Y. PAULI DEFORMATION

Two molecules, when non-interacting 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 interacting, any product-like function represents only an approximation, sometimes a very poor approximation,[1] 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 fulfil this. More exactly, the approximate wave function has to belong to the irreducible representation of the symmetry group of the Hamiltonian (see Appendix C, p. 903), 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 made antisymmetric. This causes 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 mutual pushing. The reason why two rubber balls 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 the difference between two functions: any deviation gives a contribution to the measure. We would like to know, how the electronic density has changed, where the electrons flow from, and where they go to. The electron density ρ (a function of position in space) is defined as the sum of densities ρ_i of the particular electrons:

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

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

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[1]For example, when the intermolecular distance is short, the molecules push each other and deform (maybe strongly), and the product-like function is certainly inadequate.

where $d\tau = d\tau_1 d\tau_2 \cdots d\tau_N$, and therefore the integration goes over the coordinates (space and spin) of all the electrons except electron i. In addition, there is also a summation over the spin coordinate of electron "i", simply because we are not interested in its value. As seen, the integral of $\rho(x, y, z)$ over x, y, z is equal to N, therefore $\rho(x, y, z)$ represents an electron cloud carrying N electrons, as defined in eq. (11.1) on p. 569. We make the two molecules approach 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 to ensure the proper symmetry of the wave function (the system is therefore 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 two hydrogen atoms approach and then two helium atoms.

H_2 case

In the case of two hydrogen atoms[2]

$$\varphi^{(0)} = 1s_a(1)\alpha(1)1s_b(2)\beta(2) \equiv a(1)\alpha(1)b(2)\beta(2),$$

where we have used the abbreviation $1s_a(1) \equiv a$ and $1s_b(1) \equiv b$. After inserting $\psi = \varphi^{(0)}$ into (Y.1), integration over space and summation over spin coordinates gives

$$\rho^{(0)} = \rho_1(x, y, z) + \rho_2(x, y, z),$$

where

$$\rho_1(x, y, z) = \sum_{\sigma_1 = -\frac{1}{2}}^{+\frac{1}{2}} \int \frac{d\tau}{d\tau_1} \left| a(1)\alpha(1)b(2)\beta(2) \right|^2$$

$$= \sum_{\sigma_1 = -\frac{1}{2}}^{+\frac{1}{2}} \int d\tau_2 \left| a(1)\alpha(1)b(2)\beta(2) \right|^2 = a^2.$$

Similarly,

$$\rho_2(x, y, z) = \sum_{\sigma_2 = -\frac{1}{2}}^{+\frac{1}{2}} \int \frac{d\tau}{d\tau_2} \left| a(1)\alpha(1)b(2)\beta(2) \right|^2$$

$$= \sum_{\sigma_2 = -\frac{1}{2}}^{+\frac{1}{2}} \int d\tau_1 \left| a(1)\alpha(1)b(2)\beta(2) \right|^2 = b^2.$$

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

Thus finally $\rho^{(0)} = a^2 + b^2$. This density is normalized to 2 – as it has to be, because the electron cloud $\rho(x, y, z)$ carries two electrons. Now, let us do the same for the wave function $\psi^{(0)} = N\hat{\mathcal{A}}\varphi^{(0)}$, where $\hat{\mathcal{A}}$ stands for the idempotent projection operator (13.23), and the normalization constant $N = \frac{2}{\sqrt{1+S^2}}$ with $S = (a|b)$, all quantities described in Chapter 13 on the symmetry adapted perturbation theory:

$$\rho(x, y, z) = \rho_1(x, y, z) + \rho_2(x, y, z),$$

$$\rho_1(x, y, z) = \sum_{\sigma_1 = \pm\frac{1}{2}} \int d\tau_2 \left|\psi^{(0)}\right|^2$$

$$= N^2 \frac{1}{8} \int dV_2 \left[a(1)b(2) + a(2)b(1)\right]^2 \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]^2$$

$$= N^2 \frac{1}{8} \int dV_2 \left[a(1)b(2) + a(2)b(1)\right]^2$$

$$= N^2 \frac{1}{8}\left(a^2 + b^2 + 2abS\right)$$

$$= \frac{1}{2(1 + S^2)}\left(a^2 + b^2 + 2abS\right),$$

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

As seen, the density $\rho_1(x, y, z)$ is normalized to 1 – this is what we 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 electrons[3] 1 and 2. Therefore, the *change* in the electron density due to the proper symmetry projection (including the Pauli exclusion principle) is:

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

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 $a^2S^2/(1 + S^2)$ flows from atom a, a similar thing happens to atom b, where the electronic density decreases by $b^2S^2/(1 + S^2)$. 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 middle of the bond, and of course, the integral of $\rho - \rho^{(0)}$ is equal to zero (Fig. Y.1.a).

Thus,

> in the hydrogen molecule the Pauli exclusion principle caused the two atoms to stick together (the two electrons increase their probability to be in the region between the two nuclei).
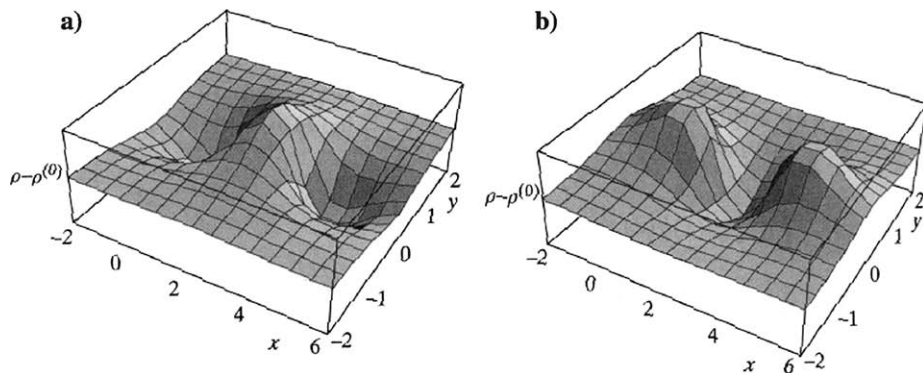
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[3]This was not the case for $\varphi^{(0)}$.

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, the other has coordinates $(0, R, 0)$, with $R = 4$ a.u. For this distance the overlap integral (see Appendix R, p. 1009) $S = (1 + R + \frac{R^2}{3}) \exp(-R)$ is 0.189. As we can see, the electron 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. The visualization of $\rho - \rho^{(0)}$ reveals a *completely different pattern*. This time the electron density has been removed from the bond region and increased in the region of the nuclei.

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

He$_2$ case

Let us see what happens if we make similar calculations for two helium atoms. To compare the future result with the H$_2$ 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 bit more tedious, because four-electron wave functions are more complicated than two-electron functions. For example, the function $\varphi^{(0)}$ this time is the product of the two Slater determinants – one for atom a, the other for atom b:

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[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 centred 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 besides the above mentioned electron–nucleus interactions (manifested by the 1s orbitals) we obtain an interesting effect: when one electron is on nucleus a, the second electron runs to nucleus b. It looks as if they have repelled each other. This is, however, at the level of the *mathematical formula of the function* ("function design"), as if the function has already been quite well designed for the future, and takes into account the physical interactions.

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

$$= N'a(1)a(2)b(3)b(4)\left[\frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2) - \alpha(2)\beta(1)\big]\right]$$

$$\times \left[\frac{1}{\sqrt{2}}\big[\alpha(3)\beta(4) - \alpha(4)\beta(3)\big]\right], \tag{Y.3}$$

where the normalization constant $N' = 1$ (easy to verify: just square the function and integrate). We obtain directly from the definition[5]

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

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

Now let us focus on $\psi^{(0)}$. Please 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 determinant[6] in such a way as to allow for the exchange of electrons between the subsystems:

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

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

where, according to (13.23), $\hat{A}$ stands for the idempotent antisymmetrization operator, and $\frac{1}{2}(1+I)$ represents an idempotent symmetrization operator acting on the nuclear coordinates. The last equality follows from the fact that this particular

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[5]This may also be calculated in your head (note that the spin functions in the square brackets are normalized).

[6]The Slater determinant containing linearly independent spinorbitals *guarantees* the antisymmetry.

Slater determinant is already symmetric with respect to the exchange of nuclei,[7] which is equivalent to $a \leftrightarrow b$.

Any determinant is invariant with respect to the addition of any linear combination of rows (columns) to a given row (column). For reasons that will become clear soon, let us make 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 subtract the first row from the third one. Then let us perform a similar series of operations on rows 2 and 4 (instead of 1 and 3), and at the end let us multiply rows 1 and 3 by $\frac{1}{\sqrt{2(1+S)}}$, and rows 2 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 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 spinorbitals 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. 1015):

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

Now let us calculate the Pauli deformation

$$\rho - \rho^{(0)} = \frac{a^2 + b^2 + 2ab}{1+S} + \frac{a^2 + b^2 - 2ab}{1-S} - 2(a^2 + b^2)$$

$$= -\frac{4S}{1-S^2}ab + \frac{2S^2}{1-S^2}a^2 + \frac{2S^2}{1-S^2}b^2. \tag{Y.4}$$

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

> 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 rubber balls squeezed together (Pauli deformation).

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[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, therefore the two exchanges leave the determinant invariant.
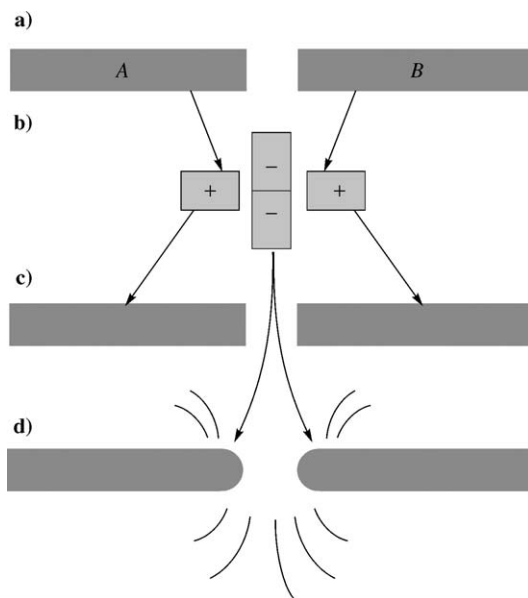
Fig. Y.2. The locality of the Pauli deformation (diagram). (a) Two polymeric chains A and B (with electronic densities in the form of the elongated rectangles corresponding to the isolated molecules A and B) approach one another (b) the Pauli deformation consists of the two density gains (the rectangles 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 molecule A and $2S^2/(1 - S^2)b^2$ on polymer B – this is why the electron density loss has a 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 molecule A has been added to the initial density distribution, and similarly for 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 at point c we subtracted the density distribution $4S/(1 - S^2)ab$ which 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 in the number of electrons from two to four (we have kept the orbital exponents equal to 1 and the internuclear distance equal to 4 a.u. unchanged). This change results in a qualitative difference in the Pauli deformation.

Two large molecules

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

The answer may be deduced from eq. (Y.4). The formula suggests that the electronic density change pertains to the whole system. When the formula was derived, we 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 the formula (Y.4) would be identical. The formula says: the three deformation contributions cancel if we integrate them over the total space.[8] The first deformation means a density deficiency (minus sign), the other two mean 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 a spatial form such that 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 is therefore similar to an inflatable balloon pressed with your finger. We have a large deformation at the contact region , what corresponds to $-\frac{4S}{1-S^2}ab$, but in fact the *whole* balloon deforms. 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 arrived at a quantum mechanical explanation.[9]

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

Two final remarks

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

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

[9]Good for both of them.