

Pauli Deformation

Two molecules, when isolated (say at infinite distance), are independent and the wave function of the total system might be taken as a *product* of the wave functions for the individual molecules. When the same two molecules are at a finite distance, then any product-like function represents only an approximation (sometimes a very poor one¹), because according to a postulate of quantum mechanics, the wave function has to be antisymmetric with respect to the exchange of electronic labels, while the product does not fulfill that. More exactly, the approximate wave function has to belong to the irreducible representation of the symmetry group of the Hamiltonian (see [Appendix C](http://booksite.elsevier.com/978-0-444-59436-5) available at booksite.elsevier.com/978-0-444-59436-5, p. e17), to which the ground-state wave function belongs. This means, first of all, that the Pauli exclusion principle is to be satisfied.

Pauli Deformation

The product-like wave function has to be antisymmetrized. This makes some changes in the electronic charge distribution (electronic density), which will be called the *Pauli deformation*.

The Pauli deformation may be viewed as a mechanical distortion of both interacting molecules due to their mutual pushing. The reason why two gumballs deform when pushed against each other is the same: the electrons of one ball cannot occupy the same space as the electrons (with the same spin coordinates) of the second ball. The most dramatic deformation takes place close to the contact area of these balls.

The norm of the difference of $\varphi^{(0)}$ and $\psi^{(0)}$ represents a very stringent measure of difference between two functions: any deviation gives a contribution to the measure. We would like to know how the electronic density changes, where the electrons flows from, and where they go. The electron density ρ (a function of the position in space) is defined as a sum of densities ρ_i of the particular electrons:

$$\rho(x, y, z) = \sum_{i=1}^N \rho_i(x, y, z)$$

¹ For instance, when the intermolecular distance is short, then the molecules push one another and deform (maybe strongly), and the product-like function is certainly inadequate.

$$\rho_i(x_i, y_i, z_i) = \sum_{\sigma_i = -\frac{1}{2}}^{+\frac{1}{2}} \int \frac{d\tau}{d\tau_i} |\psi|^2, \quad (\text{Y.1})$$

where $d\tau = d\tau_1 d\tau_2 \cdots d\tau_N$, and so the integration goes over the coordinates (space and spin) of all the electrons except the electron i . In addition, there is a summation over the spin coordinate of the electron i because we are not interested in its value. As is seen, the integral of $\rho(x, y, z)$ over x, y , and z is equal to N ; therefore, $\rho(x, y, z)$ represents an electron cloud carrying N electrons, the same as defined in Eq. (11.3) on p. 666. We make the two molecules approach each other without changing their charge distribution (the system is described by the electron density corresponding to the wave function $\psi = \varphi^{(0)}$), and then we allow the Pauli exclusion principle to operate in order to ensure the proper symmetry of the wave function (the system, therefore, is described by a new wave function $\psi = \psi^{(0)}$) by applying a suitable projection operator. What happens to the electronic density? Will it change or not?

Let us see what happens when we make such an approach of two hydrogen atoms and then of two helium atoms.

H_2 Case

In the case of two hydrogen atoms² $\varphi^{(0)} = 1s_a(1)\alpha(1)1s_b(2)\beta(2) \equiv a(1)\alpha(1)b(2)\beta(2)$, where we have used the abbreviation $1s_a(1) \equiv a$ and $1s_b(1) \equiv b$. After inserting $\psi = \varphi^{(0)}$ into Eq. (Y.1), and then integrating over space and summation over spin coordinates, we obtain $\rho^{(0)} = \rho_1(x, y, z) + \rho_2(x, y, z)$, where $\rho_1(x, y, z) = \sum_{\sigma_1 = -\frac{1}{2}}^{+\frac{1}{2}} \int \frac{d\tau}{d\tau_1} |a(1)\alpha(1)b(2)\beta(2)|^2 = \sum_{\sigma_1 = -\frac{1}{2}}^{+\frac{1}{2}} \int d\tau_2 |a(1)\alpha(1)b(2)\beta(2)|^2 = a^2$.

Similarly, $\rho_2(x, y, z) = \sum_{\sigma_2 = -\frac{1}{2}}^{+\frac{1}{2}} \int \frac{d\tau}{d\tau_2} |a(1)\alpha(1)b(2)\beta(2)|^2 = \sum_{\sigma_2 = -\frac{1}{2}}^{+\frac{1}{2}} \int d\tau_1 |a(1)\alpha(1)b(2)\beta(2)|^2 = b^2$. Thus, finally, $\rho^{(0)} = a^2 + b^2$. This density is normalized to 2, as it must, because the electron cloud $\rho(x, y, z)$ carries two electrons. Now, let us do the same for the wave function $\psi^{(0)} = N\hat{A}\varphi^{(0)}$, where \hat{A} stands for the idempotent projection operator 13.26, and the normalization constant $N = \frac{2}{\sqrt{1+S^2}}$ with $S = (a|b)$, all quantities described in Chapter 13 about the symmetry-adapted perturbation theory (SAPT):

$$\begin{aligned} \rho(x, y, z) &= \rho_1(x, y, z) + \rho_2(x, y, z), \\ \rho_1(x, y, z) &= \sum_{\sigma_1 = \pm\frac{1}{2}} \int d\tau_2 |\psi^{(0)}|^2 \end{aligned}$$

² We assign arbitrarily the spin function α to electron 1 and the spin function β to electron 2. We might have done in the opposite way; it does not change anything.

$$\begin{aligned}
&= N^2 \frac{1}{8} \int dV_2 [a(1)b(2) + a(2)b(1)]^2 \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]^2 \\
&= N^2 \frac{1}{8} \int dV_2 [a(1)b(2) + a(2)b(1)]^2 \\
&= N^2 \frac{1}{8} (a^2 + b^2 + 2abS) = \frac{1}{2(1+S^2)} (a^2 + b^2 + 2abS),
\end{aligned}$$

$$\rho_2(x, y, z) = \rho_1(x, y, z).$$

As is shown here, the density $\rho_1(x, y, z)$ is normalized to 1, which is what we would get after integration over dV_1 . A similar calculation for ρ_2 would give the same result because $|\psi^{(0)}|^2$ is symmetric with respect to the exchange of electrons³ 1 and 2. Therefore, the *change* of the electron density due to the proper symmetry projection (including the Pauli exclusion principle):

$$\rho - \rho^{(0)} = \frac{a^2 + b^2 + 2abS}{1 + S^2} - (a^2 + b^2) = \frac{2S}{1 + S^2} ab - \frac{S^2}{1 + S^2} a^2 - \frac{S^2}{1 + S^2} b^2. \quad (\text{Y.2})$$

Thus, it turns out that as a result of the Pauli exclusion principle (i.e., of the antisymmetrization of the wave function), an electron density $a^2 S^2 / (1 + S^2)$ flows from atom a, and a similar thing happens to atom b, where the electronic density decreases by $b^2 S^2 / (1 + S^2)$. Both these electronic clouds go to the bond region—we find them as an electron cloud $2abS / (1 + S^2)$ with a maximum in the bond, and of course, the integral of $\rho - \rho^{(0)}$ equals zero (Fig. Y.1a).

Thus,

in the hydrogen molecule, the Pauli exclusion principle caused the two atoms to stick together (the two electrons increase the probability that they are in the region between the two nuclei).

This is what the Pauli exclusion principle dictates. Besides that, of course, we have all the physical interactions (i.e., electron repulsion, attraction with the nuclei) and the kinetic energy, but none of these effects have been taken into account.⁴ Fig. Y.1a shows the deformation that results only from forcing the proper symmetry in the wave function.

³ This was not the case for $\varphi^{(0)}$.

⁴ Indeed, all these effects have been ignored because we neither calculated the energy nor used the Hamiltonian. However, the very fact that we write $\varphi^{(0)} = a(1)\alpha(1)b(2)\beta(2)$, where a and b stand for the properly centered $1s$ orbitals, means that the electron-nucleus interaction has been *implicitly* taken into account (this is why the $1s$ orbital appears). Similarly, when we project the product like function and obtain $\psi^{(0)}$ proportional to $[a(1)b(2) + a(2)b(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$, then in addition to the abovementioned electron-nucleus interactions (manifested by the $1s$ orbitals), we obtain an interesting effect: when one electron is on nucleus a , then the second electron runs to nucleus b . It looks as if they repelled each other. This is, however, at the level of the *mathematical formula of the function* (function design), as if the function already has been quite well designed for the *future*, taking into account the physical interactions.

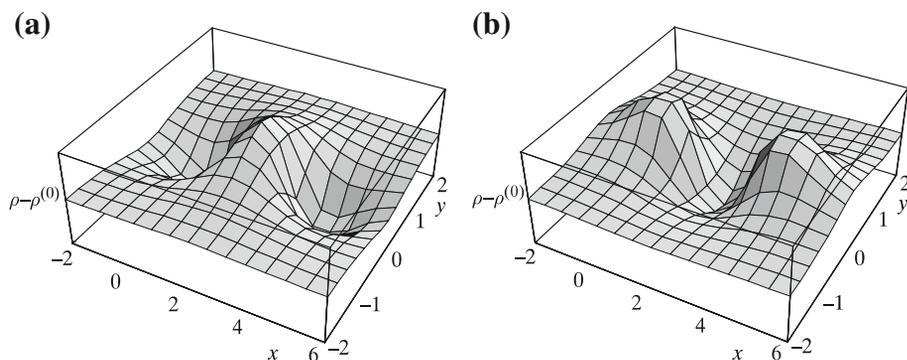


Fig. Y.1. Comparison of the Pauli deformation for two hydrogen atoms and for two helium atoms. (a) Two hydrogen atoms. Visualization of $\rho - \rho^{(0)}$ calculated in the plane containing the nuclei (the net result is zero). One of the protons is located at the origin, and the other has the coordinates $(0, R, 0)$, with $R = 1.4$ a.u. (the distance close to the equilibrium). For this distance, the overlap integral (see Appendix R available at booksite.elsevier.com/978-0-444-59436-5, p. e137) $S = (1 + R + \frac{R^2}{3})\exp(-R)$ amounts to 0.752943. As we can see, the electronic density has flown from the nuclei to the bond. (b) Two helium atoms. The only difference with respect to (a) is that two electrons have been added. But the visualization of $\rho - \rho^{(0)}$ reveals a *completely different pattern*. This time, the electronic density has been removed from the bond region and increased in the region of the nuclei.

He₂ Case

Let us see what happens if we make similar calculations for the two helium atoms. In order to compare the future result with the H₂ case, let us keep everything the same (the internuclear distance R , the atomic orbitals, the overlap integral S , etc.), except that the number of electrons changes from two to four. This time, the calculation will be a little more tedious because four-electron wave functions are more complicated than two-electron functions. For instance, the function $\varphi^{(0)}$ can be approximated as the product of the two Slater determinants—one for atom a, and the other for atom b:

$$\begin{aligned} \varphi^{(0)} &= N \begin{vmatrix} a\alpha(1) & a\alpha(2) \\ a\beta(1) & a\beta(2) \end{vmatrix} \begin{vmatrix} b\alpha(3) & b\alpha(4) \\ b\beta(3) & b\beta(4) \end{vmatrix} \\ &= N' a(1)a(2)b(3)b(4) \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \right] \\ &\quad \times \left[\frac{1}{\sqrt{2}} [\alpha(3)\beta(4) - \alpha(4)\beta(3)] \right], \end{aligned} \quad (\text{Y.3})$$

where the normalization constant $N' = 1$ (which is easy to verify: just square the function and integrate – all that by heart). Then we obtain directly from the definition⁵

$$\rho^{(0)} = \rho_1 + \rho_2 + \rho_3 + \rho_4 = 2a^2 + 2b^2,$$

which after integration gives four electrons, as it should be. The function $\varphi^{(0)}$ is “illegal” because it does not fulfill the Pauli exclusion principle; e.g., the exchange of electrons 1 and 3 does not lead to a change of sign of the wave function.

⁵ This also may be calculated in one’s head (note that the spin functions in the square brackets are normalized).

Now let us focus on $\psi^{(0)}$. Note that $\varphi^{(0)}$ of Eq. (Y.3) may be written alternatively as:

$$\varphi^{(0)} = N \begin{vmatrix} a\alpha(1) & a\alpha(2) & 0 & 0 \\ a\beta(1) & a\beta(2) & 0 & 0 \\ 0 & 0 & b\alpha(3) & b\alpha(4) \\ 0 & 0 & b\beta(3) & b\beta(4) \end{vmatrix},$$

where N is a normalization constant.

Antisymmetrization of $\varphi^{(0)}$, in which electrons 1 and 2 occupy orbital a and electrons 3 and 4 occupy orbital b , is equivalent to completing the Slater determinant⁶ in a way that allows the exchange of electrons between the subsystems:

$$\begin{aligned} \psi^{(0)} &= N \frac{1}{2} (1 + I) \hat{A} \varphi^{(0)} = N \frac{1}{2} (1 + I) \begin{vmatrix} a\alpha(1) & a\alpha(2) & a\alpha(3) & a\alpha(4) \\ a\beta(1) & a\beta(2) & a\beta(3) & a\beta(4) \\ b\alpha(1) & b\alpha(2) & b\alpha(3) & b\alpha(4) \\ b\beta(1) & b\beta(2) & b\beta(3) & b\beta(4) \end{vmatrix} \\ &= N \begin{vmatrix} a\alpha(1) & a\alpha(2) & a\alpha(3) & a\alpha(4) \\ a\beta(1) & a\beta(2) & a\beta(3) & a\beta(4) \\ b\alpha(1) & b\alpha(2) & b\alpha(3) & b\alpha(4) \\ b\beta(1) & b\beta(2) & b\beta(3) & b\beta(4) \end{vmatrix}, \end{aligned}$$

where according to 13.26, \hat{A} stands for the idempotent antisymmetrization operator and $\frac{1}{2}(1+I)$ represents an idempotent symmetrization operator acting on the nuclear coordinates. What follows from that last equality is that this particular Slater determinant is already symmetric with respect to the exchange of the nuclei,⁷ which is equivalent to $a \leftrightarrow b$.

Any determinant is invariant with respect to the addition of any linear combination of its rows (columns) to a given row (column). For reasons that soon will become clear, let us create a series of such operations. First, let us add the third row to the first one, then multiply the third row by 2 (any multiplication is harmless for the determinant, because at the end it will be normalized), and then subtract the first row from the third one. Next, let us perform a similar series of operations applied to rows 2 and 4 (instead of 1 and 3), and finally, let us multiply rows 1 and 2 by $\frac{1}{\sqrt{2(1+s)}}$, and rows 3 and 4 by $\frac{1}{\sqrt{2(1-s)}}$. The result of these operations is the Slater determinant with the doubly occupied bonding molecular orbital $\sigma = \frac{1}{\sqrt{2(1+s)}}(a + b)$ and the

⁶ The Slater determinant containing linearly independent spin orbitals *guarantees* the antisymmetry.

⁷ This corresponds to the exchange of rows in the determinant: the first with the third, and the second with the fourth. A single exchange changes the sign of the determinant, so the two exchanges leave the determinant invariant.

doubly occupied antibonding molecular orbital $\sigma^* = \frac{1}{\sqrt{2(1-S)}}(a - b)$:

$$\psi^{(0)} = \frac{1}{\sqrt{4!}} \begin{vmatrix} \sigma\alpha(1) & \sigma\alpha(2) & \sigma\alpha(3) & \sigma\alpha(4) \\ \sigma\beta(1) & \sigma\beta(2) & \sigma\beta(3) & \sigma\beta(4) \\ \sigma^*\alpha(1) & \sigma^*\alpha(2) & \sigma^*\alpha(3) & \sigma^*\alpha(4) \\ \sigma^*\beta(1) & \sigma^*\beta(2) & \sigma^*\beta(3) & \sigma^*\beta(4) \end{vmatrix}$$

All the spin orbitals involved are orthonormal (in contrast to what was in the original determinant) and the corresponding electronic density is easy to write—it is the sum of squares of the molecular orbitals multiplied by their occupancies (cf., p. e142):

$$\rho(x, y, z) = 2\sigma^2 + 2(\sigma^*)^2.$$

Now let us compute the Pauli deformation:

$$\begin{aligned} \rho - \rho^{(0)} &= \frac{a^2 + b^2 + 2ab}{1 + S} + \frac{a^2 + b^2 - 2ab}{1 - S} - 2(a^2 + b^2) \\ &= -\frac{4S}{1 - S^2}ab + \frac{2S^2}{1 - S^2}a^2 + \frac{2S^2}{1 - S^2}b^2. \end{aligned} \quad (\text{Y.4})$$

Integration of the difference gives zero, as it should. Note that the formula is similar to what we have obtained for the hydrogen molecule, but this time, the electron flow is completely different (Fig. Y.1b).

In the case of He_2 , the Pauli exclusion principle makes the electron density decrease in the region between the nuclei and increase close to the nuclei. In the case of the hydrogen molecule, the two atoms stuck together, while the two helium atoms deform as if they were gumballs squeezed together (i.e., the Pauli deformation).

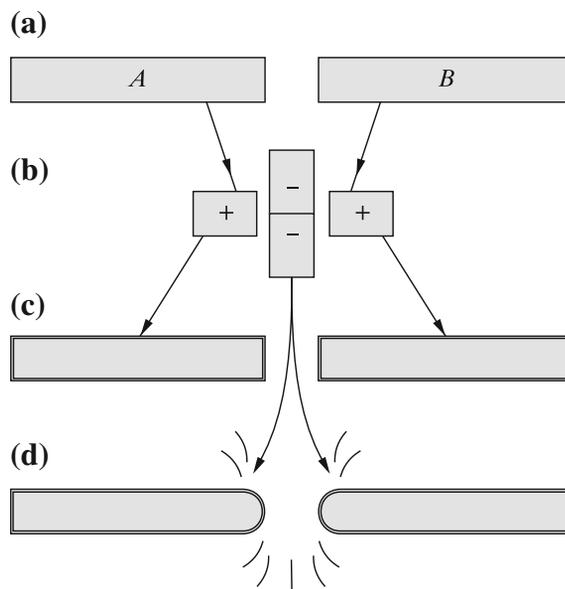


Fig. Y.2. The locality of the Pauli deformation (scheme). (a) Two polymeric chains A and B (with the electronic densities in the form of the elongated rectangles corresponding to the isolated molecules A and B) approach one another. (b) The Pauli deformation consists of the two density gains (the rectangles with +) and a single electron loss (the rectangles with -). Let us assume that the surfaces of the rectangles are equal to the corresponding integrals of the charge distributions $-4S/(1 - S^2)ab$ in the contact region, $2S^2/(1 - S^2)a^2$ on the molecule A and $2S^2/(1 - S^2)b^2$ on the polymer B. This is why the electron density loss has the rectangle twice as large as any of the electron density gains. (c) A partial Pauli deformation: the density gain $2S^2/(1 - S^2)a^2$ for the molecule A has been added to the initial density distribution, similarly for the molecule B (the rectangles became larger, but *locally the corresponding increase is small*). (d) In order to represent the total Pauli deformation from the result obtained in point c, we subtracted the density distribution $4S/(1 - S^2)ab$ that is located in the contact region. As a result, *the Pauli deformation, when viewed locally, is large only in the contact region*.

The *only* thing that has been changed with respect to the hydrogen molecule is the increase of the number of electrons from two to four (we have kept unchanged the orbital exponents equal to 1, as well as the internuclear distance, which is equal to 4 a.u.). This change resulted in a qualitative difference in the Pauli deformation.

Two Large Molecules

For two helium atoms, the Pauli deformation means a decrease in the electron density in the region between the nuclei and the corresponding increase of the density on the nuclei. This looks dangerous! What if instead of the two helium atoms, we had two closed-shell long molecules A and B, which touch each other by their terminal parts? *Would the Pauli deformation be local, or would it extend over the whole system?* Would the distant parts of the molecules deform as much as the contact regions?

The answer may be deduced from Eq. (Y.4), see Fig. Y.2. The formula suggests that the electronic density change pertains to the whole system. When the formula has been derived,

we have concentrated on two helium atoms. However, *nothing* would change in the derivation if we had in mind a doubly occupied molecular orbital a that extends over the whole polymer A and a similar orbital b that extends over B. In such a case, Eq. (Y.4) would be identical. The formula says that the three deformation contributions cancel if we integrate them over the total space.⁸ The first deformation means a density deficiency (minus sign), and the two others mean the density gains (plus sign). The first of these contributions is certainly *located close to the contact region* of A and B. The two others (of the same magnitude) have the spatial form, such as a^2 and b^2 (i.e., extend over the whole polymer chains A and B!), but are scaled by the factor $2S^2/(1 - S^2)$. Since the contributions cancel in space (when integrated), this means that *the density gain extends over the polymeric molecules and, therefore, locally is very small; the larger the interacting molecules, the smaller the local change*. The situation, therefore, is similar to an inflatable balloon being pressed by your finger. We have a large deformation at the contact region that corresponds to $-\frac{4S}{1-S^2}ab$, but in fact the *whole* balloon deforms. Just because this deformation has to extend over the whole balloon, the local deformation on the other side of the toy is extremely small. Therefore, common sense has gotten a quantum mechanical explanation.⁹

This means that the Pauli deformation has a *local character*: it takes place almost exclusively in the region of the contact of both molecules.

Two Final Remarks

- The Pauli deformation treated as a spatial charge density distribution has a region with the positive charge (some electron density flowed off there) and the negative charge (where the electron density increased). The Pauli charge distribution participates in the Coulombic interactions within the system. If such an interaction were to be represented by a multipole-multipole interaction, then the Pauli deformation has no monopole, or charge. In general, the other multipole moments of the Pauli deformation are nonzero. In particular, the Pauli deformation multipoles resulting from the exchange interaction of the molecules A and B may interact with the electric multipoles of the molecule C, thus contributing to the three-body effect.
- If the two systems A and B approach each other in such a way that $S = 0$, then the Pauli deformation is zero. $S = 0$ might occur; e.g., if the two molecules would approach along the nodal surfaces of the frontier molecular orbitals.

⁸ But of course, at a given point they do not cancel in general.

⁹ This development is good for both of them.