Comment on "The noncrossing rule and spurious avoided crossings"

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The meaning of the word "symmetry" is discussed within the context of the noncrossing rule, and some arguments concerning the rule, recently given by Hatton, are criticized.

In discussing the validity of the noncrossing rule and the published "proofs" of the rule, Hatton[1] makes several false claims for priority and advances some erroneous arguments. My purpose here is to draw attention to some relevant published work not mentioned by Hatton, and to point out some flaws in his reasoning. I will use the notation employed earlier by myself and Byers Brown.[2]

Hatton claims that the applicability of the noncrossing rule was first questioned by him. The validity of the rule was in fact first questioned by Heilmann and Lieb,[3] who cited the Hubbard Hamiltonian for benzene as a counter example, and subsequently by Valkering and Caspers.[4] Hatton also claims to have proven the noncrossing rule by redefining "symmetry;" this is not new either. Heilmann and Lieb[3] emphasized this point previously too. They pointed out that the rule depends critically on the interpretation of the word *symmetry*. The conventional meaning is that of a symmetry group independent of the parameter occurring in the Hamiltonian; Heilmann and Lieb went on to say that, if, on the other hand, one allows symmetry groups that are parameter dependent, the rule is a mere tautology because one can always invent, *post hoc*, a parameter-dependent symmetry group to account for any violations.

The concept, which plays a key role in Hatton's demonstration of the noncrossing rule, of a complete set of commuting observables (or normal constants of motion) is well known,[5,6] and has already been used by Caspers[7] for discussing the crossing of energy levels; if such a set were as readily available as Hatton suggests, one would, of course, use it to classify the energy levels; further, since the set is complete by hypothesis, intersecting levels would belong to different symmetry species, and the noncrossing rule would never be needed. The noncrossing rule is, however, *not* concerned with such operators, and it merely adds to the confusion to speak of such operators as symmetry elements of the Hamiltonian; the rule, when applied to molecules, is concerned specifically with the presence or absence of *molecular* symmetry (as defined, for example, by Longuet-Higgins[8]) and when applied to atoms, say in an external magnetic field, with levels belonging to the same value of m.[9,10]

In practice, it is very difficult, and may even be impossible, to find enough normal constants of motion of a physical character to classify all degeneracies actually occurring in nature[11]; moreover, one may often have to use noncommuting constants of motion.[6] It is precisely for dealing with such situations that the noncrossing rule is invoked. One assumes, for instance, that all the symmetry of a many-electron homonuclear (heteronuclear) diatomic molecule can be described in terms of the point group $D_{\infty h}$ ($C_{\infty v}$), and one enquires: Can two eigenstates of the same symmetry (i.e., belonging to, say, the same one-dimensional representation of the point group) be degenerate at some value of R? The noncrossing rule asserts that they cannot; but the assertion is not based on the subterfuge according to which levels of like symmetry, when found to be degenerate at some value of R, can be redefined to belong to different symmetry types; rather the assertion is based on some "proofs," which were first questioned by myself and Byers Brown.[2]

Hatton contends that the argument, advanced by myself and Byers Brown,[2] against Teller's proof is incorrect; in paraphrasing our argument, however, he distorts it. Since the original argument may have been too subtle, I will now simplify it; the simplified version is intended to be sufficiently exoteric to be within easy grasp of almost any student of science, and I am presenting it in the hope that it will generate a wider discussion than has hitherto been possible.

Consider the following theorem: The distance of a point $P(x,y)$ from the origin O is unlikely to vanish. An argument akin to that embodied in Teller's proof would prove the theorem thus: Consider the expression

$$r^2 = (x^2 + y^2)^{1/2}$$

for the distance between P and O. For r to vanish, x and y must both go to zero, and this is most unlikely; hence r is unlikely to vanish. Q.E.D.

The counterargument runs as follows: Introduce polar coordinates r and ϕ related to the Cartesian coordinates of P as

$$x = r\cos\phi, \quad y = r\sin\phi .$$

Since there is no angle ϕ for which $\sin\phi$ and $\cos\phi$ are simultaneously zero, the statement that x and y are unlikely to vanish at the same time is equivalent to the claim that r is itself unlikely to vanish, which is what we are trying to prove. The above proof of the theorem is therefore tautological.

The relevance of these remarks to Teller's proof and its refutation, impugned by Hatton[1] as well as Longuet-Higgins,[12] would become obvious if we recall the relations

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

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

derived earlier,[2] and identify $H_{11} - H_{22}$ as x, $2H_{12}$ as y, $E_1 - E_2$ as r, and 2θ as ϕ.

Since, at the time of writing our paper, we thought that the above-mentioned argument would prove sufficient for exposing the fallacy in Teller's proof, we did not present any additional arguments. All the arguments given by Hatton against Teller's proof are, however, implicit in our treatment; one of Hatton's arguments, namely "θ disappears from the Hamiltonian not because it has been specified, but because the Hamiltonian matrix of degenerate states is representation independent" was explicitly stated by Hoytink.[13]

Hatton apparently also misunderstands the proof published by Landau and Lifshitz.[14] Within the two-state model used by Landau and Lifshitz, perturbation calculations can be carried out exactly (i.e., to infinite order) and not merely to first order in δR, as Hatton argues. The perturbation, when defined correctly,[2,15] can be written

$$V \equiv \Delta H = H(R^{(0)} + \delta R) - H(R^{(0)}) .$$

There is in fact no need to equate V to $\delta R(\partial H/\partial R)$ and to calculate the energy as a power series in δR.

Since the noncrossing rule is concerned with the intersection of exact energy levels, only exact calculations can be brought to bear on the subject. Thus if the Landau-Lifshitz proof is to be restricted to energy changes of first order in δR, we must consider the special case where higher-order corrections are precisely zero. By considering such a special case I will now construct a counterexample to Hatton's claim that if, by defining V as $\delta R(\partial H/\partial R)$ and by choosing δR appropriately, the first condition for crossing

$$E_1^{(0)} - E_2^{(0)} + V_{11} - V_{22} = 0 \tag{1}$$

is satisfied to first order in δR, then the second condition

$$V_{12} = 0 \tag{2}$$

is automatically satisfied to first order in δR. The argument on which this claim is based overlooks the fact that, when the first condition is satisfied to first order in δR, $\langle\psi_1^{(0)}|\partial H/\partial R|\psi_2^{(0)}\rangle$ as well as $\langle\psi_1^{(0)}|\partial/\partial R|\psi_2^{(0)}\rangle$ and $\langle\partial\psi_1^{(0)}/\partial R|\psi_2^{(0)}\rangle$ also vanish, *however large* δR *is*. This can be seen as follows: Express the energies in a Taylor series, so that

$$E_i(R^{(0)} + \delta R) = E_i^{(0)} + \delta R\frac{\partial E_i^{(0)}}{\partial R} + \frac{1}{2}(\delta R)^2\frac{\partial^2 E_i^{(0)}}{\partial R^2} + \cdots$$

and, consequently,

$$E_2 - E_1 = E_2^{(0)} - E_1^{(0)} + \delta R\frac{\partial}{\partial R}(E_2^{(0)} - E_1^{(0)}) + \frac{1}{2}(\delta R)^2\frac{\partial^2}{\partial R^2}(E_2^{(0)} + E_1^{(0)}) + \cdots .$$

Consider now the special case in which the energy levels follow straight lines (i.e., derivatives higher than the first vanish identically), and compare the resulting expression for the energy difference with that derived in the perturbation treatment of Landau and Lifshitz; this comparison leads to the deduction:

$$\langle\psi_1^{(0)}|\frac{\partial H}{\partial R}|\psi_2^{(0)}\rangle = 0 = \langle\psi_1^{(0)}|\frac{\partial}{\partial R}|\psi_2^{(0)}\rangle .$$

Since the above deduction is independent of the choice of the starting point $R^{(0)}$, it follows that the matrix elements appearing in the above relation must vanish identically. That is, when the energy difference between the two states under consideration varies as δR, the states must have unlike symmetry; that both the crossing conditions can then be satisfied does not contradict what the Landau-Lifshitz proof says. Hatton's oversight of this point undermines his analysis of the Landau-Lifshitz proof.

The logical inadequacy of the Landau-Lifshitz proof can be demonstrated in at least two ways. First, it is enough to point out that we have, at our disposal, not one but *two* parameters, $R^{(0)}$ and δR, and thus it should not be impossible to meet the two requirements for crossing. At first sight it might seem that the choice of $R^{(0)}$ is not entirely free since it is to be chosen so as to fulfill the second condition for crossing, Eq. (2), and the additional condition of being near the crossing point R_0. That the latter restriction is unnecessary would, however, become obvious if one remember that the exactness of the two-level perturbation treatment is independent of the magnitude of the perturbation V.

Secondly, it should be recalled that, even in the Landau-Lifshitz proof, the following relations are obtained for the energy difference and the angle θ between $\psi_i(R^{(0)})$ and $\psi_i(R^{(0)}+\delta R)$:

$$E_1 - E_2 = [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2},$$

and

$$\tan 2\theta = 2H_{12}/(H_{11} - H_{22})^2 .$$

Thus the argument advanced earlier against Teller's proof applies also to the Landau-Lifshitz proof.

While discussing the inclusion of eigenfunctions other than $\psi_1^{(0)}$ and $\psi_2^{(0)}$ in the Landau-Lifshitz proof, Hatton does not mention that this extension has already been questioned by myself and Byers Brown[2]; we clearly pointed out that the contribution due to states other than E_1 and E_2 "will vanish in the limit $\delta R \to 0$ only if $E_1^{(0)} = E_2^{(0)}$ at $R = R^{(0)}$," and that a proof which hinges on the use of a truncated basis (consisting of $\psi_1^{(0)}$ and $\psi_2^{(0)}$) "loses its rigor when applied to a diatomic molecule with a plethora of energy levels many of which *may* have close values at a particular internuclear distance." However, these remarks, as well as those made by Hatton in the same context, lose their relevance on account of the conclusion, deduced in the foregoing paragraph, that even the two-level argument is logically deficient.

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