

A Two-State Model

The Schrödinger equation $\hat{H}\psi = E\psi$ is usually solved¹ by expanding the unknown wave function ψ in a series of the 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^* , $i = 1, 2, \dots, N$ and integrating, we obtain a set of N linear equations for the unknown coefficients² 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 in the energy scale practically do not count (have negligible c_j). If indeed only two states were involved (the two-state model), then 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 to be normalized and real.³ Then, for $N = 2$, we have $H_{12} = \langle \phi_1 | \hat{H} \phi_2 \rangle = \langle \hat{H} \phi_1 | \phi_2 \rangle = \langle \phi_2 | \hat{H} \phi_1 \rangle = H_{21}$, where H_{11} and H_{22} are real numbers (in most practical applications $H_{12}, H_{11}, H_{22} \leq 0$). The overlap integral will be denoted by $S \equiv \langle \phi_1 | \phi_2 \rangle = \langle \phi_2 | \phi_1 \rangle$ and the functions ϕ defined such that $S > 0$. After introducing the abbreviation $h \equiv H_{12}$, we have

$$\begin{aligned} c_1(H_{11} - E) + c_2(h - ES) &= 0 \\ c_1(h - ES) + c_2(H_{22} - E) &= 0. \end{aligned}$$

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, and MO methods discussed in [Chapters 8](#) (MO) and [10](#) (CI, VB).

² The same set of equations (secular equations) is obtained after using the Ritz method (covered in [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 solutions⁴:

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

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 $E_{ar} = \frac{H_{11} + H_{22}}{2}$ 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 1. $H_{11} = H_{22}$ 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

$$E_{\pm} = H_{11} \pm h$$

$$\left(\frac{c_1}{c_2}\right)_{\pm} = \pm 1.$$

⁴ The most practical approach is to use the 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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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

$$\begin{aligned}\psi_+ &= \frac{1}{\sqrt{2}} (\phi_1 + \phi_2), \\ \psi_- &= \frac{1}{\sqrt{2}} (\phi_1 - \phi_2).\end{aligned}$$

Case 2. $H_{11} = H_{22}$ and $S \neq 0$ (ϕ_1 and ϕ_2 correspond to the same energy, but their overlap integral is nonzero).

Then,

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

Here also, E_+ corresponds to stabilization, while E_- corresponds 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

$$\begin{aligned}\psi_+ &= \frac{1}{\sqrt{2(1+S)}} (\phi_1 + \phi_2), \\ \psi_- &= \frac{1}{\sqrt{2(1-S)}} (\phi_1 - \phi_2).\end{aligned}$$

Case 3. $H_{11} \neq H_{22}$ and $S = 0$ (ϕ_1 and ϕ_2 correspond to different energies and the overlap integral is equal to zero).

This time,

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

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

Let us consider a limited case when the mean energy in the 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 the 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 the state ψ_- , the same ratio of the coefficients is $\frac{c_1}{c_2} \simeq 0$, which means a domination of ϕ_2 .

Thus, if two states differ significantly by their energies (or h is small, which means the overlap integral is also small), they do not change (do not mix together) in any practical sense.

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