Hermitian operators

The operator P is defined as hermitian if its r,s matrix element has the property

$$P_{rs} \equiv \int \psi_r * P \ \psi_s d\tau = \int (P\psi_r)* \ \psi_s \, d\tau = \int \psi_s (P\psi_r)* \, d\tau = \int [\psi_s^* (P\psi_r^*)]^* \, d\tau \equiv P_{sr}*$$

In other words, the matrix elements related by the leading diagonal of P are complex conjugates of each other.

Operators that are hermitian enjoy certain properties. The Hamiltonian (energy) operator is hermitian, and so are the various angular momentum operators. In order to show this, first recall that the Hamiltonian is composed of a kinetic energy part which is essentially $\dfrac{p^2}{2m}$ and a set of potential energy terms which involve the distance coordinates x, y etc. If we can prove that the various terms comprising the Hamiltonian are hermitian then the whole Hamiltonian is hermitian.

The distance coordinate 'operator' x

The coordinate x is an operator insofar as it can 'operate' on a function $f(x)$ to produce another function $x f(x)$, albeit just a multiple of the original one.

$$x_{rs} \equiv \int \psi_r^* x \psi_s dx = \int \left(\psi_r x^* \psi_s^* \right)^* dx = \int (\psi_s^* x^* \psi_r)^* dx \equiv x_{sr}^*$$

which shows that x is hermitian.

The momentum operator p

The operator for the linear momentum[1] in the x direction is $p_x \equiv \dfrac{\hbar}{i} \dfrac{\partial}{\partial x}$. Let us suppose that our space is one-dimensional, along the x axis so that $\dfrac{\partial}{\partial x}$ can be written $\dfrac{d}{dx}$. Its r,s matrix element is

$$(p_x)_{rs} \equiv \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi_r^* \frac{d}{dx} \psi_s dx = \frac{\hbar}{i} \left(\left[\psi_r^* \psi_s \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi_s \frac{d}{dx} \psi_r^* dx \right)$$

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[1] We have already seen that the operator for kinetic energy is $\dfrac{p_x^2}{2m} + \dfrac{p_y^2}{2m} + \dfrac{p_z^2}{2m} = -\dfrac{\hbar^2}{2m} \left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2} \right)$,

i.e. this is the kinetic energy hamiltonian for a particle in free space.

The first term is zero (wave functions of finite systems vanish at $\pm\infty$) and the second

term is $\left[-\dfrac{\hbar}{i}\displaystyle\int_{-\infty}^{\infty}\psi_s^*\dfrac{d}{dx}\psi_r\,dx\right]^*$ which is $\left(p_x\right)_{sr}^*$. Therefore p_x is a hermitian operator.

The Hamiltonian $\mathcal{H}$

We could (but won't!) extend the above treatment for p_x to show that its

square p_x^2 is also hermitian so that the kinetic energy part of the Hamiltonian is

hermitian. If x is hermitian so also are y, z and $r = \sqrt{(x^2 + y^2 + z^2)}$ and several

functions like $\dfrac{1}{r}$ that depend on them and which appear as potential energy terms in

the Hamiltonian. Although this is not a complete argument its results strongly suggest

that the Hamiltonian operator is hermitian.

The bra and ket notation

It is convenient now to use the Dirac bra and ket notation to denote functions.

To explain their form suppose we wanted to write down the wave function for the $2p$

atomic orbital for which $m_l = -1$. Then instead of something like $\psi_{2,1,-1}$ we write

$|2\ 1\ -1\rangle$, which is called a *ket*. Then an eigenvalue equation involving the function

ψ_{pa} with eigenvalue γ previously written as $\mathcal{P}\psi_{pa} = \gamma\,\psi_{pa}$ now becomes

$$\mathcal{P}\,|pa\rangle = \gamma|pa\rangle$$

The normalisation integral of the function ψ_{pa}, i.e. $\displaystyle\int_0^{\infty}\psi_{pa}^*\psi_{pa}\,d\tau$ is written

$\langle pa|pa\rangle$ where $\langle pa|$ is the *bra* corresponding to the ket $|pa\rangle$. The function

represented by the bra is taken to have been complex conjugated and associating the

bra and ket together in this way implies integration over all the whole range of the

variables. So the overlap integral $S_{ab} \equiv \displaystyle\int_0^{\infty}\psi_a^*\psi_b\,d\tau$ is written as $\langle a|b\rangle$ and the matrix

element $V_{ab} \equiv \displaystyle\int_0^{\infty}\psi_a^*V\psi_b\,d\tau$ as $\langle a|V|b\rangle$.

Summarising,

$$\psi_a \equiv |a\rangle$$

$$\int_0^\infty \psi_a^* \psi_b \, d\tau \equiv \langle a | b \rangle$$

$$\int_0^\infty \psi_a^* V \psi_b \, d\tau \equiv \langle a | V | b \rangle$$

Properties of hermitian operators

Their eigenvalues are real

To show this consider the eigenvalue equation involving the hermitian operator $\mathcal{P}$

$$\mathcal{P} | a \rangle = \alpha | a \rangle$$

and multiply from the left with the bra $\langle a |$:

$$\langle a | \mathcal{P} | a \rangle = \alpha \langle a | a \rangle = \alpha$$

because $\langle a | a \rangle = 1$. But if $\mathcal{P}$ is hermitian the result would be the same if we were to interchange the bra and ket and take the complex conjugate of the whole element:

$$\alpha = \langle a | \mathcal{P} | a \rangle = \langle a | \mathcal{P} | a \rangle^* = \alpha^*$$

So $\alpha = \alpha^*$, i.e. the eigenvalue is real.

Since we have shown that the Hamiltonian operator is hermitian, we have the important result that all its energy eigenvalues must be real. In fact the operators of all physically measurable quantities are hermitian, and therefore have real eigenvalues.

Their eigenfunctions are orthogonal

Consider the pair of eigenvalue equations for the hermitian operator $\mathcal{P}$

$$\mathcal{P} | a \rangle = \alpha | a \rangle$$

$$\mathcal{P} | b \rangle = \beta | b \rangle$$

and suppose that the eigenvalues are non-degenerate ($\alpha \neq \beta$). Now multiply (from the left) the first equation by $\langle b |$ and the second by $| a \rangle$:

$$\langle b | P | a \rangle = \alpha \langle b | a \rangle$$

$$\langle a | P | b \rangle = \beta \langle a | b \rangle$$

But if $\mathcal{P}$ is hermitian $\langle b|P|a \rangle = \langle a|P|b \rangle^*$ and so

$$\alpha \langle b|a \rangle = \beta^* \langle a|b \rangle^* = \beta \langle a|b \rangle^* \qquad \text{because } \beta \text{ is real.}$$

So $\qquad \alpha \langle b|a \rangle = \beta \langle b|a \rangle \qquad \text{because } \langle a|b \rangle^* = \langle b|a \rangle$

But as we have stated that the eigenvalues α and β are unequal, the only way the last equation can hold is if

$$\langle b|a \rangle = 0$$

i.e. the eigenfunctions are orthogonal ($\int\limits_0^\infty \psi_a^* \psi_b d\tau = 0$).

What if $|a \rangle$ and $|b \rangle$ are degenerate?

If the eigenvalues α and β are equal the pair of equations is

$$\mathcal{P} |a \rangle = \alpha |a \rangle$$

$$\mathcal{P} |b \rangle = \alpha |b \rangle$$

And we define a ket $|A \rangle$ as a linear combination of $|a \rangle$ and $|b \rangle$:

$$|A \rangle = c_1 |a \rangle + c_2 |b \rangle .$$

Applying the operator to $|A \rangle$ we get

$$\mathcal{P} |A \rangle = c_1 P|a \rangle + c_2 P|b \rangle = c_1 \alpha |a \rangle + c_2 \alpha |a \rangle = \alpha (c_1 |a \rangle + c_2 |b \rangle) = \alpha |A \rangle$$

showing that a linear combination of the degenerate states $|a \rangle$ and $|b \rangle$ is also an eigenfunction of $\mathcal{P}$, with the same eigenvalue α. In quantum chemistry we often take combinations of degenerate functions to produce functions which are more convenient for the purpose[2]. As we have seen, in this case $|a \rangle$ and $|b \rangle$ are not necessarily orthogonal, but combinations like $|A \rangle$ and $|B \rangle$ can be constructed using coefficients c_1, c_2 etc. that ensure the orthogonality of $|A \rangle$ and $|B \rangle$.

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[2] Recall the JS course where we made two combinations of the energy-degenerate *complex* $2p$ atomic orbital functions $2p_{+1}$ and $2p_{-1}$ by adding and by subtracting them to produce the *real* orbital functions $2p_x$ and $2p_y$.

The commutation of operators

There are many sets of physical quantities (energy, momentum, position etc.) describing quantum particles which may not be *simultaneously* measurable, i.e. it may not be possible to specify simultaneous values to more than one of them at a time. They are defined by the various equations describing the Uncertainty Principle, but just which pairs of quantities A and B are related by $\delta A \times \delta B \geq \hbar$ are shown by the operators concerned. If a state ψ has exactly determinable quantities P and Q which have operators $\mathscr{P}$ and $\mathscr{Q}$ so that

$$\mathscr{P} \, \psi = p\psi \qquad \text{and} \qquad \mathscr{Q} \, \psi = q\psi$$

then the following theorem can be proved:

Theorem: A system that is specified by a set of states ψ_1, ψ_2, … has simultaneously and precisely specifiable quantities *P* and *Q if and only if their operators $\mathscr{P}$ and $\mathscr{Q}$ commute* i.e. $\mathscr{P}\mathscr{Q}\,\psi = \mathscr{Q}\mathscr{P}\,\psi$, for all the wave functions ψ.

There are two statements to be proved:

(a) **For $\mathscr{P}$ and $\mathscr{Q}$ to have a common set of eigenfunctions they must commute.**

Let one of the common eigenstates be represented by $|m\rangle$ in the eigenvalue equations

$$\mathscr{P} \, |m\rangle = p|m\rangle$$

and
$$\mathscr{Q} \, |m\rangle = q|m\rangle$$

Operate on the first equation with $\mathscr{Q}$ and on the second with $\mathscr{P}$.

$$\mathscr{Q}\mathscr{P}\,|m\rangle = p\,\mathscr{Q}\,|m\rangle = pq|m\rangle$$
$$\mathscr{P}\mathscr{Q}\,|m\rangle = q\,\mathscr{P}\,|m\rangle = pq|m\rangle$$

Therefore $\mathscr{P}$ and $\mathscr{Q}$ commute, i.e. $\mathscr{P}\mathscr{Q} = \mathscr{Q}\mathscr{P}$.

(b) **If $\mathscr{P}$ and $\mathscr{Q}$ commute they must have a common set of eigenfunctions.**

This is the more useful statement. Suppose that $|m\rangle$ is an eigenfunction of $\mathscr{P}$ with eigenvalue *p*:

$$\mathscr{P} \, |m\rangle = p|m\rangle$$

Operate on this equation with $\mathscr{Q}$:

$$\mathcal{Q}\mathcal{P}\,|m\rangle = p\,\mathcal{Q}|m\rangle$$

Because of commutation we can write it as

$$\mathcal{P}\,\mathcal{Q}\,|m\rangle = p\,\mathcal{Q}|m\rangle$$

i.e.
$$\mathcal{P}\,[\,\mathcal{Q}|m\rangle\,] = p[\,\mathcal{Q}|m\rangle\,]$$

This equation implies that $\mathcal{Q}\,|m\rangle$ is an eigenfunction of $\mathcal{P}$ with eigenvalue p. But the only way that this can be the case is if $|m\rangle$ is an eigenfunction of $\mathcal{Q}$. Therefore $|m\rangle$ must be an eigenfunction of both $\mathcal{P}$ and $\mathcal{Q}$ operators.

Application in quantum chemistry – Symmetry operators

Here is a simple Hamiltonian. It is for the H_2 molecule with two nuclei a and b and with two electrons 1 and 2, but a Hamiltonian for any atom or molecule would have the same sort of terms.

$$\mathcal{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}} - \frac{1}{r_{12}} - \frac{1}{r_{ab}}\right)$$

You recall that the Laplacian operator is $\dfrac{\partial^2}{\partial x_1^2} + \dfrac{\partial^2}{\partial y_1^2} + \dfrac{\partial^2}{\partial z_1^2}$ for the first electron and has a similar form for the second, with 2 replacing 1. Now switching the nuclei a and b and the electrons 1 and 2 means performing a symmetry operation (call it $\mathcal{P}$) on the molecule. But notice that the effect of these interchanges leaves $\mathcal{H}$ unaffected. So if the product $\mathcal{P}\mathcal{H}$ is applied to a wave function ψ we can write the operation as

$$\mathcal{P}\,(\mathcal{H}\,\psi) = \mathcal{H}\,(\mathcal{P}\psi)$$

with $\mathcal{P}$ bypassing $\mathcal{H}$ to act directly on ψ. But this means that $\mathcal{P}$ and $\mathcal{H}$ *commute*, and so should have common eigenfunctions. What does this mean?

Staying with our H_2 molecule recall that if there were no symmetry we would write its molecular orbital wave function as

$$\psi = c_1\varphi_1 + c_2\varphi_2$$

but when the values of c_1 and c_2 are found that make this an eigenfunction of $\mathcal{H}$ by applying the variation principle we get the pair

$$\psi_1 = \frac{1}{\sqrt{2}}\left(\varphi_1 + \varphi_2\right)$$

and
$$\psi_2 = \frac{1}{\sqrt{2}}\left(\varphi_1 - \varphi_2\right)$$

As eigenfunctions of the hermitian operator $\mathcal{P}$ we have seen that ψ_1 and ψ_2 are orthogonal. If you have any doubts on this, check it out:

$$<\psi_1 \mid \mathcal{P} \mid \psi_2> \quad = \int \psi_1^* \, \mathcal{P} \, \psi_2 \, d\tau = -\tfrac{1}{2}\int (\varphi_1 + \varphi_2)^* \, (\varphi_2 - \varphi_1) \, d\tau$$

$$= -\tfrac{1}{2}[\int|\varphi_1|^2 \, d\tau - \int|\varphi_2|^2] \, d\tau - \int\varphi_1^*\varphi_2 \, d\tau + \int\varphi_2^*\varphi_1 \, d\tau\,]$$

$$= -\tfrac{1}{2}[\ 1 - 1 - 0 + 0]$$

$$= 0$$

But since ψ_1 and ψ_2 are *also* eigenfunctions of $\mathcal{H}$, matrix elements H_{rs} that they form with $\mathcal{H}$ will similarly be zero:

$$<\psi_1 \mid \mathcal{H} \mid \psi_2> \, = 0$$

This is a very important result – one which deserves to be expressed verbally:

> If eigenfunctions of $\mathcal{H}$ ψ_1 and ψ_2 are found which are simultaneously eigenfunctions of a commutinmg operator $\mathcal{P}$ that *correspond to different eigenvalues of $\mathcal{P}$* then the matrix elements that they form with $\mathcal{H}$ are zero.

This is the basis of the powerful methods of symmetry theory to reduce the labour of quantum calculations and to symmetry-classify molecular wave functions and states. In the simple example illustrated above we don't need to calculate the coefficients c_1 and c_2 by solving a second-order determinant, because they have been obtained by making ψ an eigenfunction of $\mathcal{P}$. For the same reason, the application of symmetry arguments to the π MOs of pentalene C_8H_6 in our JS course enabled us to avoid solving an 8th order determinantal equation and instead to solve separately one 3rd order, two 2nd order and a 1st order equation ($3 + 2 + 2 + 1 = 8$).

Consider what would happen if you tried to form matrix elements of $\mathcal{H}$ using ψ_1 and ψ_2. Just as $\left\langle \psi_1 \middle| P \middle| \psi_2 \right\rangle = -1.\left\langle \psi_1 \middle| \psi_2 \right\rangle$ which is zero because of the orthogonality of ψ_1 and ψ_2, so also $\left\langle \psi_1 \middle| H \middle| \psi_2 \right\rangle = -\left(\alpha - \beta\right)\!\left\langle \psi_1 \middle| \psi_2 \right\rangle = 0$ and the Hamiltonian (energy) matrix is

$$\begin{pmatrix} \alpha + \beta - E & 0 \\ 0 & \alpha - \beta - E \end{pmatrix}$$

i.e. the secular determinantal equation is $\begin{vmatrix} \alpha + \beta - E & 0 \\ 0 & \alpha - \beta - E \end{vmatrix} = 0$

The matrix elements of $\mathcal{H}$ between different eigenstates of $\mathcal{P}$ are zero. The

Hamiltonian matrix has been brought to a diagonal form, or 'has been diagonalised'.

Recall the application of symmetry in the MO treatment of pentalene

(JS symmetry course)
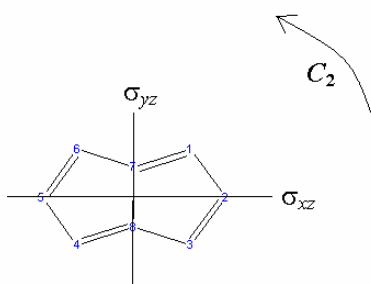
The π MOs of the pentalene molecule transform according to symmetries A_1, A_2, B_1

and B_2 in point group C_{2v}, and we showed that they were

$$
\begin{aligned}
\psi(A_1) &= c_1\tfrac{1}{2}(\varphi_1 + \varphi_3 + \varphi_4 + \varphi_6) &&+ c_2\sqrt{\tfrac{1}{2}}(\phi_2 + \phi_5) &&+ c_7\sqrt{\tfrac{1}{2}}(\phi_7 + \phi_8) \\
\psi(A_2) &= c_1{'}\,\tfrac{1}{2}(\varphi_1 - \varphi_3 + \varphi_4 - \varphi_6) \\
\psi(B_1) &= c_1{''}\,\tfrac{1}{2}(\varphi_1 + \varphi_3 - \varphi_4 - \varphi_6) &&+ c_2{''}\sqrt{\tfrac{1}{2}}(\phi_2 - \phi_5) \\
\psi(B_2) &= c_1{'''}\tfrac{1}{2}(\varphi_1 - \varphi_3 - \varphi_4 + \varphi_6) &&&&+ c_7{'''}\sqrt{\tfrac{1}{2}}(\phi_7 - \phi_8)
\end{aligned}
$$

A symmetry orbital like $\psi(A_2)$ does not interact with an orbital with different

symmetry like $\psi(B_2)$. In other words the matrix element $<\psi(A_2)\,\mathcal{H}\,\psi(B_2)>$ is zero,

as we'll demonstrate. In recognising the interactions between atomic orbitals at the

Hückel level remember that all β parameters for non-nearest neighbours are zero.

$<\psi(A_2)\,\mathcal{H}\,\psi(B_2)>$

$\quad = \int[c_1{'}\,\tfrac{1}{2}(\varphi_1 - \varphi_3 + \varphi_4 - \varphi_6)\,\mathcal{H}\,c_1{'''}\,\tfrac{1}{2}(\varphi_1 - \varphi_3 - \varphi_4 + \varphi_6) + c_7{'''}\sqrt{\tfrac{1}{2}}(\phi_7 -$

$$\phi_8)]d\tau$$

$\quad = c_1{'}\mathbf{c_1}{'''}\,(\tfrac{1}{4})[\alpha + \alpha - \alpha - \alpha + 0 + 0 \ldots] + (\tfrac{1}{2\sqrt{2}})\,c_1{'}\,c_2{'''}\,[\beta + \beta - \beta - \beta + 0\,.$

$$+\,0\ldots]$$

$\quad = 0$

So the **H** matrix elements between functions corresponding to different symmetries (here A_2 and B_2) are zero. It is for this reason that we can treat the four symmetries **A₁**, **B₁**, **A₂** and **B₂** separately.

If an operator **P** can be found which commutes with operator **H** (e.g. Hamiltonian) then any pair of non-degenerate eigenfunctions ψ_1 and ψ_2 of **P** produce zero matrix elements of **H**.

$$\text{i.e.} \quad \text{if} \quad \mathbf{HP = PH}$$

$$\text{and} \quad P\psi_i = a\psi_i \quad \text{and} \quad P\psi_j = b\psi_j$$

$$\text{then} \quad \int \psi_i^* H\psi_j \, d\tau = 0$$

Angular momentum

By considering the form of the operator for the z-component of the angular momentum operator $l_z \equiv \dfrac{\hbar}{i}\dfrac{\partial}{\partial\phi}$ it is possible to show that l_z (but not simultaneously l_x or l_y) commutes with the Hamiltonian $\mathcal{H}$. So eigenfunctions of l_z are also eigenfunctions of $\mathcal{H}$. As a result, just as the matrix elements of l_z formed from different eigenstates $|r\rangle$ and $|s\rangle$ of are zero, so also are the corresponding matrix elements of $\mathcal{H}$. (i.e. $\langle r|l_z|s\rangle = 0$ and $\langle r|H|s\rangle = 0$). We shall use this property later.

Matrix form of the Schrödinger equation

1. Solutions of the Schrödinger equation

Select a solution to $H\psi = E\psi$ which can be expressed as a linear combination of a *complete set* of basis functions $\{\varphi_i\}$:

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \ldots \tag{1}$$

Since the set $\{\varphi_i\}$:is complete the set $\{c_i\}$ of coefficients can be chosen to render ψ so flexible that it can constitute a solution (the kth, say) of the Schrödinger equation for a particular system. Inserted into the equation the latter would read

$$H \psi_k = E_k \psi_k \tag{2}$$

There are n independent ways of combining the n functions according to eqn. (1), so ψ_k is a member of n solutions like those in eqn. (2). For the moment let us consider just the kth solution: then eqn. (1) needs to be written bearing a label on the left hand side and on the set of coefficients $\{ c_i \}$:

$$\psi_k = c_{1k}\varphi_1 + c_{2k}\varphi_2 + c_{3k}\varphi_3 + \ldots + c_{nk}\varphi_n \tag{3}$$

The $\{ c_i \}$ are calculated using the Variation Principle (energy minimisation), which entails solving the secular equations.

2. The Hamiltonian matrix

In order to solve for ψ_k and E_k in eqn. (2) the energy (Hamiltonian) matrix $\mathbf{H}$ is constructed, whose general element is given by $H_{ij} \equiv \int \varphi_I^* H \varphi_j d\tau$. Obviously the elements of $\mathbf{H}$ depend on the basis functions $\{ \varphi_i \}$ used to build it. Any other set of functions, even if complete, would give rise to different matrix elements H_{ij}' and therefore to a different matrix $\mathbf{H'}$, although the energy eigenvalues obtained from $\mathbf{H}$ and $\mathbf{H'}$ would be identical.

Example: The allyl radical at Hückel level

Using the carbon $2p_z$ atomic orbitals as basis functions, the energy matrix for the allyl radical,

$$\overset{1 \quad \ 2 \quad \ 3}{H_2C\text{—}CH\text{—}CH_2} \text{ is}$$
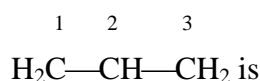
is
$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \tag{5}$$

The π MO functions and energy eigenvalues for allyl are given in the table:

k	ψ_k	E_k
1	$\frac{1}{2} (\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3)$	$\alpha - \sqrt{2}\,\beta$
2	$\frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$	α
3	$\frac{1}{2} (\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3)$	$\alpha + \sqrt{2}\,\beta$

Now instead of using the atomic orbital set (φ_1, φ_2, φ_3) as basis functions what if we had used the *molecular orbital* set to construct **H**? Let's try:

$$H_{11} = \int \psi_1^* H \psi_1 \, d\tau = \tfrac{1}{4} \int (\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3)^* \; H(\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3) \, d\tau$$

$$= \tfrac{1}{4}[\alpha + 2\alpha + \alpha - \sqrt{2}\beta - \sqrt{2}\beta - \sqrt{2}\beta - \sqrt{2}\beta]$$

$$= \alpha - \sqrt{2}\beta$$

$$H_{22} = \int \psi_2^* H \psi_2 \, d\tau = \tfrac{1}{4} \int (\varphi_1 - \varphi_3)^* \; H(\varphi_1 - \varphi_3) \, d\tau$$

$$= \tfrac{1}{2} [\alpha + \alpha]$$

$$= \alpha$$

Similarly,

$$H_{33} = \alpha + \sqrt{2}\beta$$

$$H_{12} = \frac{1}{2\sqrt{2}}\left[\alpha - \alpha - \sqrt{2}\beta + \sqrt{2}\beta\right]$$

$$= 0$$

Similarly,

$$H_{12} = 0 \quad \text{and} \quad H_{23} = 0$$

So the **H** matrix generated by the MO basis set $\{\psi_k\}$ is

$$\mathbf{H} = \begin{pmatrix} \alpha - \beta\sqrt{2} & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha + \beta\sqrt{2} \end{pmatrix} \tag{6}$$

A comparison of the matrices defined in eqns. (5) and (6) shows that the latter differs from that in (5) by the fact that the non-zero elements are confined to the diagonal positions H_{ii}, while $H_{ij} = 0$ for $i \neq j$. <u>This **H** is a diagonal matrix</u>. Using **H** given by (6) to form the secular determinantal equation produces

$$\begin{vmatrix} \alpha - \beta\sqrt{2} - E & 0 & 0 \\ 0 & \alpha - E & 0 \\ 0 & 0 & \alpha + \beta\sqrt{2} - E \end{vmatrix} = 0$$

which shows that the diagonal elements in **H** are already the energy eigenvalues E_1, E_2 and E_3 that were listed in the table. A process which transforms a matrix like the

one in eqn. (5) into a diagonal form as in (6) is said to *diagonalise* the matrix, thereby revealing the eigenvalues of the matrix in its diagonal positions.

3. Vector notation

The linear combination in eqn. (3) may be written as a *scalar product* of two vectors $\underline{c}_k$ and $\underline{\varphi}$ where the underlining means that the quantity is a *vector*. If the basis set defining ψ_k in eqn. (3) has n terms, the vectors $\underline{c}_k$ and $\underline{\varphi}$ are each rows or columns of n elements, and allow an alternative expression for ψ_k as

$$\psi_k = \underline{c}_k \bullet \underline{\varphi}$$

$$= c_{1k}\varphi_1 + c_{2k}\varphi_2 + c_{3k}\varphi_3 + \ldots + c_{nk}\varphi_n$$

To get the second of these equations from the first we form the scalar product of the vectors $\underline{c}_k$ and $\underline{\varphi}$ by supposing $\underline{c}_k$ to be a *row* vector and $\underline{\varphi}$ a *column* vector, and then using the rules of matrix multiplication. For clarity we'll adopt the convention that a vector with elements $(x_1, x_2, \ldots)$ will be written as $\underline{x}$ if it is a column vector, but as $\underline{x}^\dagger$ if it is a row vector. Doing this *transposes* a column vector $\underline{x}$ into a row vector $\underline{x}^\dagger$, and transposing $\underline{x}^\dagger$ again to $\underline{x}^{\dagger\dagger} (= \underline{x})$ restores the column vector. Note however, that as well as turning the column into a row format, converting $\underline{x}$ into $\underline{x}^\dagger$ also replaces the components x_i by their complex conjugates x_i*. We also define the transpose $\mathbf{A}^\dagger$ of a *matrix* $\mathbf{A}$ as one in which the rows have been swapped by the columns and *vice versa*, and also complex-conjugated. In other words if the general element of $\mathbf{A}$ is A_{ij}, it appears in $\mathbf{A}^\dagger$ as $A_{ji}*$.

Using this notation the above k^{th} state function becomes

$$\psi_k = \underline{c}_k^\dagger \bullet \underline{\varphi} \tag{7}$$

4. Matrix form of the eigenvalue equation. Part 1: the eigenvector matrix.

The energy E_k of the state ψ_k is normally calculated via the secular equations, which furnish both these quantities, but if ψ_k is known, E_k may be extracted from it by calculating

$$E_k = \int \psi_k* \; \mathrm{H} \; \psi_k \, d\tau$$

$$= \sum_i \sum_j c_{ik}^* c_{jk} \int \varphi_i^* \mathrm{H} \, \varphi_j \, d\tau = \sum_i \sum_j c_{ik}^* c_{jk} H_{ij}$$

So $H_{ij} \equiv \int \varphi_i^* H \varphi_j d\tau$ is the $(i, j)^{\text{th}}$ element of a matrix **H**. But using vector/matrix notation the same can also be written

$$E_k = \underline{c}_k^\dagger \, \mathbf{H} \, \underline{c}_k \qquad (8)$$

$$E_k = \underset{\mathbf{c}_k^\dagger}{\overbrace{}} \underset{\mathbf{H}}{\Box} \underset{\mathbf{c}_k}{\begin{pmatrix}\\\end{pmatrix}}$$

Check that this expression follows the rules of matrix multiplication of the three factors on the right of (8): the dimensions of the first (a row vector) are $1 \times n$, the second is a $n \times n$ matrix and the third is a column vector with dimensions $n \times 1$. The result is therefore the scalar (single number) E_k.

Until now we have considered just one solution of the Schrödinger equation — the eigenvalue E_k and the eigenvector $\underline{c}_k$. But can the whole set of solutions be handled simultaneously? Let's assemble all the eigenvectors like $\underline{c}_k$ into a matrix **c**, whose order will be $n \times n$:

$$\mathbf{c} = \begin{pmatrix} c_{11} & c_{12} & . & . & . & c_{1n} \\ c_{21} & c_{22} & . & . & . & c_{2n} \\ c_{31} & c_{32} & . & . & . & c_{3n} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ c_{n1} & c_{n2} & . & . & . & c_{nn} \end{pmatrix} \qquad (9)$$

The *columns* of **c** are the set $\{\underline{c}_k\}$, which are the eigenvectors associated with the energy eigenvalues E_1, E_2, etc. The matrix **c** is called the *eigenvector matrix*, or matrix of eigenvectors, and it has some special features.

5. Properties of the eigenvector matrix

The eigenvector matrix is an example of a type of matrix described as *unitary*. A unitary matrix **A** has the following important properties:

1. The sum of the squares of the elements of any row or column is one,

    i.e. $\sum_j |A_{ij}|^2 = 1$ and $\sum_j |A_{ji}|^2 = 1$

2. The scalar product of any two rows or of any two columns is zero,

i.e. $\sum_j A_{ij}^* A_{kj} = 0$ and $\sum_j A_{ji}^* A_{jk} = 0$

3. The transpose of the matrix is equal to its reciprocal,

i.e. $\qquad\qquad \mathbf{A}^\dagger = \mathbf{A}^{-1}$

so that $\qquad \mathbf{A}^\dagger \mathbf{A} = \mathbf{I}$ $\qquad\qquad\qquad\qquad\qquad$ (10)

where $\mathbf{I}$ is the *unit matrix* which is a matrix of the same dimension as $\mathbf{A}$, with all its

diagonal elements equal to unity and all off-diagonal elements equal to zero.

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & 0 & . & . \\ 0 & 1 & 0 & . & . \\ . & . & . & . & . \\ . & . & . & 1 & 0 \\ . & . & . & 0 & 1 \end{pmatrix}$$

A unit matrix $\mathbf{I}$ multiplying any other matrix $\mathbf{P}$ leaves it unchanged ($\mathbf{I\,P} = \mathbf{P}$). If you

think of $\mathbf{A}$ (or $\mathbf{c}$) as a matrix of LCAO coefficients, properties 1 and 2 follow from the

normalisation of the MO wave functions and from the *orthogonality* of a pair of MO

functions, respectively.

4. The eigenvector matrix $\mathbf{c}$ is such a unitary matrix. An important property

of c is its ability to diagonalise a matrix. This means that if the hamiltonian matrix $\mathbf{H}$

is subjected to a **similarity transformation** with its eigenvector matrix $\mathbf{c}$ as follows:

$$\mathbf{c}^{-1}\,\mathbf{H}\,\mathbf{c} = \mathbf{c}^\dagger\,\mathbf{H}\,\mathbf{c} = \mathbf{E_d}$$

the resulting matrix $\mathbf{E_d}$ is *diagonal*, i.e. its off-diagonal elements are zero. Those

which are on the diagonal are the *eigenvalues E_1, E_2, E_3, . . .* of $\mathbf{H}$,

i.e. $\qquad\qquad\qquad E = \begin{pmatrix} E_1 & 0 & & 0 \\ 0 & E_2 & & \\ & & & 0 \\ 0 & 0 & & E_2 \end{pmatrix}$

The procedure of finding the eigenvalues of a $\mathbf{H}$ matrix is often referred to as

'diagonalizing' it by finding a suitable matrix c to perform the similarity

transformation $\mathbf{c}^\dagger\,\mathbf{H}\,\mathbf{c.}$