The noncrossing rule and spurious avoided crossings*

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The proofs of the noncrossing rule and the problems inherent in the application of the rule are discussed. It is shown that avoided crossings cannot be rigorously predicted by the noncrossing rule. The determination of spurious avoided crossings by variational calculations is discussed. A rule is developed which establishes when variational calculations will necessarily predict avoided crossings regardless of whether the exact states cross or avoid crossing.

I. INTRODUCTION

The noncrossing rule is applicable to many eigenvalue problems, and consequently plays an important role in many fields of the sciences. The noncrossing rule[1-5] specifies the minimum number of independent parameters of a system which must be determined in order that eigenvalues of eigenstates of the same symmetry may be degenerate. (For example, in diatomic molecules, the rule predicts that energy curves of states of the same symmetry will not cross as the internuclear separation is varied.) The applicability of the noncrossing rule was first questioned by this author.[6] Two of the important points made in Ref. 6 were that (1) the noncrossing rule is applicable only if all symmetries of a system are known and the system does not have any "accidental" degeneracies, and (2) if symmetry is defined in a way which eliminates the possibility of "accidental" degeneracies, then all states are of different symmetry and the noncrossing rule is not applicable. These points and others concerning the noncrossing rule are briefly discussed in this section, and in detail in Secs. II–V.

The noncrossing rule is applicable only if all the symmetries of a system are known.[6] The rule adds to our knowledge only in systems which have not been solved exactly; in such systems it has not been shown that all the symmetries are known. In systems which have been solved exactly—and consequently provide an unambiguous test of the noncrossing rule—dynamical[7] as well as spatial and spin symmetries are present. Dynamical symmetries—which are generally more difficult to determine than spatial and spin symmetries—must be included in the analysis of these systems via the noncrossing rule, or spurious avoided crossings will be predicted (for example, see Fig. 1). In systems which have not been solved exactly, typically only simple spatial and spin symmetries are known. The assumption that other symmetries are not present is not rigorously correct, and consequently the application of the noncrossing rule to these systems may produce erroneous results.[6,8]

The noncrossing rule does not directly concern states of different symmetry. However, the usual proofs of the rule[1-5] imply that eigenvalue curves of states of different symmetry are entirely independent and will not avoid crossing. This is not the case. Many counterexamples occur in exactly solvable systems[9] (for example, see Fig. 2). The fact that states of different symmetry can exhibit avoided crossings raises questions as to the role of symmetry in the proofs of the noncrossing rule.[1-5]

Over the years, variational calculations have been performed on many systems. The crossings and avoided crossings of eigenvalue curves in these calculations are in agreement with the pre-

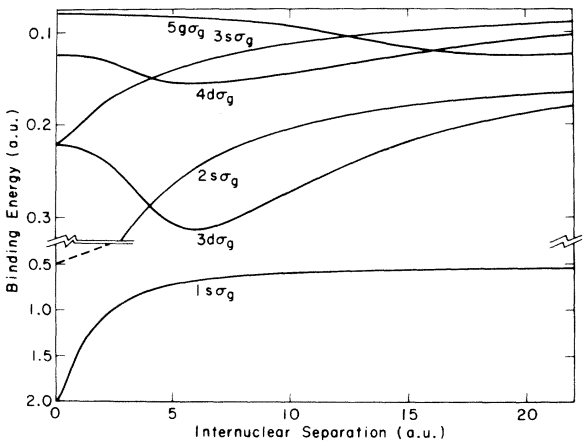

FIG. 1. Some of the lower σ_g electronic exact energy curves of the one-electron system H_2^+. All the states shown are of the same "simple" spatial symmetry, and are distinguished by dynamical symmetries (see the Appendix). None of these states avoid crossing; however, variational calculations similar to those used on many-electron systems will produce energy curves which will avoid crossing where the exact curves cross. This figure is from the work of Rosenthal (Ref. 16).

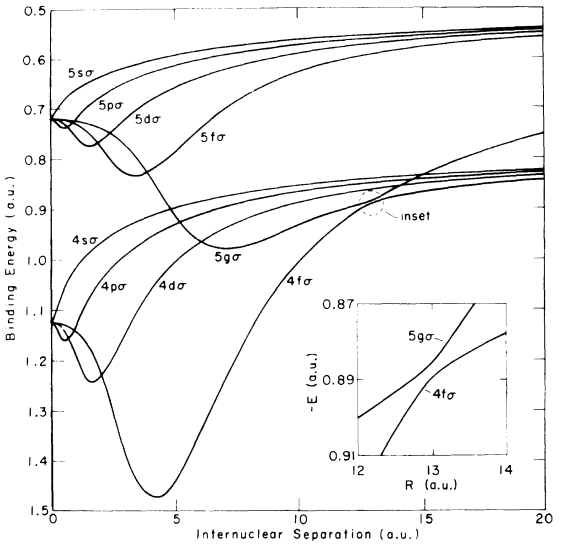

FIG. 2. Some of the electronic exact energy curves of the one-electron system BH^{5+}. All the states shown are of the same "simple" spatial symmetry, and are distinguished by dynamical symmetries (see the Appendix). The $5g\sigma$ [which asymptotically goes to $B^{5+} + H(1s)$] and the $4f\sigma$ [which asymptotically goes to $B^{4+}(4f) + H^{+}$] avoid crossing at $R \sim 13$ a.u. Also shown are many crossings of states of the same "simple" spatial symmetry. These curves were generated by the ODEM program of Power (Ref. 15).

dictions of the noncrossing rule when the symmetries of the calculation are considered. This agreement, however, does not imply that the systems do not have other symmetries, or that the noncrossing rule is correct. The resulting roots of a variational calculation may avoid crossing even though the exact eigencurves cross[8,10] (see Sec. V). This phenomenon of spurious avoided crossings is a consequence of the inadequate basis set and the variational method of calculation.[8,10] Because of this, variationally calculated avoided crossings of curves whose minimum separations are comparable to the accuracies of the calculated eigencurves may be spurious and should be investigated further.

These problems, as well as others concerning the noncrossing rule, its proofs, and its application are discussed in detail in the following sections. Before the noncrosssing rule may be rigorously used, symmetry operators must be precisely defined. The only standard definition which does not result in violations of the noncrossing rule, in exactly solvable systems, defines a set of operators which may be mapped one-to-one onto the set of constant-of-motion operators other than the Hamiltonian. This definition is discussed in Sec. II and the end of Sec. III. The beginning of Sec. III analyzes the usual proofs of the noncrossing rule. The correct meaning of symmetry in the noncrossing rule may be emphasized by replacing the word "symmetries" by the phrase "constants of motion other than the energy." With this definition of symmetry, the common belief that as a system becomes more complicated the number of symmetries decreases, is incorrect. The number of symmetries—or constants of motion other than the energy—is a function of the number of degrees of freedom of a system and not of its complexity. New proofs concerning the noncrossing rule which use these concepts are developed in Sec. IV, where it is shown that the noncrossing rule is never rigorously applicable. For complex systems not all the symmetries are known at the present time. This ignorance does not produce avoided crossings of the exact energy curves; however, as discussed in Sec. V, it does produce avoided crossings in approximate variational calculations.

II. SYMMETRY OPERATORS

The role of symmetry in most applications of group theory is to simplify rather than to completely solve a problem; only those symmetries which are readily determined are used, and the question as to whether or not all the symmetries have been found is not posed. The noncrossing rule is applicable, however, only if all the symmetries are known.[6]

Conceptually, a symmetry operator is an operator whose action on an eigenstate of the Hamiltonian produces a state of the same energy and normalization. In mathematical terms, a symmetry operator S_i of a Hamiltonian H is a well-behaved nontrivial unitary, or antiunitary, operator which commutes with H.[11] A set of commuting distinct symmetry operators of H is called a complete set if there does not exist a symmetry operator of H distinct from the set which commutes with all the operators of the set. Two states are of the same symmetry if both states are eigenstates of a complete set of symmetry operators $\{S_1, S_2, \ldots, S_n\}$ of H with the same set of eigenvalues $\{s_1, s_2, \ldots, s_n\}$. In order to emphasize the nature of the general symmetry operator, the one-electron diatomic molecule and a relation between constant-of-motion operators and symmetry operators are discussed below.

The electronic Hamiltonians of diatomic molecules in the Born-Oppenheimer approximation are functions of only one parameter, the internuclear separation. Consequently, the noncrossing rule prohibits states of the same symmetry from crossing. Since one-electron diatomic molecules are

exactly solvable in the Born-Oppenheimer approximation, the predictions of the noncrossing rule for these systems may be unambiguously checked. Often it is assumed that symmetry operators can represent only "simple" spin or spatial operations such as rotations, reflections, and inversions. If this "simplified" definition of symmetry operator is assumed, then the noncrossing rule is violated in one-electron diatomic molecules. For example, in the H_2^+ system the "simple" spatial symmetries are inversion with respect to the nuclear center of mass and rotation about the internuclear axis. If these were the only symmetries of the system, then the $2s\sigma_g$ and the $3d\sigma_g$ states—which cross (see Fig. 1)—would be of the same symmetry (as would many other pairs of crossing states of this and other one-electron diatomic molecules). It is well known, however, that these crossings are not violations of the noncrossing rule. Additional operators (see the Appendix) satisfying the formal definition of symmetry operators exist in these systems. These additional operators — sometimes called dynamical symmetry operators because of their dependence on the potential (for example, see Schiff[7])—together with the "simple" spatial symmetry operators distinguish all states of the one-electron diatomic molecules. Consequently, since all the states are of different symmetry, the noncrossing rule is not applicable to these systems. Dynamical symmetries—which are also present in the one-electron atom[7] and the three-dimensional harmonic oscillator,[7] and are necessary to "explain" the degeneracies in these systems—are often nontrivial, and were found in the cases mentioned here only when the systems were solved exactly.

For the remainder of this paper, operators which satisfy the formal definition of symmetry given in the second paragraph of this section will be called symmetry operators. Operators which correspond to "simple" spatial and spin symmetries will be called "simple" symmetry operators. The set of "simple" symmetry operators is a subset of the set of symmetry operators of a system.

Symmetry operators S_i may be related to constant-of-motion operators C_i by the following mapping:

$$S_i = e^{iC_i} . \tag{1}$$

C_i is Hermitian if and only if S_i is unitary, and C_i commutes with the Hamiltonian if and only if S_i does. This mapping is commonly used to describe the symmetry of a state. For example, in diatomic molecules the symmetry corresponding to a rotation about the internuclear axis, $S_{L_z} = e^{iL_z}$, is usually characterized by the corresponding constant of motion, the angular momentum about the axis, $L_z = -i\,\partial/\partial\phi$. The mapping is one to one except for the constant-of-motion operators, which may be expressed as simple functions of the Hamiltonian; often the corresponding trivial operators [defined by Eq. (1)], which are unitary and commute with the Hamiltonian, are excluded from the set of symmetry operators. Since the analysis which follows does not require these operators, the more restrictive definition of symmetry operator (which excludes these operators) will be used in this work.

In summary, symmetry operators (as defined in the second paragraph of this section) describe not only simple spatial and spin properties, but also more complicated properties (including those which depend on the interactions) of a system. The assumption that systems which have not been solved exactly have only simple spatial and spin symmetries is unjustified.

III. PROOFS OF THE NONCROSSING RULE

The first proof of the noncrossing rule was presented by Von Neumann and Wigner[1] in 1929. Several years later, their work was specialized to a two-state analysis by Teller.[2] This two-state proof, with or without minor changes, is currently the most commonly cited explanation of the noncrossing rule.[3] Recently, additional proofs have been proposed by Naqvi and Brown[4] (using a two-state analysis), and by Longuet-Higgins[5] (using, as did Von Neumann and Wigner, a finite-state analysis). All these works deduce the basic noncrossing rule: The crossing of two energy curves of states of the same symmetry requires the specification of at least two (three) independent real parameters of the real (complex) Hamiltonian of the system. This basic rule was extended to include manyfold crossings by Longuet-Higgins,[5] and to include sets of manyfold crossings by Von Neumann and Wigner.[1] The proofs will be discussed in three groups: (a) the work of Naqvi and Brown, (2) works using truncated basis sets, and (3) works using finite complete basis sets.

Naqvi and Brown[4] have argued that two states cross if and only if they are degenerate at some point, and are nondegenerate at neighboring points. This has led them to propose that the following two conditions are necessary for a crossing:

$$E_1(R_x) = E_2(R_x) , \tag{2}$$

$$\langle \psi_1(R_x) | \frac{\partial H}{\partial R} | \psi_2(R_x) \rangle = 0 , \tag{3}$$

where E_1 and E_2 are the energies of the exact eigenfunctions ψ_1 and ψ_2, and R_x is the crossing point. In their work, the following equivalences were deduced when $E_1(R) = E_2(R)$:

$$\langle\psi_1|\psi_2\rangle\frac{\partial E_1}{\partial R}=\langle\psi_1|\psi_2\rangle\frac{\partial E_2}{\partial R}=\langle\psi_1|\frac{\partial H}{\partial R}|\psi_2\rangle\ . \tag{4}$$

Naqvi and Brown's proof is based on the assumption that $\langle\psi_1|\psi_2\rangle$ is not necessarily zero when E_1 and E_2 are equal. This is incorrect. At a later point in this paper, it will be shown that if two states are eigenstates of a complete set of symmetry operators, then the two states are necessarily orthogonal. Naqvi and Brown's second condition [Eq. (3)] therefore follows directly from their first condition [Eq. (2)]. This point has been argued previously in a different way by Longuet-Higgins.[5]

Typical of the works which use truncated basis sets is the discussion of the noncrossing rule given by Landau and Lifshitz.[3] They consider a system which has one parameter, R. The energies $E_1(R)$ and $E_2(R)$ of the two eigenstates $\psi_1(R)$ and $\psi_2(R)$ approach each other as R is varied. At a point R_0, the energies $E_1(R_0)$ and $E_2(R_0)$ are arbitrarily close. They then ask whether or not the two energies may be degenerate at some point $R=R_0+\delta R$. This may be determined to first order in δR with the basis $\psi_1(R_0)$ and $\psi_2(R_0)$. If a higher-order answer is desired, then a more complete basis is necessary. To first order in δR the Hamiltonian at R is

$$H^{(1)}(R)=H(R_0)+\delta R\left.\frac{\partial H}{\partial R}\right|_{R_0}. \tag{5}$$

The energy separation of the eigenvalues of the Hamiltonian matrix defined by $H^{(1)}(R)$, $\psi_1(R_0)$, and $\psi_2(R_0)$ is

$$\Delta E^{(1)}=\left[\left(E_1(R_0)+\delta R\left.\frac{\partial E_1}{\partial R}\right|_{R_0}-E_2(R_0)-\delta R\left.\frac{\partial E_2}{\partial R}\right|_{R_0}\right)^2+4\delta R^2\left|\langle\psi_1(R_0)|\frac{\partial H}{\partial R}|\psi_2(R_0)\rangle_{R_0}\right|^2\right]^{1/2}. \tag{6}$$

The standard argument then concludes that since $\Delta E^{(1)}$ is the square root of the sum of two non-negative quantities (which are apparently independent), at least two parameters (one for each of the non-negative quantities) must be specified in order that $\Delta E^{(1)}$ vanish. However, since this is a calculation only to first order in δR in the energy, the non-negative quantities need only vanish to first order in δR in the energy. This may be done by the specification of one parameter. For example, if δR is chosen such that the first non-negative quantity vanishes,

$$E_1(R_0)-E_2(R_0)=\delta R\left.\frac{\partial(E_2-E_1)}{\partial R}\right|_{R_0}, \tag{7}$$

then the second non-negative quantity vanishes to first order in δR in $\Delta E^{(1)}$. This may be seen explicitly by combining Eq. (7) and the exact relation

$$2\delta R\langle\Psi_1(R_0)|\frac{\partial H}{\partial R}|\Psi_2(R_0)\rangle_{R_0}=2\delta R[E_2(R_0)-E_1(R_0)]\langle\Psi_1(R_0)|\frac{\partial}{\partial R}|\Psi_2(R_0)\rangle_{R_0}. \tag{8}$$

The result is

$$2\delta R\langle\Psi_1(R_0)|\frac{\partial H}{\partial R}|\Psi_2(R_0)\rangle_{R_0}=2\delta R^2\left.\frac{\partial(E_1-E_2)}{\partial R}\right|_{R_0}\langle\Psi_1(R_0)|\frac{\partial}{\partial R}|\Psi_2(R_0)\rangle_{R_0}. \tag{9}$$

The quantity

$$\left.\frac{\partial}{\partial R}(E_1-E_2)\right|_{R_0}\langle\Psi_1(R_0)|\frac{\partial}{\partial R}|\Psi_2(R_0)\rangle_{R_0}$$

is well behaved, and does not go as an inverse power of δR. Consequently, to first order in δR in the energy—which is the highest order in δR which may be rigorously deduced with the basis set used—the second non-negative quantity vanishes, and only one parameter need be specified in order to have a degeneracy.

The inclusion of higher orders of δR in the calculation may be done in several ways; one of the most direct is the following: the energy separation between two states deduced in degenerate perturbation theory,

$$\Delta E^{(0)}=[(H_{11}-H_{22})^2+4|H_{12}|^2]^{1/2} \tag{10}$$

(where $H_{ij}\equiv\langle\psi_i|H\psi_j\rangle$), may be corrected to give the exact energy separation by including, through nondegenerate perturbation theory or some other means, the contribution due to the states $\psi_3,\psi_4,\ldots,$ which together with ψ_1 and ψ_2 completely span the desired eigenstates. The resulting energy separation may be expressed in the form

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

where ΔE_1 and ΔE_2 are the corrections to the degenerate perturbtion theory treatment due to the inclusion of $\psi_3,\psi_4,\ldots$. If the corrections are calculated to lowest order in perturbation theory, the result is

$$\Delta E^{(1)}=[(H_{11}-H_{22})^2+4|H_{12}|^2]^{1/2}+\sum_{n=3}^{\infty}\frac{|\langle\phi_1|H\psi_n\rangle|^2}{E_1-E_n}-\sum_{n=3}^{\infty}\frac{|\langle\phi_2|H\psi_n\rangle|^2}{E_2-E_n}, \tag{12}$$

where ϕ_1, ϕ_2, E_1, and E_2 are the results of the degenerate perturbation theory treatment, and $E_3,E_4,\ldots$ are the energies of $\psi_3,\psi_4,\ldots$. Since the energy separation is no longer the square root of the sum of two non-negative quantities

[as in Eq. (10)], but is the sum of positive and negative terms, it appears that the specification of only one parameter of the Hamiltonian may be sufficient in order to obtain a crossing.

The inclusion of terms higher than first order in perturbation theory may be done in other ways. However, the problems involved in proving that even higher-order terms will not cause ΔE to vanish are nontrivial. Rather than consider perturbative proofs with incomplete bases, it is perhaps more rewarding to consider complete-basis-set proofs.

The proofs of Von Neumann and Wigner,[1] Teller,[2] and Longuet-Higgins[5] assume finite complete basis sets. (Naqvi and Brown[4] have criticized Teller's proof. Their discussion, as has been pointed out by Longuet-Higgins,[5] is incorrect. They contend that Teller's two conditions are independent only if the eigenstates do not cross, and therefore he has begged the question. Teller,[2] however, chose the two conditions on the grounds that they are simultaneously satisfied if and only if the eigenstates are degenerate. The fact that both conditions are satisfied at a crossing does not imply that they are dependent. It may be argued that Teller's conditions are dependent, but not in the manner of Naqvi and Brown.[4]) Each of the complete-basis-set proofs[1,2,5] effectively counts the number of variables required to describe the nonzero elements of a Hamiltonian matrix with and without degeneracies. The difference of these two numbers is presumed to be the number of physical parameters of the system which must be specified in order that eigencurves may cross. Critical to these proofs is the choice of representation in which the analysis is carried out. These authors use the "symmetry" representation in which all eigenstates of the same symmetry are mixed, and no eigenstates of different symmetries are mixed. If the same counting techniques are used in other representations, different noncrossing rules are obtained.

For example, the noncrossing rule of the representation which mixes states of different symmetry may be obtained in the following way: consider two eigenfunctions ϕ_1 and ϕ_2 of different symmetry. From these, two new wave functions ψ_1 and ψ_2 may be obtained by a unitary transformation U,

$$U = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}. \tag{13}$$

In general (i.e., unless $\theta = \frac{1}{2} n\pi$, or ϕ_1 and ϕ_2 are degenerate), all the elements of the Hamiltonian matrix defined by the new representation will be nonzero. The nonzero elements of the Hamiltonian matrix may be described by three variables if the eigenvalues are nondegenerate, and by one variable if the eigenvalues are degenerate, implying that the crossing of eigencurves of states of different symmetry requires the specification of two parameters of the system. The separation of the two eigenvalues resulting from diagonalization of this Hamiltonian matrix is given by Eq. (10), and leads to the same crossing conditions.

The noncrossing rule of the diagonal representation may also be easily obtained. In the diagonal representation, the number of variables of the Hamiltonian matrix is the number of distinct eigenvalues. Consequently, the crossing of eigencurves of states of the same or different symmetry requires the specification of only one parameter of the system.

The fact that different representations have different noncrossing rules is due to the presence of variables in the Hamiltonian matrix in some representations which have no physical significance. These variables, as well as physical ones, may disappear when states of the system become degenerate. Their disappearance has no physical significance and should not play a role in determining the noncrossing rule. To avoid this problem, it seems most reasonable to determine the noncrossing rule in a representation in which all the variables necessary to describe the Hamiltonian matrix correspond to physical variables of the system. Since the Hamiltonian matrix contains all the physical variables of the system in all representations, the representation most likely to contain only physical variables is the representation which requires the least number of variables to describe the Hamiltonian matrix; this is the diagonal representation. The diagonal representation leads to a noncrossing rule quite different from that obtained by Von Neumann and Wigner, Teller, and Longuet-Higgins.

Although the representation used in the noncrossing-rule proofs plays a fundamental role in these proofs, only Von Neumann and Wigner[1] explain their choice:

"In the analysis of the structure of the terms of atomic systems, one can subdivide the eigenvalues into different groups, for each group there is say an azimuthal quantum number, the reflexion character, and the multiplet system character, and so long as the reference system is not disturbed terms of one group will have no knowledge of terms of another group. Terms of different groups (terms having different transformation properties) can cross. In addition, terms of most groups are many-fold degenerate. This is however no disproof of the above because in this case the words "in general" do not apply since a suf-

ficient number of matrix elements always vanish identically. As in the theory of groups it can be assumed that no accidental degeneracy of terms takes place, we can assume here that no relationship exists which does not follow from the symmetries of the system on the basis of group theoretic considerations, and, that within a term group we always have the general case."

The justification for counting in the "symmetry" representation is that in this representation all elements of the Hamiltonian matrix are independent. The arguments supporting this choice, as well as those supporting the choice of the diagonal representaion, are fundamental in nature.

The differences between counting in the diagonal and symmetry representations may be shown explicitly by considering the real Hamiltonian matrix determined by two states of the same symmetry in the symmetry representation. If the eigenvalues are nondegenerate,

$$H = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

$$= \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix}. \tag{14}$$

If the eigenvalues are degenerate,

$$H = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

$$= \begin{pmatrix} E_1 & 0 \\ 0 & E_1 \end{pmatrix}. \tag{15}$$

If the symmetry representation is considered fundamental, then the nondegenerate Hamiltonian is described by the three quantities H_{11}, H_{22}, and H_{12}. In order to obtain a degeneracy, two conditions ($H_{11} = H_{22}$ and $H_{12} = 0$) are necessary. If the diagonal representation is considered fundamental, then the nondegenerate Hamiltonian is described by the three quantities E_1, E_2, and θ. In order to obtain a degeneracy, only one condition ($E_1 = E_2$) is necessary. θ disappears from the Hamiltonian not because it has been specified, but because the Hamiltonian matrix of degenerate states is representation independent. Therefore the disappearance of θ from the Hamiltonian does not correspond to the specification of a physical parameter of the system.

The apparent discrepancy between noncrossing rules developed in the diagonal and symmetry representations will be resolved in Sec. IV. Critical to the analysis is the definition of symmetry. At this point it is worthwhile to further discuss the definition given above by Von Neumann and Wigner.

In order to develop a rigorous noncrossing rule, the possibility of accidental degeneracies must be eliminated. Accidental degeneracies are a result of relationships among the elements of the Hamiltonian matrix which are not explained by symmetry. Thus if the possibility of accidental degeneracies is to be eliminated, the definition of symmetry operator must be general enough to allow all relationships among the elements of the Hamiltonian matrix to be explained by symmetry. This forces one to adopt a definition similar to the one given in the second paragraph of Sec. II.

Another basic point, which is not commonly understood, may be developed from Von Neumann and Wigner's statement "terms of one group will have no knowledge of terms of another group." This may be interpreted to mean that states of different symmetry will not avoid crossing. This is incorrect. Many examples of avoided crossings between states of different symmetry are known[9] (for example, the avoided crossing in BH^{5+} at $R \sim 13$ a.u. shown in Fig. 2).

IV. NEW PROOFS CONCERNING THE NONCROSSING RULE

In this section, several points concerning complete sets of symmetry operators are discussed in order to answer the questions posed in Secs. II and III.

(1) What are the roles of symmetry and the choice of representation in the noncrossing rule?

(2) How can one determine when all the symmetries of a system are known?

In fundamental developments of quantum mechanics it is usually assumed[12] or postulated[13] that a complete set of constant-of-motion operators exist, and that this complete set distinguishes all states of the system. The distinguishability of states is basic to our present understanding of quantum mechanics. It directly implies [see Eq. (1)] that states of the same symmetry cannot be degenerate. This can be shown explicitly by assuming that two states of the same symmetry are degenerate, and deducing a contradiction. The discussion will be given in terms of constant-of-motion operators rather than symmetry operators [see Eq. (1) for a relation between these operators]. Two states of the same symmetry have the same set of eigenvalues of the set of nontrivial symmetry operators of the system. Two degenerate states have the same eigenvalue of the Hamiltonian. Therefore two degenerate states of the same symmetry have the same set of eigenvalues of a complete set of constant-of-motion operators. If

the two states are not orthogonal, then an orthonormal pair of states may be constructed from them with all the same constant-of-motion eigenvalues. Let the two orthonormal degenerate states of the same symmetry be ψ_1 and ψ_2, and all the other eigenstates of the representation in which all the constant-of-motion operators are diagonal be $\psi_3, \psi_4, \ldots$. Assign to ψ_1 the superscript 2 and to all the other states the superscript 1. Then the operator

$$O_P \equiv \sum_{i=1}^{\infty} |\psi_i^{(j_i)}\rangle\, j_i\, \langle\psi_i^{(j_i)}| \tag{16}$$

is Hermitian, commutes with and is distinct from all the old constants of motion, and corresponds to a new nontrivial symmetry operator which commutes with all the old symmetry operators. Since this operator distinguishes ψ_1 and ψ_2, they cannot be of the same symmetry. [The form of the operator in Eq. (16) was chosen to emphasize the fact that the basic assumption of the proof is that eigenstates of the system exist.] When this operator acts on an eigenstate $\psi_k^{(j_k)}$ of the system, the result is the eigenstate multiplied by the superscript j_k:

$$\begin{aligned} O_P|\psi_k^{(j_k)}\rangle &= \sum_i |\psi_i^{(j_i)}\rangle\, j_i\, \langle\psi_i^{(j_i)}|\psi_k^{(j_k)}\rangle \\ &= \sum_i |\psi_i^{(j)}\rangle\, j_i \delta_{ik} \\ &= |\psi_k^{(j_k)}\rangle\, j_k = \begin{cases} 2|\psi_k\rangle, & \text{if } k=1, \\ |\psi_k\rangle, & \text{if } k\neq 1. \end{cases} \end{aligned}$$

[A new symmetry operator which distinguishes ψ_1 and ψ_2 is given directly—i.e., without considering constant-of-motion operators—by Eq. (16) if ψ_1 is assigned the superscript -1.] Thus two states of the same symmetry cannot be degenerate. States of the same symmetry, if they were degenerate, would not be distinguishable.

The statement that states of the same symmetry cannot cross is stronger than the usual noncrossing rule. The statement prohibits the crossing of states of the same symmetry no matter how many parameters of the system are varied.

The second point is that no two states are of the same symmetry. This may be shown by assuming that two states are of the same symmetry and deducing a contradiction. As was shown in the discussion above, the constant-of-motion operators which correspond to a complete set of symmetry operators, together with the Hamiltonian, form a complete set of constant-of-motion operators. No two states of the representation ($\psi_1, \psi_2, \ldots$) in which this complete set of constant-of-motion operators is diagonal have the same set of eigenvalues of these operators. Therefore all the states of the representation are orthogonal. Assume that two states ψ_1 and ψ_2 are of the same symmetry. The operator defined in Eq. (16) is—even though the energies of the two states ψ_1 and ψ_2 are no longer necessarily equal—a constant of motion, corresponding to a new nontrivial symmetry operator which commutes with all the old symmetry operators. Since this new symmetry operator distinguishes ψ_1 and ψ_2, they are of different symmetry. [A new symmetry operator which distinguishes ψ_1 and ψ_2 is given directly—i.e., without considering constant-of-motion operators—by Eq. (16) if ψ_1 is assigned the superscript -1.] Thus if a complete set of symmetry operators has been determined, then all the states are distinguished by this set. This implies that the noncrossing rule is applicable to an empty set of pairs of states, not only in the one-electron systems discussed in Sec. II, but in all systems.

At this point it is clear that any two eigenstates of a complete set of symmetry operators of a system are of different symmetry and are therefore orthogonal, as was mentioned in the discussion of the proof of Naqvi and Brown. It is also clear that the representation which does not mix states of different symmetries—the "symmetry" representation prescribed by Von Neumann and Wigner, Teller, and Longuet-Higgins—is necessarily the diagonal representation.

The above discussions do not imply that states do not avoid crossing. As was mentioned earlier, even in one-electron diatomic molecules some states avoid crossing. Rigorous noncrossing rules for the one-electron diatomic molecules may be developed (see the Appendix) if the interactions of the system are included in the analysis. In general, each particular system is expected to have its own set of noncrossing rules. Based on analyses of one-electron diatomic molecules, one expects rigorous avoided crossings in many-electron systems to be most probable when the wave functions of the two avoiding states emphasize different regions of space (such as ionic and covalent wave functions).

V. INTERPRETING THE RESULTS OF VARIATIONAL CALCULATIONS

It is well known that eigencurves of variational calculations differ quantitatively from the exact curves. However, it is not well known that they may also differ qualitatively, particularly in

regions where several curves are close. These differences are due to the inadequacies of the basis sets used for the calculation. This section will deal primarily with a qualitative difference that variational calculations are extremely susceptible to, namely the calculation of avoided crossings when the exact eigencurves cross.

Practical variational calculations are limited by the basis-set size. Since the basis set is incomplete, it cannot reflect all the symmetries of the system. The symmetries of the system which are included in the basis set will be called basis-set symmetries. States which are not distinguished by any of the basis-set symmetries will, in general, cross or avoid crossing in a variational calculation in accordance with the Von Neumann-Wigner noncrossing rule if symmetry is replaced by basis-set symmetry, regardless of whether the exact states cross or avoid crossing. This rule is developed and discussed below. First, however, the rule will be applied to a sample system in order to emphasize the difference between basis-set symmetries and the complete set of symmetries of a system.

The H_2^+ one-electron system has the following symmetries: (a) inversion through the middle of the internuclear axis, (2) rotation about the internuclear axis, and (3) dynamical symmetries (see the Appendix) which in the united-atom limit go to the symmetry corresponding to the total angular momentum squared constant of motion. Basis sets typical of those used in many-electron diatomic molecular calculations (i.e., Gaussian, atomic, or elliptical orbitals centered at both nuclei) cannot reflect all of the symmetries of the system. Symmetries (1) and (2) are easily included in these basis sets; however, symmetries (3) are not. If crossing exact eigenstates are distinguished by symmetries (1) or (2), then the variationally calculated energy curves will cross. If crossing exact eigenstates are not distinguished by either symmetry (1) or symmetry (2) (for example, the $2s\,\sigma_g$ and the $3d\,\sigma_g$ states), then the variationally calculated energy curves may cross only if at least two parameters of the system are specified. If only the internuclear separation is varied, then the calculated energy curves will, in general, not cross. At least one other variable—such as a parameter of the basis set—must be specified in order to obtain a crossing.

In a variational calculation, avoided crossings between eigencurves separated from the other eigencurves of a system may be analyzed in a two-state framework because of the extremum method of calculation. The basis for the two-state problem is the basis of the original problem with the eigenvectors of all the lower and higher eigenvalues projected out. Each of the remaining two elements of the basis and the eigenvectors ψ_1 and ψ_2 resulting from the diagonalization of the remaining 2×2 Hamiltonian matrix may be described as a linear combination of the exact eigenstates $\phi_1, \phi_2, \ldots$ of the system:

$$\psi_i = \sum_j \phi_j c_{ji} .$$

The eigenvalues obtained by diagonalization of the 2×2 Hamiltonian matrix are degenerate if and only if

$$\sum_j C_{j1}^* C_{j2} \epsilon_j = 0 , \tag{17}$$

$$\sum_j (|C_{j1}|^2 - |C_{j2}|^2)\epsilon_j = 0 , \tag{18}$$

where ϵ_j is the eigenvalue of ϕ_j. Equation (17) is trivially satisfied if ψ_1 and ψ_2 have no common element ϕ_k; in this case, however, the basis is adequate to separate the states by symmetry, and the eigencurves may cross with the specification of only one parameter. If the basis set is not adequate to distinguish the states by symmetry, then Eqs. (17) and (18) may be satisfied only by cancellation of terms. These two equations may be satisfied, in general, only if at least two parameters of the system are specified. Parameters of the basis set, as well as physical parameters of the system, may be among those specified. This analysis may be extended in a straightforward manner to include sets of manyfold degeneracies of eigenvalues of real and complex Hamiltonians. The resulting basis-set noncrossing rule is the usual noncrossing rule[1] but with symmetry replaced by basis-set symmetry, and with basis-set parameters as well as physical parameters of the system among those which may be specified in order that a crossing may occur.

A variational calculation which has been reduced (as in the preceding paragraph) to two avoiding states will maximize the eigenvalue separation between the two calculated eigenvectors.[8,10] This is done in regions where the exact eigencurves cross by making one solution as good an eigenstate of the Hamiltonian as possible, and making the other solution as poor an eigenstate as possible. This unequal treatment, although undesirable if the results of the calculation are to be used directly, allows spurious avoided crossings to be distinguished from real avoided crossings. This may be done by determining the quality of the solutions as eigenvectors of the system. The details of how this may be done are presented in another paper.[10]

VI. SUMMARY

The Von Neumann–Wigner noncrossing rule specifies the minimum number of independent parameters of a system which must be determined in order that eigenvalue curves of states of the same symmetry may cross. The application of this rule requires a clear understanding of the meaning of symmetry. The role of symmetry in most applications of group theory is to simplify—rather than to completely solve—a problem, and only those symmetries which are readily determined are considered. Typically, these are simple spatial and spin symmetries. If states are said to be of the same symmetry when they have the same simple spatial and spin symmetries, then the application of the noncrossing rule predicts spurious avoided crossings in the one-electron diatomic molecules. If the noncrossing rule is to be rigorously applicable, then a less restrictive definition of symmetry operator must be used. The general definition of a symmetry operator (i.e., a well-behaved nontrivial unitary or antiunitary operator which commutes with the Hamiltonian) includes dynamical symmetries; consequently, the application of the noncrossing rule with this definition of symmetry does not predict spurious avoided crossings in systems which have been solved exactly. However, if the general definition of symmetry operator is used, then—as was shown in Sec. IV—all states are of different symmetry and the noncrossing rule is not applicable. Thus if either of the common definitions of symmetry—one of which was probably the intended definition of the developers of the noncrossing rule—is used, then avoided crossings cannot be predicted rigorously.

This is not to imply that avoided crossings do not occur. Their occurrence, however, may depend on details of the system other than the simple spatial and spin symmetries. In general, avoided-crossing rules will be system dependent.

Variational calculations, since they are extremum calculations, tend to maximize the energy separation of nearly degenerate and degenerate states. Because of this, curves which avoid crossing by separations comparable to the accuracy of a calculation may correspond to exact curves which cross. Furthermore, states which are not distinguished by any of the basis-set symmetries will, in general, cross or avoid crossing in a variational calculation in accordance with the basis-set noncrossing rule (see Sec. V) regardless of whether the exact states cross or avoid crossing. Procedures for determining whether or not an avoided crossing is resolved in a calculation are discussed in another paper.[10]

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APPENDIX: ONE-ELECTRON DIATOMIC MOLECULE

The Schrödinger equation for the one-electron diatomic molecule may be solved by separation of variables[14] in spheroidal coordinates, λ, μ, and ϕ:

$$\lambda = (r_1 + r_2)/R\,, \quad \mu = (r_1 - r_2)/R\,.$$

ϕ is the angle about the internuclear axis, R is the internuclear separation, and r_i is the distance from the electron to nucleus i. The three separated equations (ϕ, λ, and μ equations, respectively) are

$$\left(\frac{\partial^2}{\partial\phi^2} + m^2\right) M(\phi) = 0\,,$$

$$\left(\frac{d}{d\lambda}(\lambda^2-1)\frac{d}{d\lambda} + A + \frac{R^2E}{4}\lambda^2 + R(z_1+z_2)\lambda - \frac{m^2}{\lambda^2-1}\right) N(\lambda) = 0\,,$$

$$\left(\frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu} - A - \frac{R^2E}{4}\mu^2 - R(z_1-z_2)\mu - \frac{m^2}{1-\mu^2}\right) L(\mu) = 0\,,$$

where z_i is the charge of nucleus i, E is the energy, A is a separation constant, and m^2 is the eigenvalue of the ϕ equation. The constant-of-motion operators corresponding [see Eq. (1)] to a complete set of symmetry operators are

$$A = \frac{1-\mu^2}{\lambda^2-\mu^2}\left(\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda} + (z_1+z_2)R\lambda + \frac{1}{\lambda^2-1}\frac{\partial^2}{\partial\phi^2}\right) - \frac{\lambda^2-1}{\lambda^2-\mu^2}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial}{\partial\mu} - (z_1-z_2)R\mu + \frac{1}{1-\mu^2}\frac{\partial^2}{\partial\phi^2}\right),$$

$$B = \frac{\mu^2}{\lambda^2-\mu^2}\left(\frac{\partial}{\partial_\lambda}(\lambda^2-1)\frac{\partial}{\partial_\lambda} + (z_1+z_2)R\lambda + \frac{1}{\lambda^2-1}\frac{\partial^2}{\partial\phi^2}\right) + \frac{\lambda^2}{\lambda^2-\mu^2}\left(\frac{\partial}{\partial_\mu}(1-\mu^2)\frac{\partial}{\partial_\mu} - (z_1-z_2)R\mu + \frac{1}{1-\mu^2}\frac{\partial^2}{\partial\phi^2}\right),$$

$$S_{L_z^2} = -\frac{\partial^2}{\partial\phi^2}\,.$$

In the united-atom limit the operators A and B go to the total angular momentum squared operator. These operators distinguish all states of the one-electron diatomic molecule. All states are therefore of different symmetry. This does not mean that all states may cross. For example, the $4f\sigma$ and $5g\sigma$ states of BH^{5+} (shown in Fig. 2) avoid crossing at approximately 13 a.u.

Rigorous noncrossing rules for the one-electron diatomic molecule may be obtained by Sturm-theory analysis of the separated equations. The first such rule was given by Power.[15] The more extensive rule presented here was developed by this author.[6] For a particular state, the number of nodes in the solution of each separated equation is a constant for all finite R. Consequently, the united-atom quantum numbers n, l, and m may be used to determine the number of nodes of state i in the ϕ equation $n_\phi^{(i)} = m^{(i)}$, in the λ equation, $n_\lambda^{(i)} = n^{(i)} - l^{(i)} - 1$, and in the μ equation, $n_\mu^{(i)} = l^{(i)} - m^{(i)}$. States i and j cannot cross if

$$n_m^{(i)} \leq n_m^{(j)}, \quad n_\lambda^{(i)} \leq n_\lambda^{(j)}, \quad n_\mu^{(i)} \leq n_\mu^{(j)} .$$

With this rule, the crossings and avoided crossings of BH^{5+} and the other one-electron diatomic molecules may be explained.

The sharp avoided crossings of the one-electron diatomic molecules (such as the avoided crossing between the $4f\sigma$ and $5g\sigma$ states of BH^{5+} shown in Fig. 2) were first discussed by Ponomarev and Puzynia.[9] These occur in asymmetric systems between states ϕ_1 and ϕ_2, where the electron of states ϕ_1 is fairly well localized near nucleus 1, and the electron of state ϕ_2 is fairly well localized near nucleus 2. In the crossing region, the electron of each state jumps from one nucleus to the other—resulting in a rapid change of the slopes of the energy curves.

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