

Coulomb and Resonance Integrals in Molecular Orbital Theory

The concepts of "resonance" and "exchange" have caused and will probably forever cause much confusion among chemists. Since it is hardly possible to penetrate deeper into the nature of molecules without a sound description of their binding forces, it is certainly worth while to expend some labor in making these things clear. The difficulty is to design some model which does not violate the fundamental quantum mechanical principles but, on the other hand, is simple enough to be understood by, for instance, organic chemists without too much of theoretical education.

Much of the hard mathematical labor in the ordinary textbook quantum chemistry comes from the necessity of working with central forces. Generally the theory starts with the exact model of the hydrogen atom, but as soon as the problems become of a two-center nature very serious approximations are required in an "easy" treatment. It could be questioned whether it would not be possible to obtain more instructive results by studying the one-dimensional rectangular-box potential simultaneously and treating the latter problem with and without similar approximations. The present paper deals with an illustration of how magnitudes such as Coulomb and resonance (by some authors called "exchange") integrals arise in MO LCAO (molecular orbital, linear combination of atomic orbitals) theory. Contrary to the true central-force model, the present one-dimensional model allows an easy, exact treatment, and it may also be subjected to an approximate treatment, fully analogous to the current simple treatment of H_2^+ .¹ This double treatment, which could be carried through in detail by most students of physical organic chemistry, shows how the magnitudes mentioned above arise from and thus are mere products of our crude method of LCAO approach.

The model of the particle in a one-dimensional box with slightly penetrable walls and its solutions have to be known and understood.² Also the general symmetry properties of wave functions have to be realized.

Two rectangular potential wells approach each other, corresponding to a total potential-energy function of the type illustrated in Figure 1. The one-dimensional time-independent Schrödinger equation for a single particle is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad (1)$$

In the region $x_1 < x < x_2$, $V = 0$, hence

$$\frac{d^2\psi}{dx^2} = -\frac{2mE\psi}{\hbar^2} = -\alpha^2\psi \quad (2)$$

It is obvious that ψ must be a sine function in this region, say

$$\psi_{12} = A \sin(\alpha x + \delta) \quad (3)$$

where A and δ are parameters giving the required generality. Owing to the symmetry conditions, equation (3) will also reproduce the solution in the region $-x_2 < x < -x_1$ with the same numerical values of the parameters A , α , and δ but with some obvious changes of sign (α could always be considered to be a positive quantity). For the two lowest energy levels (with which we shall be concerned here) there should be no node within these two intervals.

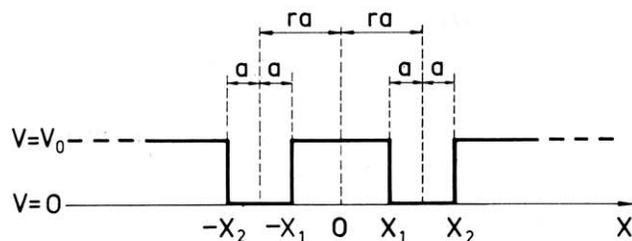


Figure 1. Double-box potential-energy function.

In the regions $x < -x_2$, $-x_1 < x < x_1$, and $x > x_2$, $V = V_0 > E$ and equation (1) becomes

$$\frac{d^2\psi}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi = \beta^2\psi \quad (4)$$

For $x > x_2$ the wave function must be of the form

$$\psi_2 = Ce^{-\beta x} \quad (5)$$

where $\beta > 0$. The same form could be used for $x < -x_2$ with proper changes of sign. In the central region, $-x_1 < x < x_1$, the wave function must (for symmetry reasons) be of the type

$$\psi_{11} = B'(e^{\beta x} \pm e^{-\beta x})$$

and it is convenient to use the hyperbolic functions. Considerations of the symmetry show that

$$\psi_1 = \begin{cases} B \cosh \beta x & \text{for the ground state} & (6a) \\ B \sinh \beta x & \text{for the first excited state} & (6b) \end{cases}$$

Some assumption about the capacity in phase space of the potential wells has to be made, and we write

$$2mV_0a^2/\hbar^2 = n^2 \quad (7)$$

where n is a pure number. From the definitions of equations (2) and (4) of α and β , respectively, the following relations are obtained:

$$\beta^2a^2 = n^2 - \alpha^2a^2 \quad (8)$$

¹ PAULING, LINUS, AND WILSON, E. BRIGHT, JR., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York and London, 1935, p. 327.

² SCHIFF, LEONARD I., "Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, Toronto, London, 1949, p. 36.

$$\frac{\beta^2}{\alpha^2} = \frac{n^2 - \alpha^2 a^2}{\alpha^2 a^2} \quad (9)$$

The usual claim for continuity of the wave function and of its first derivative is now used to solve for α . Equations (3), (5), and (6) give in this way

$$\begin{cases} \alpha \cot(\alpha x_1 + \delta) = \begin{cases} \beta \tanh \beta x_1 & \text{for the ground state} \\ \beta \coth \beta x_1 & \text{for the first excited state} \end{cases} & (10a) \\ \alpha \cot(\alpha x_2 + \delta) = -\beta & (11) \end{cases} \quad (10b)$$

If the distances of Figure 1 are introduced and further $\alpha a = z$, equations (10) and (11) could be transformed into equations (12) and (13) by means of the relations of equations (8) and (9):

$$\begin{cases} \cot[(r-1)z + \delta] = \begin{cases} \frac{\sqrt{n^2 - z^2}}{z} \tanh(r-1)\sqrt{n^2 - z^2} & \text{for the ground state} \\ \frac{\sqrt{n^2 - z^2}}{z} \coth(r-1)\sqrt{n^2 - z^2} & \text{for the first excited state} \end{cases} & (12a) \\ \cot[(r+1)z + \delta] = -\frac{\sqrt{n^2 - z^2}}{z} & (13) \end{cases} \quad (12b)$$

The system of equations (12) and (13) can now be solved empirically for z and δ if fixed values are assigned to r ($r > 1$) and n . From the expected shape of the wave function it is evident that the angle $[(r-1)z + \delta]$ must be in the first quadrant and $[(r+1)z + \delta]$ in the second (or, possibly, the third and fourth, respectively). It is then easy to plot δ as a function of z for each one of the two equations and find the point of intersection. What is needed for a reasonable degree of accuracy is an ordinary slide rule and some tables, all of which are found in, for instance, "Handbook of Chemistry and Physics."

The eigenvalue corresponding to the values chosen for r and n is easily obtained from z in terms of V_0 by means of equations (2) and (7):

$$E/V_0 = \alpha^2 \hbar^2 / 2mV_0 = \alpha^2 a^2 / n^2 = z^2 / n^2 \quad (14)$$

By varying r ($r > 1$) and keeping n at some suitable fixed value, it is possible to find how the energy of the two lowest levels changes with decreasing distance between the boxes. Figure 2 shows the result for $n = 2$

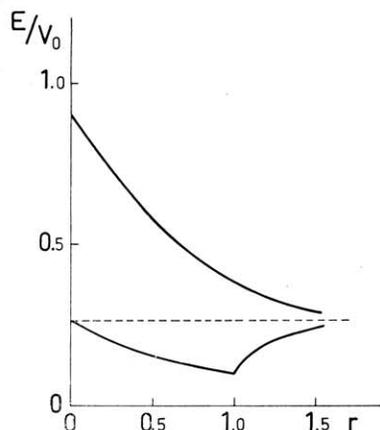


Figure 2. Energies of ground state and first excited state for a particle in the potential of Figure 1 ($r > 1$) and for a particle in a single box ($r < 1$); $n = 2$ for separate box. Dashed line indicates ground-state energy at infinite separation of boxes.

$= 2$. It is obvious that the ground state involves an attraction and the first excited state a repulsion. Figure 3 shows the shape of the eigenfunctions and the position of the energy levels for $n = 2$ and $r = 1.2$.

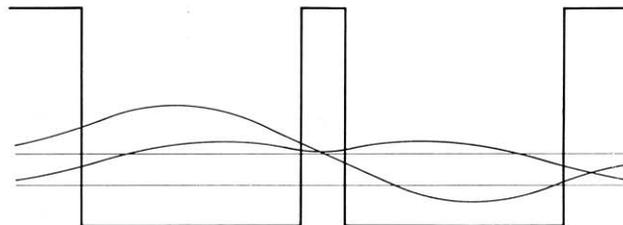


Figure 3. Exact energy levels and wave functions for the ground state and the first excited state; $n = 2, r = 1.2$.

When $r = 1$ the two boxes touch one another, and the model must be modified. It is hard to design a suitable model for $r < 1$. The assumption underlying the curve in Figure 2 is simply that of a single box of depth V_0 and length $2(r+1)a$. A convenient method for solving the single-box problem is given by Schiff.² Not too much attention should be paid to the behavior of this part of the curve, however, as the model involves serious oversimplification, as pointed out and discussed by Kauzmann.³ The most interesting phenomenon is the attraction or repulsion before the two boxes touch one another.

The eigenvalues could obviously be computed from the above equations to any desired degree of accuracy. An approximation is inherent in the model per se but no further approximations are required in the mathematics. Nothing like Coulomb or resonance integrals emerges, and no mention is made about the electron being in one or the other "atomic orbital." The situation leading to such concepts in the treatment of the perfect model could be illustrated in the following way.

Assume that the ground-state eigenvalue and eigenfunction of the single-box problem are known, but we hesitate to expend the mathematical labor involved in solving the system of equations (12) and (13). We could then try to simulate the wave function of the double-box problem by a linear combination of the known single-box wave functions. The eigenfunctions for two single boxes of length $2a$ and depth V_0 , the magnitude $2mV_0a^2/\hbar^2$ being equal to 4 as before, are shown in Figure 4. It is obvious that the combinations

$$\psi_+ = N_+(\psi_l + \psi_r) \quad (15)$$

$$\text{and} \quad \psi_- = N_-(\psi_l - \psi_r) \quad (16)$$

must bear a strong resemblance to the functions of Figure 3. N_+ and N_- are normalizing factors, and the indices l (left) and r (right) refer to the relative positions of the two boxes and functions.

The function ψ_l is the exact eigenfunction corresponding to a potential-energy function $V_l = V_0$ everywhere except for $-x_2 < x < -x_1$, where $V_l = 0$. In the same way ψ_r is the exact eigenfunction corresponding to the right-hand potential well at $x_1 < x < x_2$.

³ KAUZMANN, WALTER, "Quantum Chemistry," Academic Press, Inc., New York, 1957, p. 245.

The normalization constants are found from the conditions

$$\begin{aligned}
 1 &= N_{\pm}^2 \int_{-\infty}^{+\infty} (\psi_l \pm \psi_r)^2 dx \\
 &= N_{\pm}^2 \left(\int_{-\infty}^{+\infty} \psi_l^2 dx + \int_{-\infty}^{+\infty} \psi_r^2 dx \pm 2 \int_{-\infty}^{+\infty} \psi_l \psi_r dx \right) \\
 &= N_{\pm}^2 (2 \pm 2\Delta)
 \end{aligned}$$

$$\text{or} \quad N_{\pm}^2 = [2(1 \pm \Delta)]^{-1} \quad (17)$$

where ψ_l and ψ_r have been assumed to be normalized in themselves and Δ is the overlap integral

$$\Delta = \int_{-\infty}^{+\infty} \psi_l \psi_r dx \quad (18)$$

The magnitude of the latter depends of course strongly on the distance between the potential wells, i.e., whether there actually is a region where both functions simultaneously reach considerable values.

If the difference between the double-box Hamiltonian, H , and the single-box Hamiltonians, H_l and H_r , a difference in the potential-energy function only, is kept in mind, it is now possible to obtain an approximate expression for the energy from H and, for instance, ψ_+ :

$$\begin{aligned}
 E_+ &= \int_{-\infty}^{+\infty} \psi_+ H \psi_+ dx = N_+^2 \int_{-\infty}^{+\infty} (\psi_l + \psi_r) H (\psi_l + \psi_r) dx \\
 &= N_+^2 \left[\int_{-\infty}^{+\infty} \psi_l H \psi_l dx + \int_{-\infty}^{+\infty} \psi_r H \psi_r dx + \right. \\
 &\quad \left. \int_{-\infty}^{+\infty} \psi_l H \psi_r dx + \int_{-\infty}^{+\infty} \psi_r H \psi_l dx \right] \\
 &= N_+^2 \left[\int_{-\infty}^{+\infty} \psi_l H_l \psi_l dx - \int_{x_1}^{x_2} \psi_l V_0 \psi_l dx + \right. \\
 &\quad \left. \int_{-\infty}^{+\infty} \psi_r H_r \psi_r dx - \int_{-x_2}^{-x_1} \psi_r V_0 \psi_r dx + \right. \\
 &\quad \left. \int_{-\infty}^{+\infty} \psi_l H_r \psi_r dx - \int_{-x_2}^{-x_1} \psi_l V_0 \psi_r dx + \right. \\
 &\quad \left. \int_{-\infty}^{+\infty} \psi_r H_l \psi_l dx - \int_{x_1}^{x_2} \psi_r V_0 \psi_l dx \right] \\
 &= N_+^2 \left\{ E_s + E_s + E_s \Delta + E_s \Delta - \right. \\
 &\quad \left. V_0 \left[\int_{x_1}^{x_2} \psi_l^2 dx + \int_{-x_2}^{-x_1} \psi_r^2 dx + \int_{-x_2}^{-x_1} \psi_l \psi_r dx + \right. \right. \\
 &\quad \left. \left. \int_{x_1}^{x_2} \psi_r \psi_l dx \right] \right\} \\
 &= N_+^2 [2(1 + \Delta)E_s - V_0(\lambda + \lambda + \mu + \mu)] \\
 &= E_s - \frac{\lambda + \mu}{1 + \Delta} V_0 \quad (19)
 \end{aligned}$$

where E_s denotes the exact energy of the single-box system.

In the same way the approximate wave function ψ_- gives

$$E_- = E_s - \frac{\lambda - \mu}{1 - \Delta} V_0 \quad (20)$$

The net binding energy between the two boxes is consequently

$$\begin{aligned}
 &\frac{\lambda + \mu}{1 + \Delta} V_0 \quad \text{for the ground state} \\
 &\frac{\lambda - \mu}{1 - \Delta} V_0 \quad \text{for the first excited state}
 \end{aligned}$$

All magnitudes involved are positive quantities. From purely geometrical considerations it is obvious that μ , the product of the two different ψ 's integrated over one of the well intervals (one small and one large factor in the integrand) is larger than λ , the square of one of the ψ 's integrated over the other well (two small factors in the integrand). Hence there will be a binding force in the ground state and a repulsive force in the excited state.

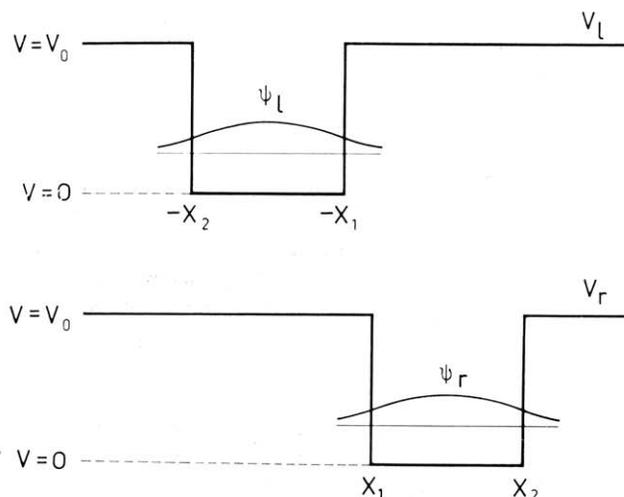


Figure 4. Single-box potential-energy functions, energy levels, and wave functions used in the approximate treatment of the double-box system.

The expressions of equations (19) and (20) are exactly analogous to the expressions obtained by the ordinary method for the energy of the molecule H_2^+ except for the internuclear repulsion term.¹ The magnitude $-\lambda V_0$ is of the same nature as the ordinary Coulomb integral, the energy of interaction between an electron in the orbital of one atom with the potential well of the other, and $-\mu V_0$ is in the same way analogous to the ordinary resonance integral.

From these two treatments of the double-box system it is evident that concepts like Coulomb and exchange or resonance integrals arise from the approximate method used to handle the mathematics and are by no means given by nature. The exact treatment is the straight-forward solution of the problem of one particle in a double-well potential, and any mention of, for instance, the interaction of an electron in one atomic orbital with the nucleus of the other atom is not required until the latter, approximate method is used because of our reluctance to make a straight-forward, exact mathematical treatment and our disposition to use what we know from a simpler problem.

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