1.29: Appendix A

Proof that the character of a matrix representative is invariant under a similarity transform

A property of traces of matrix products is that they are invariant under cyclic permutation of the matrices.

i.e. $tr\left[ABC\right] = tr\left[BCA\right] = tr\left[CAB\right]$. For the character of a matrix representative of a symmetry operation g, we therefore have:

$$\chi(g) = tr\left[\Gamma(g)\right] = tr\left[C\Gamma'(g)C^{-1}\right] = tr\left[\Gamma'(g)C^{-1}C\right] = tr\left[\Gamma'(g)\right] = \chi'(g) \tag{29.1}$$

The trace of the similarity transformed representative is therefore the same as the trace of the original representative.

Proof that the characters of two symmetry operations in the same class are identical

The formal requirement for two symmetry operations g and g' to be in the same class is that there must be some symmetry operation f of the group such that $g' = f^{-1}gf$ (the elements g and g' are then said to be *conjugate*). If we consider the characters of g and g' we find:

$$\chi(g') = tr\left[\Gamma(g')\right] = tr\left[\Gamma^{-1}(f)\Gamma(g)\Gamma(f)\right] = tr\left[\Gamma(g)\Gamma(f)\Gamma^{-1}(f)\right] = tr\left[\Gamma(g)\right] = \chi(g) \tag{29.2}$$

The characters of g and g' are identical.

Proof of the Variation Theorem

The variation theorem states that given a system with a Hamiltonian H, then if ϕ is any normalized, well-behaved function that satisfies the boundary conditions of the Hamiltonian, then

$$\langle\phi|H|\phi\rangle \geq E_0 \tag{29.3}$$

where E_0 is the true value of the lowest energy eigenvalue of H. This principle allows us to calculate an upper bound for the ground state energy by finding the trial wavefunction ϕ for which the integral is minimized (hence the name; trial wavefunctions are varied until the optimum solution is found). Let us first verify that the variational principle is indeed correct.

We first define an integral

$$\begin{aligned} I &= \langle\phi| - E_0|\phi\rangle \\ &= \langle\phi|H|\phi\rangle - \langle\phi|E_0|\phi\rangle \\ &= \langle\phi|H|\phi\rangle - E_0\langle\phi|\phi\rangle \\ &= \langle\phi|H|\phi\rangle - E_0 \qquad \text{since } \phi \text{ is normalized} \end{aligned} \tag{29.4}$$

If we can prove that $I \geq 0$ then we have proved the variation theorem.

Let Ψ_i and E_i be the true eigenfunctions and eigenvalues of H, so $H\Psi_i = E_i\Psi_i$. Since the eigenfunctions Ψ_i form a complete basis set for the space spanned by H, we can expand any wavefunction ϕ in terms of the Ψ_i (so long as ϕ satisfies the same boundary conditions as Ψ_i).

$$\phi = \sum_k a_k\Psi_k \tag{29.5}$$

Substituting this function into our integral I gives

$$\begin{aligned} I &= \left\langle \sum_k a_k\Psi_k|H - E_0|\sum_j a_j\Psi_j\right\rangle \\ &= \langle\sum_k a_k\Psi_k|\sum_j (H - E_0)a_j\Psi_j\rangle \end{aligned} \tag{29.6}$$

If we now use $H\Psi + E\Psi$, we obtain

$$\begin{aligned} I &= \langle\sum_k a_k\Psi_k|\sum_j a_j(E_j - E_0)\Psi_j\rangle \\ &= \sum_k\sum_j a_k^* a_j(E_j - E_0)\langle\Psi_k|\Psi_j\rangle \\ &= \sum_k\sum_j a_k^* a_j(E_j - E_0)\delta_{jk} \end{aligned} \tag{29.7}$$

We now perform the sum over j, losing all terms except the $j = k$ term, to give

$$\begin{aligned} I &= \sum_k a_k^* a_k (E_k - E_0) \\ &= \sum_k |a_k|^2 (E_k - E_0) \end{aligned} \tag{29.8}$$

Since E_0 is the lowest eigenvalue, $E_k - E_0$ must be positive, as must $|a_k|^2$. This means that all terms in the sum are non-negative and $I \geq 0$ as required.

For wavefunctions that are not normalized, the variational integral becomes:

$$\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_0 \tag{29.9}$$

Derivation of the secular equations – the general case of the linear variation method

In the study of molecules, the variation principle is often used to determine the coefficients in a *linear variation function*, a linear combination of n linearly independent functions $(f_1, f_2, \ldots, f_n)$ (often atomic orbitals) that satisfy the boundary conditions of the problem. i.e. $\phi = \sum_i c_i f_i$. The coefficients c_i are parameters to be determined by minimizing the variational integral. In this case, we have:

$$\begin{aligned} \langle\phi|H|\phi\rangle &= \langle \sum_i c_i f_i | H | \sum_j c_j f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j \langle f_i | H | f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j H_{ij} \end{aligned} \tag{29.10}$$

where H_{ij} is the Hamiltonian matrix element.

$$\begin{aligned} \langle\phi|\phi\rangle &= \langle \sum_i c_i f_i | \sum_j c_j f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j \langle f_i | f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j S_{ij} \end{aligned} \tag{29.11}$$

where S_{ij} is the overlap matrix element.

The variational energy is therefore

$$E = \frac{\sum_i \sum_j ci^* c_j H_{ij}}{\sum_i \sum_J c_i^* c_j S_{ij}} \tag{29.12}$$

which rearranges to give

$$E \sum_i \sum_j c_i^* c_j S_{ij} = \sum_i \sum_j c_i^* c_j H_{ij} \tag{29.13}$$

We want to minimize the energy with respect to the linear coefficients c_i, requiring that $\dfrac{\partial E}{\partial c_i}$ for all i. Differentiating both sides of the above expression gives,

$$\frac{\partial E}{\partial c_k} \Sigma_i \Sigma_j c_i^* c_j S_{ij} + E \Sigma_i \Sigma_j \left[\frac{\partial c_i^*}{\partial c_k} c_j + \frac{\partial c_j}{\partial c_k} c_i^* \right] S_{ij} + \Sigma_i \Sigma_j \left[\frac{\partial c_i^*}{\partial c_k} c_j + \frac{\partial c_j}{\partial c_k} c_i^* \right] H_{ij} \tag{29.14}$$

Since $\frac{\partial c_i^*}{\partial c_k} = \delta_{ik}$ and $S_{ij} = S_{ji}$, $H_{ij} = H_{ji}$, we have

$$\frac{\partial E}{\partial c_k} \Sigma_i \Sigma_j c_i^* c_j S_{ij} + 2E \Sigma_i S_{ik} = 2\Sigma_i c_i H_{ik} \tag{29.15}$$

When $\frac{\partial E}{\partial c_k} = 0$, this gives

$$\boxed{\Sigma_i c_i (H_{ik} - E S_{ik}) = 0} \quad \text{for all k} \quad \text{SECULAR EQUATIONS} \tag{29.16}$$