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Mathematical Foundations

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In physics and chemistry it is not possible to develop any useful model of matter without a basic knowledge of some elementary mathematics. This involves use of some elements of linear algebra, such as the solution of algebraic equations (at least quadratic), the solution of systems of linear equations, and a few elements on matrices and determinants.

1.1 MATRICES AND SYSTEMS OF LINEAR EQUATIONS

We start from matrices, limiting ourselves to the case of a *square matrix* of order two, namely a matrix involving two rows and two columns. Let us denote this matrix by the boldface capital letter **A**:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \quad (1.1)$$

where A_{ij} is a number called the *ijth element* of matrix \mathbf{A} . The elements A_{ii} ($j = i$) are called diagonal elements. We are interested mostly in *symmetric* matrices, for which $A_{21} = A_{12}$. If $A_{21} = A_{12} = 0$, the matrix is *diagonal*. Properties of a square matrix \mathbf{A} are its *trace* ($\text{tr } \mathbf{A} = A_{11} + A_{22}$), the sum of its diagonal elements, and its *determinant*, denoted by $|\mathbf{A}| = \det \mathbf{A}$, a number that can be evaluated from its elements by the rule:

$$|\mathbf{A}| = A_{11}A_{22} - A_{12}A_{21} \quad (1.2)$$

Two 2×2 matrices can be multiplied rows by columns by the rule:

$$\mathbf{AB} = \mathbf{C} \quad (1.3)$$

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} \quad (1.4)$$

the elements of the product matrix \mathbf{C} being:

$$\begin{cases} C_{11} = A_{11}B_{11} + A_{12}B_{21}, & C_{12} = A_{11}B_{12} + A_{12}B_{22}, \\ C_{21} = A_{21}B_{11} + A_{22}B_{21}, & C_{22} = A_{21}B_{12} + A_{22}B_{22}. \end{cases} \quad (1.5)$$

So, we are led to the *matrix multiplication rule*:

$$C_{ij} = \sum_{\kappa=1}^2 A_{i\kappa}B_{\kappa j} \quad (1.6)$$

If matrix \mathbf{B} is a simple number a , Equation (1.6) shows that *all* elements of matrix \mathbf{A} must be multiplied by this number. Instead, for $a|\mathbf{A}|$, we have from Equation (1.2):

$$a|\mathbf{A}| = a(A_{11}A_{22} - A_{12}A_{21}) = \begin{vmatrix} aA_{11} & aA_{12} \\ A_{21} & A_{22} \end{vmatrix} = \begin{vmatrix} aA_{11} & A_{12} \\ aA_{21} & A_{22} \end{vmatrix}, \quad (1.7)$$

so that, multiplying a determinant by a number is equivalent to multiplying just *one* row (or *one* column) by that number.

We can have also *rectangular* matrices, where the number of rows is different from the number of columns. Particularly important is the 2×1 *column vector* \mathbf{c} :

$$\mathbf{c} = \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (1.8)$$

or the 1×2 *row vector* $\tilde{\mathbf{c}}$:

$$\tilde{\mathbf{c}} = (c_{11} \ c_{12}) = (c_1 \ c_2) \quad (1.9)$$

where the tilde \sim means interchanging columns by rows or vice versa (the *transposed* matrix).

The linear *inhomogeneous* system:

$$\begin{cases} A_{11}c_1 + A_{12}c_2 = b_1 \\ A_{21}c_1 + A_{22}c_2 = b_2 \end{cases} \quad (1.10)$$

can be easily rewritten in matrix form using matrix multiplication rule (1.3) as:

$$\mathbf{A}\mathbf{c} = \mathbf{b} \quad (1.11)$$

where \mathbf{c} and \mathbf{b} are 2×1 column vectors.

Equation (1.10) is a system of two algebraic equations linear in the *unknowns* c_1 and c_2 , the elements of matrix \mathbf{A} being the *coefficients* of the linear combination. Particular importance has the case where \mathbf{b} is proportional to \mathbf{c} through a number λ :

$$\mathbf{A}\mathbf{c} = \lambda\mathbf{c} \quad (1.12)$$

which is known as the *eigenvalue equation* for matrix \mathbf{A} . λ is called an *eigenvalue* and \mathbf{c} an *eigenvector* of the square matrix \mathbf{A} . Equation (1.12) is equally well written as the *homogeneous* system:

$$(\mathbf{A} - \lambda\mathbf{1})\mathbf{c} = \mathbf{0} \quad (1.13)$$

where $\mathbf{1}$ is the 2×2 diagonal matrix having 1 along the diagonal, called the *identity* matrix, and $\mathbf{0}$ is the zero vector matrix, a 2×1 column of zeros. Written explicitly, the homogeneous system (Equation 1.13) is:

$$\begin{cases} (A_{11} - \lambda)c_1 + A_{12}c_2 = 0 \\ A_{21}c_1 + (A_{22} - \lambda)c_2 = 0 \end{cases} \quad (1.14)$$

Elementary algebra then says that the system of equations (1.14) has acceptable solutions if and only if the determinant of the coefficients vanishes, namely if:

$$|\mathbf{A} - \lambda\mathbf{1}| = \begin{vmatrix} A_{11} - \lambda & A_{12} \\ A_{21} & A_{22} - \lambda \end{vmatrix} = 0 \quad (1.15)$$

Equation (1.15) is known as the *secular equation* for matrix \mathbf{A} . If we expand the determinant according to the rule of Equation (1.2), we obtain

for a symmetric matrix \mathbf{A} :

$$(A_{11}-\lambda)(A_{22}-\lambda)-A_{12}^2 = 0 \quad (1.16)$$

giving the *quadratic* equation in λ :

$$\lambda^2-(A_{11}+A_{22})\lambda+A_{11}A_{22}-A_{12}^2 = 0 \quad (1.17)$$

which has the two *real*¹ solutions (the eigenvalues, the roots of the equation):

$$\begin{cases} \lambda_1 = \frac{A_{11}+A_{22}}{2} + \frac{\Delta}{2} \\ \lambda_2 = \frac{A_{11}+A_{22}}{2} - \frac{\Delta}{2} \end{cases} \quad (1.18)$$

where Δ is the *positive* quantity:

$$\Delta = \left[(A_{22}-A_{11})^2 + 4A_{12}^2 \right]^{1/2} > 0 \quad (1.19)$$

Inserting each root in turn in the homogeneous system (Equation 1.14), we obtain the corresponding solutions (the eigenvectors, our unknowns):

$$\begin{cases} c_{11} = \left(\frac{\Delta + (A_{22}-A_{11})}{2\Delta} \right)^{1/2}, & c_{21} = \left(\frac{\Delta - (A_{22}-A_{11})}{2\Delta} \right)^{1/2} \\ c_{12} = -\left(\frac{\Delta - (A_{22}-A_{11})}{2\Delta} \right)^{1/2}, & c_{22} = \left(\frac{\Delta + (A_{22}-A_{11})}{2\Delta} \right)^{1/2} \end{cases} \quad (1.20)$$

where the second index (a column index, shown in bold type in Equations 1.20) specifies the eigenvalue to which the eigenvector refers. All such results can be collected in the 2×2 square matrices:

$$\mathbf{A} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \quad \mathbf{C} = (\mathbf{c}_1 \quad \mathbf{c}_2) = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \quad (1.21)$$

the first being the diagonal matrix of the eigenvalues (the *roots* of our secular equation 1.17), the second the row matrix of the eigenvectors (the *unknowns* of the homogeneous system 1.14). Matrix multiplication rule shows that:

$$\tilde{\mathbf{C}}\mathbf{A}\mathbf{C} = \mathbf{A}, \quad \tilde{\mathbf{C}}\mathbf{C} = \mathbf{C}\tilde{\mathbf{C}} = \mathbf{1} \quad (1.22)$$

¹This is a mathematical property of real symmetric matrices.

We usually say that the first of Equations (1.22) expresses the *diagonalization* of the symmetric matrix \mathbf{A} through a transformation with the complete matrix of its eigenvectors, while the second equations express the *normalization* of the coefficients (i.e., the resulting vectors are chosen to have modulus 1).²

Equations (18–20) simplify noticeably in the case $A_{22} = A_{11} = \alpha$. Then, putting $A_{12} = A_{21} = \beta$, we obtain:

$$\begin{cases} \lambda_1 = \alpha + \beta, & \lambda_2 = \alpha - \beta \\ \mathbf{c}_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}, & \mathbf{c}_2 = \begin{pmatrix} -1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \end{cases} \quad (1.23)$$

Occasionally, we shall need to solve the so called *pseudosecular equation* for the symmetric matrix \mathbf{A} arising from the *pseudoeigenvalue equation*:

$$\mathbf{Ac} = \lambda \mathbf{Sc} \Rightarrow |\mathbf{A} - \lambda \mathbf{S}| = \begin{vmatrix} A_{11} - \lambda & A_{12} - \lambda S \\ A_{21} - \lambda S & A_{22} - \lambda \end{vmatrix} = 0 \quad (1.24)$$

where \mathbf{S} is the *overlap matrix*:

$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \quad (1.25)$$

Solution of Equation (1.24) then gives:

$$\begin{cases} \lambda_1 = \frac{A_{11} + A_{22} - 2A_{12}S}{2(1-S^2)} - \frac{\Delta}{2(1-S^2)} \\ \lambda_2 = \frac{A_{11} + A_{22} - 2A_{12}S}{2(1-S^2)} + \frac{\Delta}{2(1-S^2)} \end{cases} \quad (1.26)$$

$$\Delta = \left[(A_{22} - A_{11})^2 + 4(A_{12} - A_{11}S)(A_{12} - A_{22}S) \right]^{1/2} > 0 \quad (1.27)$$

The eigenvectors corresponding to the roots (Equations 1.26) are rather complicated (Magnasco, 2007), so we shall content ourselves here by giving only the results for $A_{22} = A_{11} = \alpha$ and $A_{21} = A_{12} = \beta$:

²The length of the vectors. A matrix satisfying the second of Equations (1.22) is said to be an *orthogonal* matrix.

$$\begin{cases} \lambda_1 = \frac{\alpha + \beta}{1 + S}, & \mathbf{c}_{11} = (2 + 2S)^{-1/2}, & \mathbf{c}_{21} = (2 + 2S)^{-1/2} \\ \lambda_2 = \frac{\alpha - \beta}{1 - S}, & \mathbf{c}_{12} = -(2 - 2S)^{-1/2}, & \mathbf{c}_{22} = (2 - 2S)^{-1/2} \end{cases} \quad (1.28)$$

under these assumptions, these are the elements of the square matrices Λ and \mathbf{C} (Equations 1.21). Matrix multiplication shows that these matrices satisfy the generalization of Equations (1.22):

$$\tilde{\mathbf{C}}\mathbf{A}\mathbf{C} = \Lambda, \quad \tilde{\mathbf{C}}\mathbf{S}\mathbf{C} = \mathbf{C}\tilde{\mathbf{S}} = \mathbf{1} \quad (1.29)$$

so that matrices \mathbf{A} and \mathbf{S} are simultaneously diagonalized under the transformation with the orthogonal matrix \mathbf{C} .

All previous results can be extended to square symmetric matrices of order N , in which case the solution of the corresponding secular equations must be found by numerical methods, unless use can be made of symmetry arguments.

1.2 PROPERTIES OF EIGENVALUES AND EIGENVECTORS

It is of interest to stress some properties hidden in the eigenvalues $(\lambda_1 \ \lambda_2)$ and eigenvectors $\begin{pmatrix} \mathbf{c}_1 \\ \mathbf{c}_2 \end{pmatrix}$, (Equations 1.23), of the symmetric matrix \mathbf{A} of order 2 with $A_{22} = A_{11} = \alpha$ and $A_{21} = A_{12} = \beta$.

In fact, Equation (1.17) can be written:

$$(\lambda_1 - \lambda)(\lambda_2 - \lambda) = \lambda_1\lambda_2 - (\lambda_1 + \lambda_2)\lambda + \lambda^2 = 0 \quad (1.30)$$

so that:

$$\lambda_1\lambda_2 = A_{11}A_{22} - A_{12}^2 = \alpha^2 - \beta^2 = \det \mathbf{A} \quad (1.31)$$

$$\lambda_1 + \lambda_2 = A_{11} + A_{22} = 2\alpha = \text{tr } \mathbf{A} \quad (1.32)$$

In Equation (1.17), therefore, the coefficient of λ^0 , the determinant of matrix \mathbf{A} , is expressible as the *product* of the two eigenvalues; the coefficient of λ , the trace of matrix \mathbf{A} , is expressible as the *sum* of the two eigenvalues.

From the eigenvectors of Equations (1.23) we can construct the two square symmetric matrices of order 2:

$$\mathbf{P}_1 = \mathbf{c}_1 \tilde{\mathbf{c}}_1 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \quad (1.33)$$

$$\mathbf{P}_2 = \mathbf{c}_2 \tilde{\mathbf{c}}_2 = \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \quad (1.34)$$

The two matrices \mathbf{P}_1 and \mathbf{P}_2 do not admit inverse (the determinants of both are zero) and have the properties:

$$\mathbf{P}_1^2 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \mathbf{P}_1 \quad (1.35)$$

$$\mathbf{P}_2^2 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \mathbf{P}_2 \quad (1.36)$$

$$\mathbf{P}_1 \mathbf{P}_2 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} = \mathbf{0} \quad (1.37)$$

$$\mathbf{P}_2 \mathbf{P}_1 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} = \mathbf{0} \quad (1.38)$$

$$\mathbf{P}_1 + \mathbf{P}_2 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{1} \quad (1.39)$$

In mathematics, matrices having these properties (idempotency, mutual exclusivity, completeness³) are called *projectors*. In fact, acting on matrix \mathbf{C} of Equation (1.21)

$$\mathbf{P}_1 \mathbf{C} = \mathbf{P}_1 \mathbf{c}_1 + \mathbf{P}_1 \mathbf{c}_2 = \mathbf{c}_1 \quad (1.40)$$

since:

$$\mathbf{P}_1 \mathbf{c}_1 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \frac{1}{\sqrt{2}} + \frac{1}{2} \frac{1}{\sqrt{2}} \\ \frac{1}{2} \frac{1}{\sqrt{2}} + \frac{1}{2} \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \mathbf{c}_1 \quad (1.41)$$

$$\mathbf{P}_1 \mathbf{c}_2 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} \frac{1}{\sqrt{2}} + \frac{1}{2} \frac{1}{\sqrt{2}} \\ -\frac{1}{2} \frac{1}{\sqrt{2}} + \frac{1}{2} \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = \mathbf{0} \quad (1.42)$$

so that, acting on the complete matrix \mathbf{C} of the eigenvectors, \mathbf{P}_1 selects its eigenvector \mathbf{c}_1 , at the same time annihilating \mathbf{c}_2 . In the same way:

$$\mathbf{P}_2 \mathbf{C} = \mathbf{P}_2 \mathbf{c}_1 + \mathbf{P}_2 \mathbf{c}_2 = \mathbf{c}_2 \quad (1.43)$$

This makes evident the projector properties of matrices \mathbf{P}_1 and \mathbf{P}_2 .

Furthermore, matrices \mathbf{P}_1 and \mathbf{P}_2 allow one to write matrix \mathbf{A} in the so-called *canonical* form:

$$\mathbf{A} = \lambda_1 \mathbf{P}_1 + \lambda_2 \mathbf{P}_2 \quad (1.44)$$

³Often referred to as resolution of the identity.

Equation (1.44) is easily verified:

$$\left\{ \begin{aligned} \lambda_1 \mathbf{P}_1 + \lambda_2 \mathbf{P}_2 &= (\alpha + \beta) \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} + (\alpha - \beta) \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \\ &= \begin{pmatrix} \frac{\alpha + \beta}{2} + \frac{\alpha - \beta}{2} & \frac{\alpha + \beta}{2} - \frac{\alpha - \beta}{2} \\ \frac{\alpha + \beta}{2} - \frac{\alpha - \beta}{2} & \frac{\alpha + \beta}{2} + \frac{\alpha - \beta}{2} \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} = \mathbf{A} \end{aligned} \right. \quad (1.45)$$

The same holds true for any analytical function⁴ F of matrix \mathbf{A} :

$$F(\mathbf{A}) = F(\lambda_1)\mathbf{P}_1 + F(\lambda_2)\mathbf{P}_2 \quad (1.46)$$

Therefore, it is easy to calculate, say, the inverse or the square root of matrix \mathbf{A} . For instance, we obtain for the *inverse* matrix ($F = {}^{-1}$):

$$\left\{ \begin{aligned} \lambda_1^{-1} \mathbf{P}_1 + \lambda_2^{-1} \mathbf{P}_2 &= \begin{pmatrix} \frac{1}{2(\alpha + \beta)} & \frac{1}{2(\alpha + \beta)} \\ \frac{1}{2(\alpha + \beta)} & \frac{1}{2(\alpha + \beta)} \end{pmatrix} + \begin{pmatrix} \frac{1}{2(\alpha - \beta)} & -\frac{1}{2(\alpha - \beta)} \\ -\frac{1}{2(\alpha - \beta)} & \frac{1}{2(\alpha - \beta)} \end{pmatrix} \\ &= \frac{1}{2(\alpha^2 - \beta^2)} \begin{pmatrix} (\alpha - \beta) + (\alpha + \beta) & (\alpha - \beta) - (\alpha + \beta) \\ (\alpha - \beta) - (\alpha + \beta) & (\alpha - \beta) + (\alpha + \beta) \end{pmatrix} = \frac{1}{2(\alpha^2 - \beta^2)} \begin{pmatrix} 2\alpha & -2\beta \\ -2\beta & 2\alpha \end{pmatrix} \\ &= \frac{1}{\alpha^2 - \beta^2} \begin{pmatrix} \alpha & -\beta \\ -\beta & \alpha \end{pmatrix} = \mathbf{A}^{-1} \end{aligned} \right. \quad (1.47)$$

and we obtain the usual result for the inverse matrix ($\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{1}$).

In the same way, provided $\sqrt{\lambda_1}$ and $\sqrt{\lambda_2}$ are positive, we can calculate the *square root* of matrix \mathbf{A} ($F = \sqrt{}$):

$$\left\{ \begin{aligned} \sqrt{\mathbf{A}} &= \sqrt{\alpha + \beta} \mathbf{P}_1 + \sqrt{\alpha - \beta} \mathbf{P}_2 \\ &= \frac{1}{2} \begin{pmatrix} \sqrt{\alpha + \beta} + \sqrt{\alpha - \beta} & \sqrt{\alpha + \beta} - \sqrt{\alpha - \beta} \\ \sqrt{\alpha + \beta} - \sqrt{\alpha - \beta} & \sqrt{\alpha + \beta} + \sqrt{\alpha - \beta} \end{pmatrix} = \begin{pmatrix} \frac{A+B}{2} & \frac{A-B}{2} \\ \frac{A-B}{2} & \frac{A+B}{2} \end{pmatrix} \end{aligned} \right. \quad (1.48)$$

⁴Any function expressible as a power series, e.g. inverse, square root, exponential.

where we have put:

$$A = \sqrt{\alpha + \beta}, \quad B = \sqrt{\alpha - \beta} \quad (1.49)$$

Then, we can easily check that:

$$\left\{ \begin{aligned} \sqrt{\mathbf{A}}\sqrt{\mathbf{A}} &= \frac{1}{4} \begin{pmatrix} A+B & A-B \\ A-B & A+B \end{pmatrix} \begin{pmatrix} A+B & A-B \\ A-B & A+B \end{pmatrix} \\ &= \frac{1}{4} \begin{pmatrix} (A+B)^2 + (A-B)^2 & 2(A^2 - B^2) \\ 2(A^2 - B^2) & (A-B)^2 + (A+B)^2 \end{pmatrix} \\ &= \frac{1}{4} \begin{pmatrix} 2(A^2 + B^2) & 2(A^2 - B^2) \\ 2(A^2 - B^2) & 2(A^2 + B^2) \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 4\alpha & 4\beta \\ 4\beta & 4\alpha \end{pmatrix} = \mathbf{A} \end{aligned} \right. \quad (1.50)$$

as it must be. These examples show how far we can go when eigenvalues and eigenvectors of a symmetric matrix are known.

1.3 VARIATIONAL APPROXIMATIONS

For our description of atoms and molecules, we rely on the *orbital model*, where atoms or molecules are described by one or more point-like positively charged nuclei surrounded by a cloud of negatively charged electrons, whose density is distributed in space in terms of atomic orbitals (one-centre, AOs) or molecular orbitals (multicentre, MOs) $\psi(\mathbf{r})$, one-electron wavefunctions, such that

$$|\psi(\mathbf{r})|^2 d\mathbf{r} \quad (1.51)$$

gives the probability of finding at $d\mathbf{r}$ an electron in state $\psi(\mathbf{r})$, provided $\psi(\mathbf{r})$ satisfies the *normalization* condition:

$$\int d\mathbf{r} |\psi(\mathbf{r})|^2 = 1 \quad (1.52)$$

the integration being extended over all space. The AOs are functions of the space point \mathbf{r} in the three spherical coordinates (r, θ, φ) that depend on the three quantum numbers n, l, m and have radial and angular dependence. As well known, they are classified as $1s, 2s, 2p, 3s, 3p, 3d$, etc. and we shall

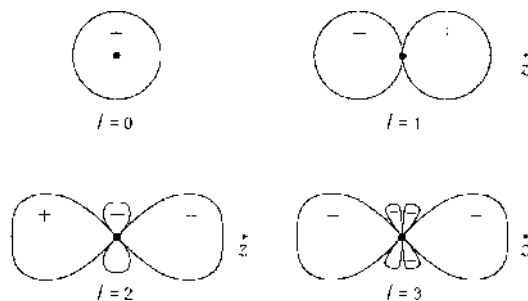


Figure 1.1 Polar diagrams of the angular part of s , p , d , and f AOs with $m=0$. Reprinted from Magnasco, V., *Methods of Molecular Quantum Mechanics: An Introduction to Electronic Molecular Structure*. Copyright (2009) with permission from John Wiley and Sons

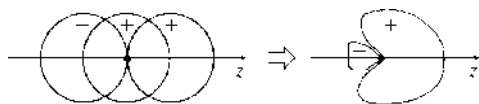


Figure 1.2 Schematic drawing of the formation of an sp hybrid AO

assume that they are real *regular*⁵ functions showing an exponential (Slater-type, STO) or gaussian (GTO) radial decay. Figure 1.1 shows schematically the polar diagrams of the angular parts of s , p , d , and f AOs with $l = 0, 1, 2, 3$, respectively, and $m = 0$.

Hybrid orbitals are AOs mixed on the same centre (e.g. s and p). Figure 1.2 sketches the formation of an sp hybrid directed along the z axis (right of the figure) from the mixing of a spherical $2s$ orbital with a $2p_z$ orbital (left of the figure). Because its form is nonsymmetric with respect to the nucleus on which it is centred, the hybrid AO acquires an intrinsic dipole moment, called by Coulson (1961) the *atomic dipole*, which is very important in the theoretical interpretation of the observed dipole moment in the molecule (see the case of first-row hydrides in Chapter 2). We are not interested in further details about AOs here, but more can be learned elsewhere (Magnasco, 2007, 2009a).

The AOs are obtained by solving some kind of differential Schrödinger-type eigenvalue equation, which for a single electron can be written:

$$\hat{H}\psi = \varepsilon\psi \quad (1.53)$$

⁵A *regular* function is a mathematical function satisfying the three conditions of being: (i) single-valued; (ii) continuous with its first derivatives; and (iii) quadratically integrable, i.e. vanishing at infinity.

where $\hat{H} = \hat{T} + V$ is the total (kinetic + potential) energy or *Hamiltonian* operator⁶, ψ a wavefunction (the *eigenfunction* of Equation 1.53), and ε (the *eigenvalue*) an orbital energy. In our model, \hat{H} will be replaced by a symbol H , where we suppress the caret characterizing the operator.

Since equations as (1.53) are difficult to solve exactly, practically all results in the applications of quantum mechanics to chemistry rely on a general method of approximation due to Rayleigh and known as the *variational method* (Magnasco, 2007, 2009a), which we summarize briefly in the following.

Let φ be a normalized⁷ regular *trial* (or *variational*) function. We define the Rayleigh ratio as the functional:⁸

$$\varepsilon[\varphi] = \frac{\int dx \varphi^*(x) H \varphi(x)}{\int dx \varphi^*(x) \varphi(x)} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \quad (1.54)$$

where x are the electronic coordinates, $\varphi^*(x)$ the function complex conjugate to $\varphi(x)$, and H the Hamiltonian of the system. In the last term on the right-hand side of the equation we have introduced the so-called Dirac notation for the integrals. Then, the Rayleigh variational principle states that, if E_0 is the *true* energy of the ground state (the state of lowest energy):

$$\varepsilon[\varphi] \geq E_0 \quad (1.55)$$

In other words, any approximate energy must lie *above* the true energy of the ground state, giving an *upper bound* to the electronic energy. Variational approximations to energy and wavefunction can then be simply worked out by introducing some *variational parameters* $\{c\}$ in the trial function φ , then evaluating the integrals in the functional (1.54), in order to obtain an ordinary function of the parameters $\{c\}$ that can be *minimized* against these parameters. Therefore, for a single parameter c :

$$\varepsilon[\varphi] = \frac{\int dx \varphi^*(x, c) H \varphi(x, c)}{\int dx \varphi^*(x, c) \varphi(x, c)} = \varepsilon(c) \Rightarrow \min \quad (1.56)$$

The necessary condition for the minimum of $\varepsilon(c)$ will be:

$$\frac{d\varepsilon}{dc} = 0 \Rightarrow c_{\min} \quad (1.57)$$

⁶An operator is a rule changing a regular function into another one, and is denoted by the caret sign ^.

⁷A function satisfying Equation (1.52).

⁸A function of function $\varphi(x)$.

an algebraic equation which must be solved for the *best* value of parameter c , giving in this way the best variational energy and wavefunction.

The most interesting application for our purposes is to construct MOs by the linear combination of atomic orbitals (LCAO) method, where the variable parameters are the coefficients of the linear combination of some basic orbitals $\{\chi\}$ ⁹ (Ritz method). It can be shown that, in this case, *the best orbitals are obtained by solving the eigenvalue equation for matrix H*:

$$\mathbf{H}\mathbf{c} = \varepsilon\mathbf{c} \Rightarrow (\mathbf{H} - \varepsilon\mathbf{1})\mathbf{c} = \mathbf{0} \quad (1.58)$$

where:

$$H_{ij} = \langle \chi_i | H | \chi_j \rangle, \quad S_{ij} = \langle \chi_i | \chi_j \rangle = \delta_{ij} \quad (1.59)$$

For molecules, all elements of matrix \mathbf{H} are negative numbers. The homogeneous system (Equation 1.58) has nontrivial solutions if and only if:

$$|\mathbf{H} - \varepsilon\mathbf{1}| = 0 \quad (1.60)$$

The solution of the secular equation (1.60) for our simple case of a 2×2 symmetric matrix \mathbf{H} (a basis of *two* AOs) yields as *best* values for the variational energy the *two* real roots (eigenvalues) ε_1 and ε_2 , that are usually written in ascending order, with the corresponding *two* eigenvectors \mathbf{c}_1 and \mathbf{c}_2 determining the *two* molecular orbitals φ_1 and φ_2 (Equations 18–20 with $\lambda = \varepsilon$, or the simpler Equations 1.23 when the diagonal elements are equal):

$$\begin{cases} \varepsilon_1 \leq \varepsilon_2 \\ \mathbf{c}_1, \mathbf{c}_2 \\ \varphi_1, \varphi_2 \end{cases} \quad (1.61)$$

$\varepsilon < 0$ means *bonding*, $\varepsilon > 0$ means *antibonding*, with a corresponding notation for the resulting MOs.

The same procedure can be applied to find approximations to the second-order energy E_2 of Section 4.2 of Chapter 4 in the context of the Hylleraas variational method (Magnasco, 2007, 2009a), as we shall illustrate in the simple case of two functions. We start from a convenient set of basis functions χ written as the (1×2) row vector:

$$\chi = (\chi_1 \quad \chi_2) \quad (1.62)$$

⁹Assumed normalized and orthogonal to each other, namely $\langle \chi_i | \chi_j \rangle = \delta_{ij}$, where δ is the Kronecker' symbol (=1 for $j = i$, = 0 for $j \neq i$).

possibly orthonormal in themselves but necessarily *orthogonal* to ψ_0 . We shall assume that:

$$\boldsymbol{\chi}^\dagger \boldsymbol{\chi} = \mathbf{1}, \quad \boldsymbol{\chi}^\dagger \psi_0 = 0 \quad (1.63)$$

If the $\boldsymbol{\chi}$ s are not orthogonal they must first be orthogonalized by the Schmidt method (Magnasco, 2007). Then, we construct the matrices:

$$\mathbf{M} = \boldsymbol{\chi}^\dagger (\hat{H}_0 - E_0) \boldsymbol{\chi} \quad (1.64)$$

the (2×2) Hermitian matrix of the *excitation energies*, and:

$$\boldsymbol{\mu} = \boldsymbol{\chi}^\dagger (\hat{H}_1 \psi_0) \quad (1.65)$$

the (2×1) column vector of the transition moments.

By expanding the first-order function ψ_1 in the *finite* set of the $\boldsymbol{\chi}$ s, we can write:

$$\psi_1 = \boldsymbol{\chi} \mathbf{C} = \sum_{\kappa=1}^2 \chi_\kappa C_\kappa \quad (1.66)$$

$$E_2 = \mathbf{C}^\dagger \mathbf{M} \mathbf{C} + \mathbf{C}^\dagger \boldsymbol{\mu} + \boldsymbol{\mu}^\dagger \mathbf{C} \quad (1.67)$$

which is minimum for:

$$\frac{\delta E_2}{\delta \mathbf{C}^\dagger} = \mathbf{M} \mathbf{C} + \boldsymbol{\mu} = \mathbf{0} \Rightarrow \mathbf{C}(\text{best}) = -\mathbf{M}^{-1} \boldsymbol{\mu} \quad (1.68)$$

giving as *best* variational approximation to the second-order energy E_2 :

$$E_2(\text{best}) = -\boldsymbol{\mu}^\dagger \mathbf{M}^{-1} \boldsymbol{\mu} \quad (1.69)$$

The symmetric matrix \mathbf{M} can be reduced to *diagonal* form by a unitary transformation¹⁰ \mathbf{U} among its basis functions $\boldsymbol{\chi}$:

$$\boldsymbol{\psi} = \boldsymbol{\chi} \mathbf{U}, \quad \mathbf{U}^\dagger \mathbf{M} \mathbf{U} = \boldsymbol{\varepsilon}, \quad \mathbf{U}^\dagger \boldsymbol{\mu} = \boldsymbol{\mu}_\psi \quad (1.70)$$

where $\boldsymbol{\varepsilon}$ is here the (2×2) diagonal matrix of the (positive) *excitation energies*:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \quad (1.71)$$

¹⁰A unitary matrix \mathbf{U} satisfies $\mathbf{U}^{-1} = \mathbf{U}^\dagger$, where \mathbf{U}^{-1} is the inverse and $\mathbf{U}^\dagger = (\tilde{\mathbf{U}})^\dagger$ the adjoint matrix (Magnasco, 2007). A matrix is said Hermitian if $\mathbf{U} = \mathbf{U}^\dagger$. For *real* elements, unitary and orthogonal matrices coincide, so that we can use either of them indistinctly.

The ψ s are called *pseudostates*, and give best E_2 in the form:

$$E_2(\text{best}) = -\boldsymbol{\mu}_\psi^\dagger \boldsymbol{\varepsilon}^{-1} \boldsymbol{\mu}_\psi = -\sum_{\kappa=1}^2 \frac{|\langle \psi_\kappa | \hat{H}_1 | \psi_0 \rangle|^2}{\varepsilon_\kappa} \quad (1.72)$$

which is known as *sum-over-pseudostates* expression. Equation (1.72) has the same form as the analogous expression that would arise from the discrete *eigenstates* of \hat{H}_0 , but with definitely better convergence properties, reducing the infinite summation to a sum of a *finite* number of terms, and avoiding the need of considering the contribution from the continuous part of the spectrum (Magnasco, 2007).

1.4 ATOMIC UNITS

To get rid of all fundamental physical constants in our mathematical formulae we shall introduce consistently a system of *atomic units* (au), by putting:

$$e = \hbar = m = 4\pi\varepsilon_0 = 1 \quad (1.73)$$

The basic atomic units are obtained from the SI values of the fundamental physical constants given in Table 1.1 (Mohr and Taylor, 2003).

The basic au of charge, length, energy and time are then expressed by:

$$\left\{ \begin{array}{ll} \text{Charge} & e = 1.602\,176 \times 10^{-19} \text{ C} \\ \text{Length, Bohr} & a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{me^2} = 5.291\,772 \times 10^{-11} \text{ m} \\ \text{Energy, Hartree} & E_b = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{a_0} = 4.359\,744 \times 10^{-18} \text{ J} \\ \text{Time} & \tau = \frac{\hbar}{E_b} = 2.418\,884 \times 10^{-17} \text{ s} \end{array} \right. \quad (1.74)$$

When the atomic unit of energy is referred to molar quantities, we have the different SI equivalents:

$$\left\{ \begin{array}{l} N_A E_b = 2625.499 \text{ kJ mol}^{-1} = 27.211\,38 \text{ eV mol}^{-1} \\ \quad = 219.474\,6 \times 10^3 \text{ cm}^{-1} \text{ mol}^{-1} = 315.774\,6 \times 10^3 \text{ K mol}^{-1} \end{array} \right. \quad (1.75)$$

Table 1.1 Fundamental physical constants

Physical quantity	Value in SI units
Elementary charge	$e = 1.602\,176 \times 10^{-19} \text{ C}$
Electron mass	$m = 9.109\,382 \times 10^{-31} \text{ kg}$
Reduced Planck's constant	$\hbar = 1.054\,572 \times 10^{-34} \text{ J s}$
Vacuum permittivity	$4\pi\epsilon_0 = 1.112\,650 \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Light velocity in vacuum	$c = 2.997\,925 \times 10^8 \text{ m s}^{-1}$
Avogadro number	$N_A = 6.022\,142 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k = 1.380\,650 \times 10^{-23} \text{ J K}^{-1}$

with the submultiples:

$$10^{-3}E_b = mE_b \quad [\text{milliHartree}] \quad (1.76)$$

$$10^{-6}E_b = \mu E_b \quad [\text{microHartree}] \quad (1.77)$$

etc. The milliHartree is the characteristic unit for the energy of the chemical bond, the microHartree is that for the energy of the Van der Waals bond. The hydrogen bond has an intermediate energy, corresponding to that of a weak chemical bond.

The basic au for dipole, quadrupole and octupole electric moments are given as:

$$\left\{ \begin{array}{l} \text{Dipole moment, } ea_0 \quad = 8.478 \times 10^{-30} \text{ C} \times \text{m} \\ \quad \quad \quad \quad \quad = 2.542 \times 10^{-18} \text{ esu} \times \text{cm} = 2.542 \text{ D} \\ \text{Quadrupole moment, } ea_0^2 \quad = 4.486 \times 10^{-40} \text{ C} \times \text{m}^2 \\ \quad \quad \quad \quad \quad = 1.345 \times 10^{-26} \text{ esu} \times \text{cm}^2 = 1.345 \text{ B} \\ \text{Octupole moment, } ea_0^3 \quad = 2.374 \times 10^{-50} \text{ C} \times \text{m}^3 \\ \quad \quad \quad \quad \quad = 7.117 \times 10^{-35} \text{ esu} \times \text{cm}^3 \end{array} \right. \quad (1.78)$$

In the expressions above, D is the Debye unit of electric dipole moment, and B the Buckingham unit for the electric quadrupole moment.

At the end of a calculation in atomic units, as we shall usually do, the actual SI values can be obtained by taking into account the SI equivalents (1.74) and (1.78). As an example, we give below the calculation of the SI equivalent of the Hartree unit to seven significant figures:

$$\left\{ \begin{aligned} E_b &= \frac{1}{4\pi\epsilon_0} \frac{e^2}{a_0} = \frac{me^4}{(4\pi\epsilon_0)^2 \hbar^2} \\ &= \frac{9.109\,382 \times 10^{-31} \times (1.602\,176 \times 10^{-19})^4}{(1.112\,650 \times 10^{-10})^2 \times (1.054\,571 \times 10^{-34})^2} \frac{\text{kg C}^4}{\text{C}^4 \text{m}^{-2} \text{J}^2 \text{s}^2} \\ &= 4.359\,744 \times 10^{-18} \text{ J.} \end{aligned} \right. \quad (1.79)$$

1.5 THE ELECTRON DISTRIBUTION IN MOLECULES

The one-electron spatial function $P(\mathbf{r})$ describing the distribution of the electrons (the *electron density*) in the doubly occupied MO $\phi(\mathbf{r})$:

$$\phi(\mathbf{r}) = \chi_A(\mathbf{r})c_A + \chi_B(\mathbf{r})c_B = \frac{\chi_A(\mathbf{r}) + \lambda\chi_B(\mathbf{r})}{\sqrt{1 + \lambda^2 + 2\lambda S}} \quad (1.80)$$

where $\lambda = c_B/c_A$ denotes here the *polarity parameter* of the bond orbital and $S = \langle \chi_A | \chi_B \rangle$ the *overlap* integral, is simply given by:

$$P(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) = 2\phi(\mathbf{r})\phi^*(\mathbf{r}) = 2|\phi(\mathbf{r})|^2 \quad (1.81)$$

the factor 2 comes from the equal contribution of electrons with either spin ($\alpha = \text{spin-up}$, $\beta = \text{spin-down}$).

The electron density can be further analysed in terms of elementary contributions from the AOs, giving the so-called *population analysis*,¹¹ which shows how the electrons are distributed between the different atomic orbitals in the molecule. We obtain from Equation (1.81):

$$P(\mathbf{r}) = q_A \chi_A^2(\mathbf{r}) + q_B \chi_B^2(\mathbf{r}) + q_{AB} \frac{\chi_A(\mathbf{r})\chi_B(\mathbf{r})}{S} + q_{BA} \frac{\chi_B(\mathbf{r})\chi_A(\mathbf{r})}{S} \quad (1.82)$$

where $\chi_A^2(\mathbf{r})$ and $\chi_B^2(\mathbf{r})$ are *atomic densities*, $\frac{\chi_A(\mathbf{r})\chi_B(\mathbf{r})}{S}$ and $\frac{\chi_B(\mathbf{r})\chi_A(\mathbf{r})}{S}$ are *overlap densities*, all normalized to 1, while the coefficients:

$$q_A = \frac{2}{1 + \lambda^2 + 2\lambda S}, \quad q_B = \frac{2\lambda^2}{1 + \lambda^2 + 2\lambda S} \quad (1.83)$$

¹¹The extension to N-electron LCAO-MO wave functions is due to Mulliken (1955).

are *atomic charges*, and:

$$q_{AB} = q_{BA} = \frac{2\lambda S}{1 + \lambda^2 + 2\lambda S} \quad (1.84)$$

overlap charges. The charges are normalized so that:

$$q_A + q_B + q_{AB} + q_{BA} = \frac{2 + 2\lambda^2 + 4\lambda S}{1 + \lambda^2 + 2\lambda S} = 2 \quad (1.85)$$

the total number of electrons in the bond orbital $\phi(\mathbf{r})$.

For a *homopolar bond*, $\lambda = 1$:

$$q_A = q_B = \frac{1}{1+S} \quad q_{AB} = q_{BA} = \frac{S}{1+S} \quad (1.86)$$

so that for $S > 0$, in the bond, the charge on the atoms is decreased, electrons being transferred to the region between nuclei to an extent described by q_{AB} and q_{BA} . This reduces internuclear repulsion and means *bonding*.

For a *heteropolar bond*, $\lambda \neq 1$, and we define *gross charges* on A and B as:

$$Q_A = q_A + q_{AB} = \frac{2 + 2\lambda S}{1 + \lambda^2 + 2\lambda S} \quad (1.87)$$

$$Q_B = q_B + q_{BA} = \frac{2\lambda^2 + 2\lambda S}{1 + \lambda^2 + 2\lambda S} \quad (1.88)$$

and *formal charges* on A and B as:

$$\delta_A = 1 - Q_A = \frac{\lambda^2 - 1}{1 + \lambda^2 + 2\lambda S} \quad (1.89)$$

$$\delta_B = 1 - Q_B = -\frac{\lambda^2 - 1}{1 + \lambda^2 + 2\lambda S} \quad (1.90)$$

If $\lambda > 1$, $\delta_A = \delta > 0$, $\delta_B = -\delta_A = -\delta < 0$, and we have the dipole $A^{+\delta}B^{-\delta}$ (e.g. the LiH molecule).

In our model, an essential role will be assigned to the *exchange-overlap densities* (Magnasco and McWeeny, 1991; Magnasco, 2007, 2008, 2009a):

$$\chi_A(\mathbf{r})\chi_B(\mathbf{r}) - S\chi_A^2(\mathbf{r}), \quad \chi_B(\mathbf{r})\chi_A(\mathbf{r}) - S\chi_B^2(\mathbf{r}) \quad (1.91)$$

which have the properties:

$$\int d\mathbf{r}[\chi_A(\mathbf{r})\chi_B(\mathbf{r}) - S\chi_A^2(\mathbf{r})] = 0, \quad \int d\mathbf{r}[\chi_B(\mathbf{r})\chi_A(\mathbf{r}) - S\chi_B^2(\mathbf{r})] = 0 \quad (1.92)$$

1.6 EXCHANGE-OVERLAP DENSITIES AND THE CHEMICAL BOND

This section aims to illustrate the origin of the quantum mechanical exchange-overlap densities and their different behaviour in the case of the chemical bond in ground state H_2 and the Pauli repulsion in He_2 . We choose as starting point for the $^1\Sigma_g^+$ ground state of the systems the normalized Heitler–London (HL) wave functions (Magnasco, 2008):

$$\Psi(\text{H}_2) = \frac{||\bar{a}\bar{b}|| + ||b\bar{a}||}{\sqrt{2 + 2S^2}} = \frac{a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)}{\sqrt{2 + 2S^2}} \frac{\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)}{\sqrt{2}} \quad (1.93)$$

$$\Psi(\text{He}_2) = ||a\bar{a}\bar{b}\bar{b}|| = ||a(\mathbf{r}_1)\alpha(s_1) \quad a(\mathbf{r}_2)\beta(s_2) \quad b(\mathbf{r}_3)\alpha(s_3) \quad b(\mathbf{r}_4)\beta(s_4)|| \quad (1.94)$$

where \mathbf{r} and s are space and spin variables, the bar denotes β spin, $a(\mathbf{r}) = 1s_A(\mathbf{r})$ and $b(\mathbf{r}) = 1s_B(\mathbf{r})$ are AOs centred at A and B , the double bar standing for a normalized Slater determinant (Magnasco, 2007, 2009a)¹².

If $\mathbf{x} = \mathbf{r}s$ denotes the space-spin variable, we recall from first principles (Magnasco, 2007, 2009a) that, for a normalized N -electron wavefunction satisfying the Pauli antisymmetry principle, the one-electron density function is defined as:

$$\rho(\mathbf{x}; \mathbf{x}) = N \int d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N \overline{\Psi(\mathbf{x}, \mathbf{x}_2, \cdots, \mathbf{x}_N)} \Psi^*(\mathbf{x}, \mathbf{x}_2, \cdots, \mathbf{x}_N) \quad (1.95)$$

where the first set of variables in ρ comes from Ψ , the second from Ψ^* . The physical meaning of ρ is:

$$\rho(\mathbf{x}; \mathbf{x})d\mathbf{x} = \text{probability of finding an electron at } d\mathbf{x} \quad (1.96)$$

where $d\mathbf{x} = d\mathbf{r}ds$ is an elementary volume at a *fixed* point in space-spin space. In this way, ρ determines the probability distribution in space of

¹²It should be remarked that, while the Heitler–London function (1.93) for H_2 is a two-determinant wave function, the Heitler–London function (1.94) for He_2 is a single determinant wave function, so that in this case HL and MO approaches coincide.

electrons of either spin. If:

$$\begin{cases} \rho^\alpha(\mathbf{r}; \mathbf{r}) d\mathbf{r} = \text{probability of finding at } d\mathbf{r} \text{ an electron with spin } \alpha \\ \rho^\beta(\mathbf{r}; \mathbf{r}) d\mathbf{r} = \text{probability of finding at } d\mathbf{r} \text{ an electron with spin } \beta \end{cases} \quad (1.97)$$

with $\rho^\alpha(\mathbf{r}; \mathbf{r}) = \rho^\alpha(\mathbf{r})$ and $\rho^\beta(\mathbf{r}; \mathbf{r}) = \rho^\beta(\mathbf{r})$ the (spatial) coefficients of $\alpha(s)\alpha^*(s)$ and $\beta(s)\beta^*(s)$ in ρ , the (spatial) *electron density*, as observed from experiment, is defined as:

$$P(\mathbf{r}; \mathbf{r}) = \rho^\alpha(\mathbf{r}; \mathbf{r}) + \rho^\beta(\mathbf{r}; \mathbf{r}) \quad (1.98)$$

The electron densities for the $^1\Sigma_g^+$ states of H_2 and He_2 resulting from these Heitler–London wave functions are then:

$$\begin{cases} P(\mathbf{r}; \mathbf{r}) = \rho^\alpha(\mathbf{r}; \mathbf{r}) + \rho^\beta(\mathbf{r}; \mathbf{r}) \\ = \frac{a(\mathbf{r})a^*(\mathbf{r}) + b(\mathbf{r})b^*(\mathbf{r}) + S[a(\mathbf{r})b^*(\mathbf{r}) + b(\mathbf{r})a^*(\mathbf{r})]}{1 + S^2} \end{cases} \quad (1.99)$$

for the two-electron system H_2 , and:

$$\begin{cases} P(\mathbf{r}; \mathbf{r}) = \rho^\alpha(\mathbf{r}; \mathbf{r}) + \rho^\beta(\mathbf{r}; \mathbf{r}) \\ = 2 \frac{a(\mathbf{r})a^*(\mathbf{r}) + b(\mathbf{r})b^*(\mathbf{r}) - S[a(\mathbf{r})b^*(\mathbf{r}) + b(\mathbf{r})a^*(\mathbf{r})]}{1 - S^2} \end{cases} \quad (1.100)$$

for the four-electron system He_2 .

We give in detail below the calculation of the electron density for the Heitler–London wavefunction (1.93) of ground state H_2 , when $a(\mathbf{r})$, $b(\mathbf{r})$, $\alpha(s)$, $\beta(s)$ are all normalized to one:

$$\begin{aligned} \rho(\mathbf{x}_1; \mathbf{x}_1) &= 2 \int d\mathbf{x}_2 \frac{a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)}{\sqrt{2+2S^2}} \frac{\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)}{\sqrt{2}} \\ &\quad \frac{[a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)]^*}{\sqrt{2+2S^2}} \frac{[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]^*}{\sqrt{2}} \\ &= (2+2S^2)^{-1} \int d\mathbf{r}_2 \frac{[a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)]}{[a^*(\mathbf{r}_1)b^*(\mathbf{r}_2) + b^*(\mathbf{r}_1)a^*(\mathbf{r}_2)]} \int ds_2 \frac{[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]}{[\alpha^*(s_1)\beta^*(s_2) - \beta^*(s_1)\alpha^*(s_2)]} \\ &= \frac{a(\mathbf{r}_1)a^*(\mathbf{r}_1) + b(\mathbf{r}_1)b^*(\mathbf{r}_1) + S[a(\mathbf{r}_1)b^*(\mathbf{r}_1) + b(\mathbf{r}_1)a^*(\mathbf{r}_1)]}{2+2S^2} [\alpha(s_1)\alpha^*(s_1) + \beta(s_1)\beta^*(s_1)] \end{aligned}$$

so that:

$$\rho^\alpha(\mathbf{r}_1; \mathbf{r}_1) = \rho^\beta(\mathbf{r}_1; \mathbf{r}_1) = \frac{a(\mathbf{r}_1)a^*(\mathbf{r}_1) + b(\mathbf{r}_1)b^*(\mathbf{r}_1) + S[a(\mathbf{r}_1)b^*(\mathbf{r}_1) + b(\mathbf{r}_1)a^*(\mathbf{r}_1)]}{2 + 2S^2} \quad (1.101)$$

and we obtain the result of Equation (1.99) if we leave out the now useless suffix 1 on the space-spin variables.

(i) The ${}^1\Sigma_g^+$ state of H_2 (two-electron interaction)

The *spinless* 1-electron density (Equation 1.99) satisfies the conservation relation:

$$\int d\mathbf{r} P(\mathbf{r}; \mathbf{r}) = 2 \quad (1.102)$$

the total number of electrons in H_2 .

Using the identity:

$$(1 + S^2)^{-1} = 1 - S^2(1 + S^2)^{-1} \quad (1.103)$$

we see that the electron density (real orbitals) can be *partitioned* into:

$$\left\{ \begin{array}{l} P(\mathbf{r}; \mathbf{r}) = [a^2(\mathbf{r}) + b^2(\mathbf{r})] + \frac{S}{1 + S^2} \{ [a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})] + [b(\mathbf{r})a(\mathbf{r}) - Sb^2(\mathbf{r})] \} \\ = P^{cb}(\mathbf{r}; \mathbf{r}) + P^{exch-ov}(\mathbf{r}; \mathbf{r}) \end{array} \right. \quad (1.104)$$

where:

$$P^{cb}(\mathbf{r}; \mathbf{r}) = a^2(\mathbf{r}) + b^2(\mathbf{r}) = P^{cl}(\mathbf{r}; \mathbf{r}) \quad (1.105)$$

is the *quasi-classical* contribution to the molecular density, and:

$$P^{exch-ov}(\mathbf{r}; \mathbf{r}) = \frac{S}{1 + S^2} \{ [a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})] + [b(\mathbf{r})a(\mathbf{r}) - Sb^2(\mathbf{r})] \} = P^l(\mathbf{r}; \mathbf{r}) \quad (1.106)$$

the quantum mechanical *exchange-overlap* (or *interference*) density. Equations (1.105) and (1.106) satisfy the relations:

$$\int d\mathbf{r} P^{cl}(\mathbf{r}; \mathbf{r}) = \int d\mathbf{r} [a^2(\mathbf{r}) + b^2(\mathbf{r})] = 2 \quad (1.107)$$

the number of electrons in the H₂ molecule, and:

$$\left\{ \begin{aligned} & \int d\mathbf{r} P^{exch-ov}(\mathbf{r}; \mathbf{r}) \\ &= \frac{S}{1+S^2} \int d\mathbf{r} \{ [a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})] + [b(\mathbf{r})a(\mathbf{r}) - Sb^2(\mathbf{r})] \} \\ &= \frac{S}{1+S^2} (2S - 2S) = 0 \end{aligned} \right. \quad (1.108)$$

in agreement with Equations (1.92). However, the energy changes associated with the quantum mechanical exchange-overlap component (Equation 1.106) of the interaction energy are the greatest contributors to the energy of the chemical bond (see Table 1.2).

Equations (1.105) and (1.106) are the Heitler–London counterpart of the corresponding quantities (Equations 3.4 and 3.5 on page 340 of Ruedenberg’s paper (1962), which refers to a LCAO-MO wave function. Ruedenberg calls Equation (1.106) ‘the modification of the quasi-classical density due to the *interference* effect’, while we, more literally, speak of *exchange*[$a(\mathbf{r})b(\mathbf{r})$], [$b(\mathbf{r})a(\mathbf{r})$] and *overlap*[$-Sa^2(\mathbf{r})$], [$-Sb^2(\mathbf{r})$] densities.

Finally, it is worth noting that, while:

$$q_A^{cl} = q_B^{cl} = 1 \quad (1.109)$$

is the classical electron charge on separate A and B (one electron on each H atom),

$$q_{AB}^{exch-ov} = q_{BA}^{exch-ov} = \frac{S}{1+S^2} > 0 \quad (1.110)$$

is the fraction of electronic charge transferred in the bond region, due to what Ruedenberg calls the ‘constructive interference’, and which means *bonding*.

Table 1.2 Optimized bond energies and their components ($10^{-3}E_b$) for ground state H₂

R/a_0	ΔE^{cb}	$\Delta E^{exch-ov}$	$\Delta E(^1\Sigma_g^+)$
1	15.85	-104.43	-88.58
1.2	-9.93	-119.03	-128.96
1.4	-19.42	-119.63	-139.05
1.6	-21.83	-112.54	-134.37
1.8	-21.08	-101.60	-122.68
2	-18.99	-89.02	-108.01
4	-1.68	-9.68	-11.36
6	-0.06	-0.45	-0.51
8	-0.00 ₂	-0.01 ₅	-0.01 ₇

So, a complete equivalence exists between our notation (Magnasco and McWeeny, 1991; Magnasco, 2004a, 2007, 2008, 2009a) and that of Ruedenberg (1962).

(ii) The $^1\Sigma_g^+$ state of He_2 (four-electron interaction)

The same argument can be applied to the electron density (Equation 1.100), which satisfies the conservation relation:

$$\int d\mathbf{r} P(\mathbf{r};\mathbf{r}) = 4 \quad (1.111)$$

the total number of electrons in He_2 .

Using the identity:

$$(1-S^2)^{-1} = 1 + S^2(1-S^2)^{-1} \quad (1.112)$$

the electron density (real orbitals) can be *partitioned* into:

$$\left\{ \begin{aligned} P(\mathbf{r};\mathbf{r}) &= 2[a^2(\mathbf{r}) + b^2(\mathbf{r})] - \frac{2S}{1-S^2} \{ [a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})] + [b(\mathbf{r})a(\mathbf{r}) - Sb^2(\mathbf{r})] \} \\ &= P^{cb}(\mathbf{r};\mathbf{r}) + P^{exch-ov}(\mathbf{r};\mathbf{r}), \end{aligned} \right. \quad (1.113)$$

where:

$$P^{cb}(\mathbf{r};\mathbf{r}) = 2[a^2(\mathbf{r}) + b^2(\mathbf{r})] = P^{cl}(\mathbf{r};\mathbf{r}) \quad (1.114)$$

is the *quasi-classical* contribution to the molecular density, and:

$$\left\{ \begin{aligned} P^{exch-ov}(\mathbf{r};\mathbf{r}) &= \\ &= -\frac{2S}{1-S^2} \{ [a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})] + [b(\mathbf{r})a(\mathbf{r}) - Sb^2(\mathbf{r})] \} = P^I(\mathbf{r};\mathbf{r}) \end{aligned} \right. \quad (1.115)$$

the quantum mechanical *exchange-overlap* (or *interference*) density. Even in this case it is evident that:

$$\int d\mathbf{r} P^{cl}(\mathbf{r};\mathbf{r}) = 4 \quad (1.116)$$

$$\int d\mathbf{r} P^{exch-ov}(\mathbf{r};\mathbf{r}) = 0 \quad (1.117)$$

While the ‘exchange-overlap’ (or ‘interference’) density still does not give any contribution to the electron population, it is now at the origin of

Table 1.3 Optimized Pauli repulsions and their components ($10^{-3}E_h$) for the He–He interaction in the medium range

R/a_0	ΔE^{cb}	$\Delta E^{exch-ov}$	$\Delta E(^1\Sigma_g^+)$
2	-27.28	163.90	136.62
2.5	-7.55	50.22	42.67
3	-1.93	14.89	12.96
3.5	-0.47	4.27	3.80
4	-0.11	1.18	1.07
4.5	-0.02	0.32	0.30
5	-0.00 ₅	0.08	0.07 ₅

the *strong repulsion* occurring at short range between two neutral He atoms (Pauli repulsion, see Table 1.3), since in this case:

$$q_{AB}^{exch-ov} = q_{BA}^{exch-ov} = -\frac{2S}{1-S^2} < 0 \quad (1.118)$$

so that, now, electrons escape from the region between the nuclei, giving what Ruedenberg calls ‘a destructive interference’. The same behaviour occurs for the triplet $^3\Sigma_u^+$ excited state of H_2 .

Hence, we conclude, first, that there is a complete equivalence between Ruedenberg’s (1962) and our formulation (Magnasco and McWeeny, 1991; Magnasco, 2004a, 2007, 2008, 2009a) in terms of quantum densities, and, next, that the different behaviour of the quantum ‘exchange-overlap’ (or ‘interference’) density for the $^1\Sigma_g^+$ states of H_2 (chemical bonding) and He_2 (Pauli repulsion) is evident from the opposite signs of the $q_{AB}^{exch-ov}$ terms occurring in H_2 and He_2 . The latter originate the main contribution to the respective $\Delta E^{exch-ov}$ components of the bond energy in H_2 (*attractive* contribution) and of the Pauli repulsion in He_2 (*repulsive* contribution).

Numerical values of the interaction energies for these Heitler–London wavefunctions, taken from Magnasco (2008), are given in Tables 1.2 and 1.3. The energies are optimized variationally with respect to the values of the orbital exponents c_0 of the atomic $1s$ STOs on A and B .

It can be seen from Table 1.2 that the optimized value resulting for the bond energy of H_2 at the equilibrium bond length, $\Delta E_e(^1\Sigma_g^+) = -139.05 \times 10^{-3}E_b$ at $R_e = 1.40a_0$, is within 80% of the theoretical value $\Delta E_e(^1\Sigma_g^+) = -174.45 \times 10^{-3}E_b$ given by Wolniewicz (1993) in his accurate calculation using a 279-term expansion in spheroidal coordinates for the two electrons, including powers of the inter-electronic distance. It must be admitted that our results are particularly satisfying for such a simple wavefunction!

The He–He optimized Pauli repulsion at medium range resulting from Table 1.3 at $R = 3a_0$, $\Delta E(^1\Sigma_g^+) = 12.96 \times 10^{-3}E_b$, turns out to be within 96% of the accurate result $\Delta E(^1\Sigma_g^+) = 13.52 \times 10^{-3}E_b$, obtained by Liu and McLean (1973) from an accurate SCF Hartree–Fock calculation using a $4s3p2d1f$ basis of STOs on each centre. At $R = 4a_0$, the optimized result, $\Delta E(^1\Sigma_g^+) = 1.07 \times 10^{-3}E_b$, is still within 80% of the accurate value given by the same authors, $\Delta E(^1\Sigma_g^+) = 1.35 \times 10^{-3}E_b$. Apparently, our results would be even better when compared with experiment¹³ (Feltgen *et al.*, 1982), but in this case we must expect that our SCF values, underestimating the interaction, compensate in part for the effect of the attractive London forces not considered in the calculation.

These numerical results confirm the validity of our simple analysis based on the exchange-overlap densities either for the chemical bond (H_2) or the Pauli repulsion (He–He). Even at the simple MO level, which we know to behave correctly in the bond region (Magnasco, 2007, 2009a), a model representing at its best such quantum densities in terms of the single one-electron Hückel parameter $[(\beta - \alpha S)/(1 + S)] < 0$ (Magnasco, 2004a) is expected to give a qualitatively correct representation of the chemical bond and its properties. This is what we want to present in the next chapter.

¹³Our calculated value at $R = 3.5a_0$ would exceed by less than 2% the experimental value of $\Delta E = 3.74 \times 10^{-3}E_b$.

