0) + \{H'(R_0) - E_1'(R_0)\}\psi_1^0 = 0$$

If we multiply the complex conjugate of this equation by  $\psi_2^0$  and integrate, we obtain

$$(13) \quad \langle \psi_1^0 | H'(R_0) | \psi_2^0 \rangle = E_1' \langle \psi_1^0 | \psi_2^0 \rangle$$

Differentiation of the Schrödinger equation for the second state, and multiplication by the complex conjugate of  $\psi_1^0$  gives

$$(14) \quad \langle \psi_1^0 | H'(R_0) | \psi_1^0 \rangle = E_2' \langle \psi_1^0 | \psi_2^0 \rangle$$

Subtraction of Equation (14) from Equation (13) yields

$$(15) \quad \{E_1'(R_0) - E_2'(R_0)\} \langle \psi_1^0 | \psi_2^0 \rangle = 0$$

If the contact is of zero order, so that  $E_1(R_0) = E_2(R_0)$  but  $E_1'(R_0) \neq E_2'(R_0)$ , we must have, as we found earlier in the text

$$(8') \quad S \equiv \langle \psi_1^0 | \psi_2^0 \rangle = 0$$

If  $E_1(R_0) = E_2(R_0)$ , and also  $E_1'(R_0) = E_2'(R_0)$ , but  $E_1''(R_0) \neq E_2''(R_0)$ , i.e. if the contact is of first order, we differentiate Equation (15) with respect to  $R$  and find

$$S\{E_1''(R_0) - E_2''(R_0)\} + S'(R_0)\{E_1'(R_0) - E_2'(R_0)\} = 0$$

which again leads to Equation (8) of the text.

In general, if the contact is of order  $n$ , we differentiate Equation (15)  $n$  times and, remembering the set of Equations (11), arrive, in the last step, at Equation (8). The curves intersect, or do not intersect, at the point of contact according as  $n$  is even or odd.

Substitution of Equation (8) into Equation (13) gives us the equation

$$\langle \psi_0^1 | H'(R_0) | \psi_2^0 \rangle = 0$$

which is identical with the second of the pair of Equations (10) of the text. We have thus established that the requirements which must be met, if two energy curves are to have a contact at  $R_0$ , are the same as those expressed by Equations (10) which were derived earlier in the text.

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