D. A TWO-STATE MODEL

The Schrödinger equation $\hat{H}\psi = E\psi$ is usually solved by expanding the unknown wave function ψ in a series[1] of complete basis set $\{\phi_i\}_{i=1}^{N}$ of states ϕ_i, where N in principle equals ∞ (instead in practice we end up with a chosen large value of N). The expansion gives $\hat{H}\sum_j c_j\phi_j = E\sum_j c_j\phi_j$, or $\sum_j c_j(\hat{H}\phi_j - E\phi_j) = 0$. By multiplying this equation successively by ϕ_i^*, $i = 1, 2, \ldots, N$, and integrating we obtain a set of N linear equations for the unknown coefficients[2] c_i:

$$\sum_j c_j(H_{ij} - ES_{ij}) = 0,$$

where the Hamiltonian matrix elements $H_{ij} \equiv \langle\phi_i|\hat{H}\phi_j\rangle$, and the overlap integrals $S_{ij} \equiv \langle\phi_i|\phi_j\rangle$. The summation going to infinity makes impossible any simple insight into the physics of the problem. However, in many cases what matters most are only *two* states of comparable energies, while other states, being far away on the energy scale, do not count in practice (have negligible c_j). If indeed only two states were in the game (the two-state model), the situation could be analyzed in detail. The conclusions drawn are of great conceptual (and smaller numerical) importance.

For the sake of simplicity, in further analysis the functions ϕ_j will be assumed normalized and real.[3] Then, for $N = 2$ we have $H_{12} = \langle\phi_1|\hat{H}\phi_2\rangle = \langle\hat{H}\phi_1|\phi_2\rangle = \langle\phi_2|\hat{H}\phi_1\rangle = H_{21}$, and all H_{ij} are real numbers (in most practical applications $H_{12}, H_{11}, H_{22} \leqslant 0$). The overlap integral will be denoted by $S \equiv \langle\phi_1|\phi_2\rangle = \langle\phi_2|\phi_1\rangle$. After introducing the abbreviation $h \equiv H_{12}$ we have

$$c_1(H_{11} - E) + c_2(h - ES) = 0,$$
$$c_1(h - E) + c_2(H_{22} - ES) = 0.$$

A non-trivial solution of these secular equations exists only if the secular determinant satisfies

$$\begin{vmatrix} H_{11} - E & h - ES \\ h - ES & H_{22} - E \end{vmatrix} = 0.$$

[1] As a few examples just recall the CI, VB (Chapter 10), and MO (Chapter 8) methods.

[2] The same set of equations ("secular equations") is obtained after using the Ritz method (Chapter 5).

[3] This pertains to almost all applications. For complex functions the equations are only slightly more complicated.

After expanding the determinant, we obtain a quadratic equation for the unknown energy E:

$$(H_{11} - E)(H_{22} - E) - (h - ES)^2 = 0$$

with its two solutions[4]

$$E_\pm = \frac{1}{1-S^2}\left\{\frac{H_{11}+H_{22}}{2} - hS \right.$$
$$\left. \mp \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + \left(h - S\sqrt{H_{11}H_{22}}\right)^2 + 2hS\left(\sqrt{H_{11}H_{22}} - \frac{H_{11}+H_{22}}{2}\right)}\right\}.$$

After inserting the above energies into the secular equations we obtain the following two sets of solutions c_1 and c_2:

$$\left(\frac{c_1}{c_2}\right)_\pm = \frac{1}{(h - H_{11}S)}\left\{\frac{H_{11}-H_{22}}{2} \pm \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + (h - H_{11}S)(h - H_{22}S)}\right\}.$$

Using the abbreviations

$$\Delta = \frac{H_{11}-H_{22}}{2},$$

and $E_{ar} = (H_{11} + H_{22})/2$ for the arithmetic mean, as well as $E_{geom} = \sqrt{H_{11}H_{22}}$ for the geometric mean, we get a simpler formula for the energy

$$E_\pm = \frac{1}{1-S^2}\left\{E_{ar} - hS \mp \sqrt{\Delta^2 + (h - SE_{geom})^2 + 2hS(E_{geom} - E_{ar})}\right\}.$$

Now, let us consider some important special cases.

Case I. $H_{11} = H_{22}$ and $S = 0$ (ϕ_1 and ϕ_2 correspond to the same energy and do not overlap).

Then, $\Delta = 0$, $E_{ar} = E_{geom} = H_{11}$ and we have

$$E_\pm = H_{11} \pm h, \qquad \left(\frac{c_1}{c_2}\right)_\pm = \pm 1.$$

For $h < 0$ this means that E_+ corresponds to stabilization (with respect to ϕ_1 or ϕ_2 states), while E_- corresponds to destabilization (by the same value of $|h|$). The wave functions contain equal contributions of ϕ_1 and ϕ_2 and (after normalization) are

[4] It is most practical to use Mathematica coding:

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Solve[(H11-EdS)*(H22-EdS)-(h-EdS*S)^2==0,EdS]
Solve[(H11-EdS)*(H22-EdS)-(h-EdS*S)^2==0
&&c1*(H11-EdS)+c2*(h-EdS*S)==0
&&c1*(h-EdS*S)+c2*(H22-EdS)==0,{c1,c2},{EdS}]
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$$\psi_+ = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2), \qquad \psi_- = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2).$$

Case II. $H_{11} = H_{22}$ and $S \neq 0$ (ϕ_1 and ϕ_2 correspond to the same energy, but their overlap integral is non-zero).

Then,

$$E_\pm = \frac{H_{11} \pm h}{1 \pm S}, \qquad \left(\frac{c_1}{c_2}\right)_\pm = \pm 1.$$

Here also E_+ corresponds to stabilization, and E_- to destabilization (because of the denominator, this time the destabilization is larger than the stabilization). The wave functions have the same contributions of ϕ_1 and ϕ_2 and (after normalization) are equal to

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(\phi_1 + \phi_2), \qquad \psi_- = \frac{1}{\sqrt{2(1-S)}}(\phi_1 - \phi_2).$$

Case III. $H_{11} \neq H_{22}$ and $S = 0$ (ϕ_1 and ϕ_2 correspond to different energies and the overlap integral equals zero).

This time

$$E_\pm = E_{\text{ar}} \mp \sqrt{\Delta^2 + h^2},$$
$$\left(\frac{c_1}{c_2}\right)_\pm = \frac{1}{h}\left(\Delta \pm \sqrt{\Delta^2 + h^2}\right). \tag{D.1}$$

Here also the state of E_+ means stabilization, while E_- corresponds to destabilization (both effects are equal).

Let us consider a limiting case when the mean energy in state ϕ_1 is much lower than that in ϕ_2 ($H_{11} \ll H_{22}$), and in addition $\frac{\Delta}{h} \gg 0$. For the state with energy E_+ we have $\frac{c_1}{c_2} \simeq \frac{2\Delta}{h}$, i.e. c_1 is very large, while c_2 is very small (this means that ψ_+ is very similar to ϕ_1). In state ψ_- the same ratio of coefficients equals $\frac{c_1}{c_2} \simeq 0$, which means a domination of ϕ_2.

> Thus, if two states differ very much in their energies (or h is small, which means the overlap integral is also small), they do not change in practice (do not mix together).

This is why at the beginning of this appendix, we admitted only ϕ_1 and ϕ_2 of comparable energies.