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Joseph O. Hirschfelder and Donald K. Harriss

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Joseph O. Hirschfelder and Donald K. Harriss+

University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin

ABSTRACT

The various orders of the wave functions for a perturbed Hamiltonian can be resolved into components which transform in accordance with the irreducible representations of the unperturbed Hamiltonian. Each of these components satisfies a separate perturbation equation. It is hoped that this approach will be especially useful in considering the perturbation of degenerate states.

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+ Present address: Department of Chemistry, University of Minnesota, Duluth.

Consider a perturbation problem in which the perturbation destroys a part of the symmetry of the unperturbed state. The following treatment serves to resolve the perturbed wave function into components each of which transforms in accordance with irreducible representations of the unperturbed Hamiltonian. Thus, for example, if the perturbation destroys the spherical symmetry of a system, the perturbed wave function can be expanded into spherical harmonics.

The zeroth order Hamiltonian H_o of a molecular system commutes with a group G composed of g transformations R_i. This group has a set of s irreducible representations with matrix elements $D^{(\ell)}(R_i)_{jk}$. The ℓ-th irreducible representation is h_ℓ dimensional. The Hilbert space of H_o is spanned by functions which transform according to these irreducible representations.

If Φ is an arbitrary function in this Hilbert space, then ${}^{\ell}\Phi_j = A_{\ell j}\Phi$ transforms as the j-th row of the ℓ-th irreducible representation.[1] Here

$$A_{\ell j} = (h_\ell/g) \sum_i D^{(\ell)}(R_i)_{jj}^{*} R_i \quad . \tag{1}$$

In general, the functions ${}^{\ell}\Phi_j$ do not form a basis, (i.e. are not "partner" functions), but they do form a resolution of Φ,

$$\Phi = \sum_\ell \sum_j {}^{\ell}\Phi_j \quad , \tag{2}$$

by the completeness theorem for the projection operators. Since R_i commutes with H_o, it follows that the $A_{\ell j}$ also commute with H_o.

If G is a continuous, rather than a finite group, then the summation over the R_i must be replaced by integration over all of the transformations using weight functions appropriate to the parametrization. Thus, if H_o has spherical symmetry, then

$$A_{\ell j} = Y_{\ell j}(\theta,\phi) \int_0^{\pi} \int_0^{2\pi} Y_{\ell j}(\theta,\phi)^* \; (\qquad) \sin\theta \, d\phi \, d\theta \tag{3}$$

where the $Y_{\ell j}(\theta,\phi)$ are the normalized surface spherical harmonics. Similarly, if H_o has cylindrical symmetry then

$$A_{\ell} = (1/2\pi) \exp(i\ell\phi) \int_0^{2\pi} \exp(-i\ell\phi) \; (\qquad) \, d\phi \tag{4}$$

Now let us consider a perturbation problem where the Hamiltonian for the perturbed system is $H = H_o + V$. The usual Rayleigh-Schrödinger perturbation equations are

$$(H_o - \varepsilon_o) \Psi_o = 0 \tag{5}$$

$$(H_o - \varepsilon_o) \Psi_o^{(1)} + (V - \varepsilon_o^{(1)}) \Psi_o = 0 \tag{6}$$

$$(H_o - \varepsilon_o) \Psi_o^{(2)} + (V - \varepsilon_o^{(1)}) \Psi_o^{(1)} = \varepsilon_o^{(2)} \Psi_o \tag{7}$$

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Since the zeroth order wavefunction Ψ_o is an eigenfunction of H_o it must belong to an irreducible representation of G . Furthermore, each of the $\Psi_o^{(n)}$ can be resolved into a set of functions $A_{\ell j} \Psi_o^{(n)}$ which transform in accordance with a particular row of a particular irreducible representation,

$$\Psi_o^{(n)} = \sum_{\ell,j} A_{\ell j} \Psi_o^{(n)} \tag{8}$$

The equation for $A_{\ell j} \Psi_o^{(n)}$ is obtained by multiplying the equation for $\Psi_o^{(n)}$ by $A_{\ell j}$. Thus,

$$(H_o - \mathcal{E}_o) A_{\ell j} \Psi_o^{(1)} + A_{\ell j}[(V- \mathcal{E}_o^{(1)}) \Psi_o] = 0 \tag{9}$$

$$(H_o - \mathcal{E}_o) A_{\ell j} \Psi_o^{(2)} + A_{\ell j}[(V- \mathcal{E}_o^{(1)}) \Psi_o^{(1)}] = \mathcal{E}_o^{(2)} A_{\ell j} \Psi_o \tag{10}$$

$$(H_o - \mathcal{E}_o) A_{\ell j} \Psi_o^{(n)} + A_{\ell j}[(V- \mathcal{E}_o^{(1)}) \Psi_o^{(n-1)}]$$

$$= \sum_{k=0}^{n-2} \mathcal{E}_o^{(n-k)} A_{\ell j} \Psi_o^{(k)} , \quad n > 1 \tag{11}$$

The normalization condition for the components of the perturbed wavefunctions are given by

$$\sum_{\ell,j} \sum_{k=0}^{n} < A_{\ell j} \Psi_o^{(n-k)} | A_{\ell j} \Psi_o^{(k)} > = 0 , \ n > 0 \tag{12}$$

In the calculation of the terms contributing to a particular order of the perturbed energy, the most important consideration is that the direct product of all representations in the integrand must contain the identity representation $D^{(0)}(R)$. A direct product of two unitary irreducible representations $D^{(k)}(R)^* \times D^{(n)}(R)$ can have a component transforming as the identity representation[2] only if $k=n$.

For the three-dimensional rotation group we have the Clebsch-Gordan series

$$D^{(k)}(R)^* \times D^{(n)}(R) = D^{(k)}(R) \times D^{(n)}(R) = D^{(|k-n|)}(R) + D^{(|k-n|+1)}(R) + \ldots + D^{(k+n)}(R)$$

where a necessary condition[3] for a representation $D^{(m)}(R)$ to be contained in the direct product $D^{(k)}(R) \times D^{(n)}(R)$ is that $|k-n| \leq m \leq k+n$. Let us suppose that $\Psi_o = A_{oo} \Psi_o$; then the various orders of the perturbed energy are given by:

$$\mathcal{E}_o^{(1)} = \langle \Psi_o | A_{oo}[V \Psi_o] \rangle \quad (13)$$

$$\mathcal{E}_o^{(2)} = \langle \Psi_o | A_{oo}[(V - \mathcal{E}_o^{(1)}) \Psi_o^{(1)}] \rangle \quad (14)$$

$$\mathcal{E}_o^{(3)} = \sum_{\ell,j} \langle A_{\ell j} \Psi_o^{(1)} | A_{\ell j}[(V - \mathcal{E}_o^{(1)}) \Psi_o^{(1)}] \rangle \quad (15)$$

It is easy to discuss any specific case in terms of the properties of the group under consideration.

The simplest illustration of this type of resolution corresponds to Ψ_o transforming as the identity representation and V transforming as the k-th irreducible representation (which has h_k dimensions). It follows from Eqs. (9) and (12) that $\Psi^{(1)}$ can have non-zero projections only for A_{kj} . Thus,

$$\Psi^{(1)} = \sum_{j=1}^{h_k} A_{kj} \Psi^{(1)}$$

and therefore, from Eq. (13), $\mathcal{E}_0^{(1)} \equiv 0$. We see from Eq. (14) that, if V is Hermitian, $\mathcal{E}_0^{(2)}$ is not identically zero since $D^{(k)*}(R) \times D^{(k)}(R)$ contains $D^{(0)}(R)$. From Eq. (15) we see that $\mathcal{E}_0^{(3)}$ is identically zero unless $D^{(k)}(R) \times D^{(k)}(R)$ contains $D^{(k)}(R)$. From the second order equation, (10), $\psi_0^{(2)}$ can have non-zero components $A_{ji}\ \psi_0^{(2)}$ only for those irreducible representations $D^{(j)}(R)$ contained in $D^{(k)}(R) \times D^{(k)}(R)$. Similarly for the third order equation, non-zero projections $A_{ji}\ \psi_0^{(3)}$ can exist only for those $D^{(j)}(R)$ contained in $D^{(k)*}(R) \times D^{(k)}(R) \times D^{(k)}(R)$.

A system exhibiting this type of behavior is the ground state hydrogen atom in a uniform electric field. In this example ψ_o is spherically symmetric, transforming as $D^{(0)}(R)$. For unit field strength the perturbation may be taken as $-Z$ which has the symmetry of $Y_{10}(0,\emptyset)$, transforming as $D^{(1)}(R)$. Since Y_{10} is only one of the three partners which form the basis for the representation $D^{(1)}(R)$, the product $Y_{10} \times Y_{10}$ need not have components transforming as all of the representations included in the Clebsch-Gordan series. Examination of the products shows that they reduce as:

$$Y_{10} \times Y_{10} \longrightarrow Y_{00}, Y_{20}$$

$$Y_{10} \times Y_{10} \times Y_{10} \longrightarrow Y_{10}, Y_{30}$$

$$Y_{10} \times Y_{10} \times Y_{10} \times Y_{10} \longrightarrow Y_{00}, Y_{20}, Y_{40}$$

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This reduction is sufficient to show that all odd order energies are zero and, since for the ground state $\mathcal{E}_0^{(2n)} \leqslant 0$, that the energy of the perturbed system is a sum of negative numbers. It can also be seen that $\Psi^{(n)}$ can have $(n+2)/2$ components for n even, $(A_{00}\Psi^{(n)}, A_{20}\Psi^{(n)}, \ldots, A_{n0}\Psi^{(n)})$, and $(n+1)/2$ components for n odd, $(A_{10}\Psi^{(n)}, A_{30}\Psi^{(n)}, \ldots, A_{n0}\Psi^{(n)})$. Each of the components has known symmetry and the projected equations can be treated as one-dimensional problems.