

# HERMITIAN ADJOINT

$$\int dx \varphi_i^*(x) A(x) \varphi_j(x) = \int dx (A^\dagger \varphi_i)^* \varphi_j(x)$$

definition of adjoint.

For matrices  $A_{ij}^\dagger = A_{ji}^*$  (not  $= A_{ij}$  in general).

Example  $\begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix} \neq \begin{pmatrix} 1 & 2 \\ 0 & 1 \end{pmatrix}$  not Hermitian  
 $A \neq A^\dagger$

$$\begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix} \text{ Hermitian.}$$
$$B = B^\dagger$$

Consider  $AA^\dagger$

$$AA^\dagger = \begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 \\ 2 & 5 \end{pmatrix} = C$$

~~$$A^\dagger A = \begin{pmatrix} 1 & 2 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix} = \begin{pmatrix} 5 & 2 \\ 2 & 1 \end{pmatrix} = C^*$$~~

$$C^\dagger = \begin{pmatrix} 1 & 2 \\ 2 & 5 \end{pmatrix} \therefore C = C^\dagger$$

Product of  $A$  and  $A^\dagger$  is Hermitian.

You show in general.

# Uncertainty Relation

$$\langle \psi | B B^\dagger | \psi \rangle = \int dx \psi^\dagger B B^\dagger \psi = \int dx (B^\dagger \psi)^* B^\dagger \psi$$

$\geq 0$  since last form is manifestly positive.

$$B = C + i\lambda D \quad B^\dagger = C^\dagger - i\lambda D^\dagger \quad \text{w } C \text{ and } D \text{ assumed Hermitian.}$$

$$0 \leq \langle B B^\dagger \rangle = \langle C^2 \rangle + \lambda^2 \langle D^2 \rangle - i\lambda (\langle CD - DC \rangle) \equiv f(\lambda)$$

minimize  $f(\lambda)$ :  $df/d\lambda = 0$

$$2\lambda \langle D^2 \rangle - i (\langle CD - DC \rangle) = 0$$

$$\lambda = \frac{i}{2} \frac{\langle (CD - DC) \rangle}{\langle D^2 \rangle}$$

$$f_{\min} = \langle C^2 \rangle - \frac{1}{4} \frac{\langle (CD - DC) \rangle^2}{\langle D^2 \rangle} + \frac{1}{2} \frac{\langle (CD - DC) \rangle^2}{\langle D^2 \rangle}$$

$$= \langle C^2 \rangle + \frac{1}{4} \frac{\langle (CD - DC) \rangle^2}{\langle D^2 \rangle} \geq 0$$

$$\text{Thus } \langle C^2 \rangle \langle D^2 \rangle \geq -\frac{1}{4} \langle (CD - DC) \rangle^2$$

$$(C + i\lambda D)(C - i\lambda D) = C^2 + \lambda^2 D^2 + i\lambda(DC - CD)$$

8. For the hydrogen atom  $H = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r} = T + V$ , and hence  $E_n = \langle T \rangle_{nlm} - e^2 \langle r^{-1} \rangle$ . Since  $E_n = -e^2/2ar^2$ , we find by using (7.5) that

$$E_n = \langle T \rangle_{nlm} - \frac{e^2}{ar^2} = \langle T \rangle_{nlm} + 2E_n,$$

hence

$$E_n = -\langle T \rangle_{nlm}.$$

he relation between the mean value of the potential energy and that of the kinetic energy is thus

$$\langle V \rangle_{nlm} = -2\langle T \rangle_{nlm}. \quad (8.1)$$

9. Consider  $\Psi$  to be normalized to unity. By differentiating the defining relation (III.3) we obtain

$$\frac{d\langle A \rangle}{dt} = \left\langle \frac{\partial \Psi}{\partial t} \Psi, A \right\rangle + \left\langle \Psi, A \frac{\partial \Psi}{\partial t} \right\rangle + \left\langle \Psi, \frac{\partial A}{\partial t} \Psi \right\rangle. \quad (9.1)$$

ut, from the Schrödinger equation, we have that

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar} H\Psi, \quad \frac{\partial \Psi^*}{\partial t} = -\frac{1}{i\hbar} (H\Psi)^*.$$

nd thus, from (9.1), equation (9a) can be obtained.

If the observable  $A$  is not explicitly time-dependent, then  $\frac{\partial A}{\partial t} = 0$  and equation (9a) is the form

$$i\hbar \frac{d\langle A \rangle}{dt} = \langle [A, H] \rangle. \quad (9.2)$$

is equation expresses a very important fact, namely, that the mean value of an observable which commutes with the Hamiltonian is a constant of the motion. In particular, if  $H$  is not explicitly time-dependent, the total energy of the system is conserved and the system is said to be conservative.

10. Since the Hamiltonian of the particle is

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = T + V(\mathbf{r}),$$

follows from (9.2) that

$$\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{p} \rangle = \frac{1}{i\hbar} \langle [\mathbf{r} \cdot \mathbf{p}, H] \rangle = 2\langle T \rangle - \langle \mathbf{r} \cdot \nabla V \rangle.$$

aking into account the fact that  $\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{p} \rangle = 0$ , the virial theorem follows immediately.

$$\begin{aligned} (\hat{x}\hat{p} - \hat{p}\hat{x})f(x) &= x \frac{\hbar}{i} \frac{d}{dx} f - \frac{\hbar}{i} \frac{d}{dx} x f = x \frac{\hbar}{i} \frac{d}{dx} f - \frac{\hbar}{i} x \frac{d}{dx} f - \frac{\hbar}{i} f \\ &= -\frac{\hbar}{i} f = i\hbar f \end{aligned}$$

If the potential energy is proportional to  $r^n$ , we have

$$\langle \mathbf{r} \cdot \nabla V \rangle = n\langle V \rangle$$

and (10a) becomes

$$2\langle T \rangle = n\langle V \rangle.$$

Note that for the harmonic oscillator potential ( $n = 2$ ) and for the Coulomb  $p$  ( $n = -1$ ) the relations (4.6) and (8.1) follow directly from (10.1).

11. Consider an arbitrary operator  $B$ . The mean value in a state  $\psi$  of a physical quantity associated with the Hermitian operator  $BB^+$  will be

$$\langle BB^+ \rangle = \langle \psi, BB^+\psi \rangle = \langle B^+\psi, B^+\psi \rangle \geq 0.$$

Now let  $C$  and  $D$  be two Hermitian operators and  $\lambda$  a real number. Taking  $B = C - i\lambda D$  we have  $B^+ = C + i\lambda D$  and

$$0 \leq \langle BB^+ \rangle = \langle C^2 \rangle + \lambda^2 \langle D^2 \rangle - i\lambda \langle CD - DC \rangle = f(\lambda),$$

say, when function  $f(\lambda)$  has no maximum, and its minimum is given by the condition  $(df/d\lambda) = 0$ . After some simple algebra we find that

$$f_{\min} = \langle C^2 \rangle + \frac{\langle CD - DC \rangle^2}{4\langle D^2 \rangle} \geq 0,$$

whence

$$\langle C^2 \rangle \langle D^2 \rangle \geq -\frac{1}{4} \langle CD - DC \rangle^2.$$

Let  $u$  and  $v$  be the dynamical variables associated with the Hermitian operators  $U$  and  $V$  of the uncertainty relation (III.7). The deviations

$$\delta U \equiv U - \langle U \rangle, \quad \delta V \equiv V - \langle V \rangle,$$

of  $U$  and  $V$  from their mean values  $\langle U \rangle$  and  $\langle V \rangle$  will also be Hermitian operators satisfying the commutation rule

$$[\delta U, \delta V] = [U, V].$$

If we now take  $C = \delta U$  and  $D = \delta V$ , (11.4) becomes

$$\langle (\delta U)^2 \rangle \langle (\delta V)^2 \rangle \geq -\frac{1}{4} \langle UV - VU \rangle^2.$$

Defining the root mean square deviations

$$\Delta U = \sqrt{\langle (\delta U)^2 \rangle} \quad \text{and} \quad \Delta V = \sqrt{\langle (\delta V)^2 \rangle},$$

we obtain from (11.7) the uncertainty relation

$$\Delta U \Delta V \geq \sqrt{-\frac{1}{4} \langle [U, V] \rangle^2}.$$

$$[\hat{x}, \hat{p}] = i\hbar$$

$$\Delta x \Delta p \geq \sqrt{-\frac{1}{4} (i\hbar)^2} = \sqrt{-\frac{1}{4} (-1)\hbar^2} = \frac{\hbar}{2}$$

Minimum uncertainty wavepackets are Gaussian wavepackets

with two arbitrary functions  $u$  and  $v$ , both complex and only chosen so that the integrals exist. With  $\Omega$  the operator (7.3) and  $\alpha$  real, this yields

$$\frac{\hbar}{i} \int d^3x u^* \left[ (1-\alpha)x \frac{\partial v}{\partial x} + \alpha \frac{\partial(xv)}{\partial x} \right] = -\frac{\hbar}{i} \int d^3x \left[ (1-\alpha)x \frac{\partial u^*}{\partial x} + \alpha \frac{\partial(xu^*)}{\partial x} \right] v$$

or

$$\int d^3x u^* \left[ x \frac{\partial v}{\partial x} + \alpha v \right] = - \int d^3x \left[ x \frac{\partial u^*}{\partial x} + \alpha u^* \right] v.$$

Reordering leads on to

$$\int d^3x x \frac{\partial}{\partial x} (u^* v) = -2\alpha \int d^3x u^* v$$

or, by partial integration on the left-hand side, to

$$- \int d^3x u^* v = -2\alpha \int d^3x u^* v$$

which, of course, yields the result of  $\alpha = \frac{1}{2}$ , Eq. (7.5), again.

### Problem 8. Derivatives of an operator

Let  $f(p, x)$  be an integer function of the operators  $p_k, x_k$ . Then the general relations

$$\frac{\partial f}{\partial x_k} = - [f, p_k] \quad (8.1)$$

and

$$\frac{\partial f}{\partial p_k} = [f, x_k] \quad (8.2)$$

with the abbreviation

$$[f, g] = \frac{i}{\hbar} (fg - gf)$$

shall be derived from the commutation rules.

**Solution.** The commutation rules are

$$[p_k, p_l] = 0; \quad [x_k, x_l] = 0; \quad [p_k, x_l] = \delta_{kl}. \quad (8.3)$$

From these we construct (8.1) and (8.2) in four consecutive steps:

1. Let  $f = p_l$ , then we have  $\partial f / \partial x_k = 0$  and  $\partial f / \partial p_k = \delta_{kl}$ . Hence, Eqs. (8.1) and (8.2) become  $[p_k, p_l] = 0$  and  $[p_l, x_k] = \delta_{kl}$ ; i.e. they are satisfied according to (8.3). In the same way, for  $f = x_l$ ,  $\partial f / \partial x_k = \delta_{kl}$ ,  $\partial f / \partial p_k = 0$ , they may be proved to hold.

$$[p, x] = -i\hbar$$

# Schrödinger EOMS TDEOMS

$$i\hbar \dot{\psi} = H \psi \quad -i\hbar \dot{\psi}^* = H^+ \psi^* = H \psi^* \quad H \text{ hermitian}$$

$$\frac{d}{dt} \int \psi^* A \psi = \int (\dot{\psi}^* A \psi + \psi^* A \dot{\psi})$$

$$= \int \left( \frac{i}{\hbar} H \psi^* \right) A \psi - \psi^* \frac{i}{\hbar} H \psi$$

$$= \frac{i}{\hbar} \left( \int \psi^* H A \psi - \int \psi^* \right)$$

$$= \frac{i}{\hbar} \int \psi^* (H A - A H) \psi = \frac{i}{\hbar} \langle [H, A] \rangle$$

$$\frac{d \langle A \rangle}{dt} = \frac{i}{\hbar} \langle [H, A] \rangle$$

Apply to  $A = x$

$$\frac{d \langle x \rangle}{dt} = \frac{i}{\hbar} \langle [H, x] \rangle$$

You showed  $[p, f(x)] = -i\hbar df/dx$

in momentum space, can show  $[x, f(p)] = i\hbar df(p)/dp$

$$\text{So } [p^2, x] = -2i\hbar p$$

$$[H, x] = \left[ \frac{p^2}{2m}, x \right] + [V(x), x] = \frac{-i\hbar p}{m}$$

$$\frac{d \langle x \rangle}{dt} = \frac{i}{\hbar} \left( -\frac{i\hbar \langle p \rangle}{m} \right) = \frac{\langle p \rangle}{m} = \langle \partial H / \partial p \rangle$$

And  $\frac{d\langle p \rangle}{dt} = \frac{i}{\hbar} \langle [H, p] \rangle$

$$\langle [H, p] \rangle = \langle \left[ \frac{p^2}{2m}, p \right] + [V(x), p] \rangle = \langle [V(x), p] \rangle$$

And from  $[f(x), p] = i\hbar df/dx$ , we get

$$\langle [H, p] \rangle = i\hbar \langle dV(x)/dx \rangle$$

so  $\frac{d\langle p \rangle}{dt} = - \langle dV(x)/dx \rangle = \langle F(x) \rangle$ . "

or  $\left. \begin{array}{l} \boxed{\frac{d\langle p \rangle}{dt} = - \langle \partial H / \partial x \rangle} \\ \boxed{\frac{d\langle x \rangle}{dt} = \langle \partial H / \partial p \rangle} \end{array} \right\} \text{Ehrenfest}$

time  $t_0$ , one is thus able to predict the statistical distribution of the results of any measurement performed upon the system at a given later time  $t_1$ . Indeed, the dynamical state of the system at the instant when the measurement begins is

$$|\psi(t_1)\rangle = U(t_1, t_0)|\psi\rangle,$$

and consequently, the probability of finding the system in a given state  $|x\rangle$  is

$$|\langle x|\psi(t_1)\rangle|^2 = |\langle x|U(t_1, t_0)|\psi\rangle|^2. \quad (\text{VIII.36})$$

In the above description of phenomena, the state of the system is represented by a moving ket vector  $|\psi(t)\rangle$ . On the other hand, the physical quantities, or at least those which do not depend upon the time explicitly, are represented by stationary observables of  $\mathcal{E}$  space; likewise, the eigenvectors of these observables are stationary vectors of  $\mathcal{E}$  space, as is the case for the vectors  $|x\rangle$  and  $|\psi\rangle$  of expression (VIII.36). This mode of description of quantum phenomena is called the *Schrödinger "representation"*<sup>1)</sup>.

### 10. Heisenberg "Representation"

One obtains a mode of description of phenomena that is strictly equivalent to the foregoing one by performing a unitary transformation on the kets and observables of the Schrödinger "representation", and assigning to the transformed quantities the same physical significance as to those from which they originated. In such a transformation the observables transform into observables possessing the same eigenvalue spectrum; the eigenvectors transform into eigenvectors; the algebraic relations, the conjugation relations, and the scalar products are conserved. Since the only measurable quantities are moduli of scalar products [cf. eq. (VIII.36)], it is clear that the

<sup>1)</sup> One must not confuse this concept of "representation" with the notion of the representation of vectors and operators of vector space by matrices. The "representation" with which we are dealing here is that of the motion of the quantum system. In order to avoid confusion, it would be preferable here to speak of the Schrödinger "mode of description". The term "representation" is unfortunately entrenched by usage. In order to distinguish the two concepts, we agree to place the word "representation" between quotation marks whenever it is used in its present sense. The distinction to be made here is analogous to the distinction between unitary transformation of matrices and unitary transformation of vectors and operators (cf. Ch. VII, Sec. III).

predictions made by means of the new quantities are identical to the predictions made with the old quantities.

In particular, one defines the *Heisenberg "representation"* by performing upon the kets and observables of the Schrödinger "representation" the unitary, time-dependent transformation  $U^t(t, t_0)$ . Let us attach the subscript S to the old quantities, and the subscript H to the new quantities. The ket

$$|\psi_S(t)\rangle = U(t, t_0)|\psi_S(t_0)\rangle$$

which represents the dynamical state of the system at time  $t$  is transformed into a stationary ket

$$|\psi_H\rangle = U^t(t, t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle. \quad (\text{VIII.37})$$

Conversely, an observable  $A_S$  of the Schrödinger "representation" transforms into

$$A_H(t) = U^t(t, t_0)A_S U(t, t_0). \quad (\text{VIII.38})$$

In general,  $A_H$  is not stationary, even when  $A_S$  does not depend upon the time explicitly. Indeed, if one takes into account differential equation (VIII.32) and its Hermitian conjugate equation, one obtains, on differentiating the last equation term by term

$$\begin{aligned} i\hbar \frac{dA_H}{dt} &= -U^t H A_S U + i\hbar U^t \frac{\partial A_S}{\partial t} U + U^t A_S H U \\ &= U^t [A_S, H] U + i\hbar U^t \frac{\partial A_S}{\partial t} U. \end{aligned} \quad (\text{VIII.39})$$

In this equation,  $H$  is the Hamiltonian of the Schrödinger "representation". Introducing the Hamiltonian of the Heisenberg "representation":

$$H_H = U^t H U,$$

one has

$$U^t [A_S, H] U = [A_H, H_H].$$

On the other hand,  $A_S$ , a function of the fundamental observables of the Schrödinger "representation", may depend upon the time explicitly; the right-hand side of (VIII.39) takes account of this fact.  $\partial A_S / \partial t$  is some function of the observables of the Schrödinger "representation". If  $\partial A_H / \partial t$  is the function obtained by replacing the latter

observables by the corresponding observables of the Heisenberg "representation", it is clear that

$$\frac{\partial A_{\mathbb{H}}}{\partial t} = U^\dagger \frac{\partial A_S}{\partial t} U.$$

Equation (VIII.39) is therefore written

$$i\hbar \frac{dA_{\mathbb{H}}}{dt} = [A_{\mathbb{H}}, H_{\mathbb{H}}] + i\hbar \frac{\partial A_{\mathbb{H}}}{\partial t}.$$

(VIII.40)

This equation is known as the *Heisenberg equation*.

In conclusion, the Heisenberg "representation" is obtained by imposing upon the vector space of the Schrödinger "representation" an overall motion chosen in such a way that the dynamical state of the quantum system is represented by a stationary ket  $|\psi_{\mathbb{H}}\rangle$ . In other words, *any stationary ket of the Heisenberg "representation" represents a possible motion of the quantum system*. Conversely, the various physical quantities are represented by observables evolving in the course of time according to the law (VIII.38) or, what amounts to the same thing, according to the Heisenberg equation (VIII.40) with the initial condition  $A_{\mathbb{H}}(t_0) = A_S(t_0)$ .

Equations (VIII.38) and (VIII.40) apply equally well to any function of the observables of the Heisenberg representation, and especially to the expression  $\exp(i\xi A_{\mathbb{H}})$  or to the projector  $P_D^{(\mathbb{H})}$  upon the subspace of the eigenvectors belonging to the eigenvalues of a given domain  $D$  of the spectrum of  $A_{\mathbb{H}}$ .

Likewise, a ket  $|\chi_{\mathbb{H}}\rangle$  representing an ensemble of compatible variables generally depends upon the time and is deduced from its homologue  $|\chi_S\rangle$  of the Schrödinger "representation" by the formula

$$|\chi_{\mathbb{H}}(t)\rangle = U^\dagger(t, t_0)|\chi_S\rangle. \quad (\text{VIII.41})$$

Let us suppose that the motion of the quantum system is represented after time  $t_0$  by the (stationary) ket  $|\psi_{\mathbb{H}}\rangle$ . The probability of finding it in the state  $|\chi_{\mathbb{H}}\rangle$  upon performing a measurement at the later time  $t_1$  is

$$|\langle \chi_{\mathbb{H}}(t_1) | \psi_{\mathbb{H}} \rangle|^2,$$

a quantity which is obviously equal to the one obtained with the corre-

sponding kets of the Schrödinger "representation" [eq. (VIII.36)], since the scalar product is invariant under the unitary transformation  $U^\dagger(t_1, t_0)$ .

### 11. Heisenberg "Representation" and Correspondence Principle

As shown above, the "representations" of Schrödinger and of Heisenberg are strictly equivalent. In practice, the Schrödinger "representation" is more often used, because it lends itself better to calculations. In fact, the Schrödinger equation, an equation between vectors, is *a priori* easier to solve than the Heisenberg equation which is an equation between operators. However, certain general properties of quantum systems are more immediately apparent in the Heisenberg "representation".

The formal analogy between the Classical Theory and the Quantum Theory is particularly striking in the Heisenberg "representation". The motion of a quantum system in fact, just like the motion of a classical system, appears in the Heisenberg "representation" as a motion of the dynamical variables which are associated with it.

Let us consider a quantum system possessing a classical analogue, and let us compare the motions of the two systems. To every physical quantity of the classical system corresponds a physical quantity of the quantum system. The only difference lies in the fact that the physical quantities of the classical system are quantities obeying the rules of ordinary algebra, whereas their quantum analogues are operators obeying the rules of a non-commutative algebra. But, to the extent that one can identify the expressions of a non-commutative algebra with expressions of ordinary algebra, the equations of motion of the quantized quantities are identical to those of their classical analogues. Indeed, the Heisenberg equations for the variables  $q_1, \dots, q_N$  and  $p_1, \dots, p_N$  are written

$$\begin{aligned} \frac{dq_i}{dt} &= \frac{1}{i\hbar} [q_i, H] = \frac{\partial H}{\partial p_i} & (i = 1, 2, \dots, N) \\ \frac{dp_i}{dt} &= \frac{1}{i\hbar} [p_i, H] = -\frac{\partial H}{\partial q_i} & (i = 1, 2, \dots, N). \end{aligned} \quad (1)$$

To obtain these expressions, the fundamental commutation relations between the  $q$ 's and the  $p$ 's as well as the properties (V.67) and (V.68) to which they give rise, have been taken into account. The



system of equations (I) is formally identical to Hamilton's canonical equations of Classical Mechanics.

More generally, a classical dynamical variable  $A_{cl.} = A(q_1, \dots, q_N; p_1, \dots, p_N; t)$  obeys the equation of motion

$$\frac{dA_{cl.}}{dt} = \{A_{cl.}, H_{cl.}\} + \frac{\partial A_{cl.}}{\partial t}, \quad (\text{VIII.42})$$

where  $\{A_{cl.}, H_{cl.}\}$  designates the Poisson bracket of  $A_{cl.}$  and  $H_{cl.}$  according to the definition

$$\{A, H\} \equiv \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right).$$

We see that the classical equation (VIII.42) is identical to the corresponding Heisenberg equation to the extent that one can identify the Poisson bracket  $\{A, H\}$  with the commutator  $[A_H, H_H]/i\hbar$ . Making use of the fundamental commutation relations and of the similarity between the rules of commutator algebra and the rules of Poisson bracket algebra, one can actually prove the identity of these two expressions provided one makes a suitable choice of the order of the  $q$ 's and the  $p$ 's in the explicit expression of the Poisson bracket.

## 12. Constants of the Motion

The notion of constant of the motion is particularly simple to grasp in the Heisenberg "representation". A dynamical variable *which does not depend upon the time explicitly* is a constant of the motion if the observable  $C_H$  representing it in the Heisenberg "representation" remains constant in time. Consequently, its system of eigenvectors remains stationary and the statistical distribution of the results of a possible measurement of this quantity is always independent of the time at which this measurement is undertaken.

According to the above definition of the constant of the motion

$$i\hbar \frac{d}{dt} C_H = [C_H, H_H] = 0.$$

The constants of the motion are thus represented by *observables which commute with the Hamiltonian*. This result holds true equally well in the Schrödinger "representation" and in the Heisenberg "representation"

since the commutation relations are conserved in passing from one to the other. *← as you will show*

Moreover, since  $C_H$  is time-independent, it is equal to its initial value  $C_S$

$$C_H(t) = C_H(t_0) = C_S = C.$$

$$U^\dagger C_S U = C_S \quad C_S U = U C_S$$

If, in particular, the dynamical state of the system is represented by an eigenvector of  $C$  in the Heisenberg "representation",

$$C|\psi_H\rangle = c|\psi_H\rangle,$$

the variable  $C$  keeps the same well-defined value  $c$  in the course of time; the eigenvalue  $c$  is then said to be a *good quantum number*. As can easily be shown,  $C$  commutes with the evolution operator  $U(t, t_0)$ ; hence, the ket  $|\psi_S(t)\rangle$  of the Schrödinger "representation" remains forever in the subspace of the eigenvalue  $c$ ,

$$C|\psi_S(t)\rangle = c|\psi_S(t)\rangle.$$

$$\begin{aligned} C|\psi_H\rangle &= CU|\psi_S\rangle \\ &= UC|\psi_S\rangle = cU|\psi_S\rangle \\ &= Uc|\psi_S\rangle = c|\psi_S\rangle \end{aligned}$$

## 13. Equations of Motion for the Mean Values. Time-Energy Uncertainty Relation

Starting from the Heisenberg "representation", it is particularly simple to write down a differential equation for the mean value of a given observable  $A_H$ . Indeed, since  $|\psi_H\rangle$  is time-independent,

$$\frac{d\langle A \rangle}{dt} = \frac{d}{dt} \langle \psi_H | A_H | \psi_H \rangle = \langle \psi_H | \frac{dA_H}{dt} | \psi_H \rangle.$$

Using the Heisenberg equation, we arrive at eq. (V.72) once again:

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle [A, H] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle. \quad (\text{VIII.43})$$

In particular, one obtains the Ehrenfest equations (Ch. VI, § 2) by carrying out this manipulation on system (I).

As an application of eq. (VIII.43), we shall give a precise statement of the time-energy uncertainty relation (cf. Ch. IV, § 10). Consider a system whose Hamiltonian  $H$  does not explicitly depend upon the time, and let  $A$  be another observable of this system which does not depend upon the time explicitly. We consider the dynamical state of the system at a given time  $t$ . Let  $|\psi\rangle$  be the vector representing

that state. Call  $\Delta A$ ,  $\Delta E$  the root-mean-square deviations of  $A$  and of  $H$ , respectively. Applying the Schwarz inequality to the vectors  $(A - \langle A \rangle)|\psi\rangle$  and  $(H - \langle H \rangle)|\psi\rangle$  and carrying out the same manipulations as in § 4, we find after some calculations

$$\Delta A \cdot \Delta E > \frac{1}{2} |\langle [A, H] \rangle|, \quad (\text{VIII.44})$$

the equality being realized when  $|\psi\rangle$  satisfies the equation

$$(A - \alpha)|\psi\rangle = i\gamma(H - \epsilon)|\psi\rangle$$

where  $\alpha$ ,  $\gamma$ , and  $\epsilon$  are arbitrarily real constants [cf. eq. (VIII.10)]. However, according to eq. (VIII.43),  $\langle [A, H] \rangle = i\hbar d\langle A \rangle/dt$ ; the inequality (VIII.44) may equally well be written

$$\frac{\Delta A}{|d\langle A \rangle/dt|} \cdot \Delta E > \frac{1}{2}\hbar,$$

or else

$$\tau_A \cdot \Delta E > \frac{1}{2}\hbar \quad (\text{VIII.45})$$

if one puts

$$\tau_A = \frac{\Delta A}{|d\langle A \rangle/dt|}; \quad (\text{VIII.46})$$

$\tau_A$  appears as a time characteristic of the evolution of the statistical distribution of  $A$ . It is the time required for the center  $\langle A \rangle$  of this distribution to be displaced by an amount equal to its width  $\Delta A$ ; in other words, it is the time necessary for this statistical distribution to be appreciably modified. In this manner we can define a characteristic evolution time for each dynamical variable of the system.

Let  $\tau$  be the shortest of the times thus defined.  $\tau$  may be considered as a characteristic time of evolution of the system itself: whatever the measurement carried out on the system at an instant of time  $t'$ , the statistical distribution of the results is essentially the same as would be obtained at the instant  $t$ , as long as the difference  $|t - t'|$  is less than  $\tau$ .

According to the inequality (VIII.45), this time  $\tau$  and the energy spread  $\Delta E$  satisfy the time-energy uncertainty relation

$$\tau \cdot \Delta E > \frac{1}{2}\hbar. \quad (\text{VIII.47})$$

If, in particular, the system is in a stationary state,  $d\langle A \rangle/dt = 0$  no matter what  $A$ , and consequently  $\tau$  is infinite; however,  $\Delta E = 0$ , in conformity with relation (VIII.47).

#### 14. Intermediate "Representations"

The Schrödinger and Heisenberg "representations" are not the only possible ones. Any unitary transformation of the vectors and the observables of the Schrödinger (or Heisenberg) "representations" defines a new "representation". All these "representations" furnish strictly equivalent descriptions of quantum phenomena. In practice, one therefore adopts the "representation" which lends itself best to the solution of each particular problem.

Any problem of Quantum Mechanics essentially consists of a more or less complete and more or less precise determination of the properties of the unitary operator  $U(t, t_0)$ ; indeed, all the predictions of the theory are given by matrix elements of  $U(t, t_0)$  such as the one occurring in eq. (VIII.36). The solution of equation (VIII.32) is thus the central problem of the theory. When one knows an approximate solution  $U^{(0)}(t, t_0)$  of this equation, it is often convenient to set

$$U = U^{(0)}U'. \quad (\text{VIII.48})$$

Substituting this expression in eq. (VIII.32) and multiplying both sides from the left by the unitary operator  $U^{(0)\dagger}$ , we obtain the differential equation

$$i\hbar \frac{d}{dt} U' = U^{(0)\dagger} \left( H U^{(0)} - i\hbar \frac{dU^{(0)}}{dt} \right) U'; \quad (\text{VIII.49})$$

$U'$  is the solution of this equation satisfying the initial condition

$$U'(t_0, t_0) = 1.$$

If the approximation is justified,  $U'$  is an operator changing slowly as a function of time; this is actually quite evident from eq. (VIII.49), since in that case, the operator  $H U^{(0)} - i\hbar(dU^{(0)}/dt)$  almost vanishes. Equation (VIII.49), therefore, lends itself better than equation (VIII.32) to an approximate solution<sup>1)</sup>.

Since  $U^{(0)}$  is unitary, the operator

$$H^{(0)}(t) \equiv i\hbar \left[ \frac{d}{dt} U^{(0)}(t, t_0) \right] U^{(0)\dagger}(t, t_0)$$

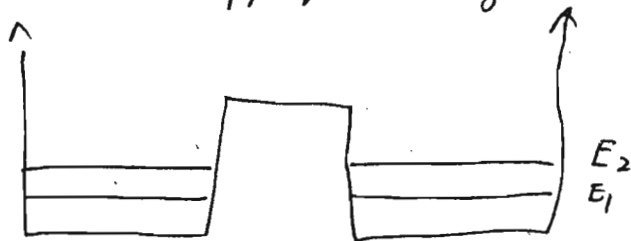
<sup>1)</sup> The procedure discussed here is the generalization to the differential equations between operators, of the method of variation of constants of the elementary theory of differential equations.

You saw that in Ohain 314 for

$$\psi(x,t) = a_1 e^{-E_1 t/\hbar} \varphi_1(x) + a_2 e^{-E_2 t/\hbar} \varphi_2(x)$$

that  $|\psi(x,t)|^2 = \text{const} + (\ ) \cos \frac{(E_2 - E_1)t}{\hbar}$

This would be applicable e.g. to a syst.



This frequency  $\omega = (E_2 - E_1)/\hbar$  means that for this non-stationary state, the probability oscillates from one side to the other in period  $T = 2\pi/\omega$ .

This is resonance (responsible for bonding)

One cannot observe both the going back and forth and the splitting of the energy at the same time.

To see resonance oscillations, need to make the time of observation considerably less than one period. The uncertainty in the time measurement must be much less than  $2\pi/\omega$ . But, by the uncertainty principle, the uncertainty in energy must be much larger than  $\hbar\omega$ , which is the splitting.

Thus, the splitting would be unobservable. To tell which state the system is, need to observe it for a time much longer than the period to reduce the uncertainty to less than  $\hbar\omega$  - then can't see the oscillation.

## APPENDIX

*Review of pertinent quantum mechanics***A.1 The standard two-state system**

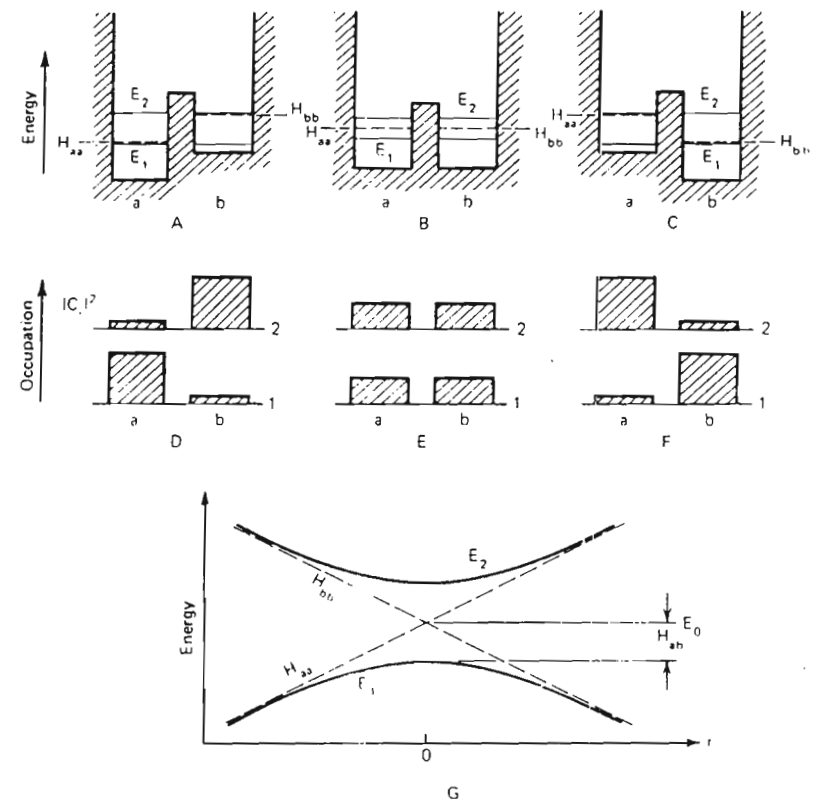
This review is intended to aid the dispersion to experimental workers in the biological field of the pertinent present knowledge of quantum mechanics which has grown up in the fields of physics and chemistry. For many readers this appendix is unnecessary but my own experience and the lessons of the Philadelphia Tunnelling Conference (November 1977), Chance *et al.* (eds.) (1979a), show that many of us need at least parts of it. I assume the reader has an elementary knowledge of quantum mechanics, at least as taught in general physics and chemistry courses: uncertainty principle. Schrodinger equation, etc. I suppose not all readers are familiar with transformation theory (Dirac, 1927, 1935; Jordan, 1927a, b) (how to change from one representation of a system to another) and some other concepts very pertinent to tunnelling discussion which I will try to define and explain in elementary terms. An excellent beginning text for further reading is the Feynman lectures (Feynman, Leighton & Sands, 1965). A few notions which the reader undoubtedly knows already will be repeated anyway for emphasis and completeness.

Quantum mechanics attempts to tell us what we can know about the future of a system, given what we know about it now. Since scientific knowledge is always of a statistical nature and never complete, quantum mechanics quite properly deals with *probabilities*. However, it does not deal with the probabilities directly. It deals with an underlying structure of 'probability *amplitudes*' from which probabilities can be calculated by taking the squares of the absolute values of the probability amplitudes. The 'amplitudes' themselves are, in general, complex numbers but the probabilities, of course, must be real and positive.

One describes a system in terms of a set of 'base-states'. The set must

be *complete* in that any state of the system to be contemplated must be describable as a combination of the base-states. Also the base-states must be *orthogonal* and *normalized*, that is, if the system is known to be in a single base-state it must have zero amplitude to be in any other and unit amplitude to be in itself. Different sets of base-states may be used to describe the same system. Sometimes one set or 'representation' is more convenient and sometimes another.

Fig. A.1. Tunnelling between two boxes. (A)-(C) Energy  $v$ , particle coordinate, as in Fig. 5.8. Boundaries of shaded areas are potential energy. Solid horizontal lines within boxes represent the energy eigenvalues, dashed lines the values of  $H_{aa}$  and  $H_{bb}$ . (A) Box  $a$  has lower energy than  $b$ . (B) Boxes have equal energy. (C) Box  $a$  has higher energy than  $b$ . (D), (E) and (F): Graphs of occupation of states corresponding to the potential-energy diagrams (A), (B) and (C), respectively. The occupations or probabilities are shown partitioned between base-states  $a$  and  $b$  and between eigenstates 1 and 2 according to equations (A.11). (G) A plot of the energies  $v$ , a continuous scale of separation between  $H_{aa}$  and  $H_{bb}$ . The abscissa is  $r = (H_{aa} - H_{bb})/2|H_{ab}|$ . See equations (A.9).



Physical quantities are represented as *operators* which affect the probability amplitudes by operating on them. Here we will be concerned mainly with the energy operator which is also called the '*Hamiltonian*'. We will discuss how this works in the case of a system which has only two base-states. This may sound like an oversimplified system but actually a large number of physical problems can be discussed in terms of the standard two-state system (Feynman *et al.*, 1965), including many of the tunnelling concepts.

Consider a system that consists of two boxes with one particle which can be in either box. There is a wall between the boxes that the particle cannot penetrate in a classical manner because it does not have enough kinetic energy. (This 'wall' is not a real one, penetration of which requires loss of energy (to heat) through inelastic collision with its material, but is, rather, a force-field which classically slows the particle on entering (to stopping if the particle does not have enough momentum to get over the hump) and speeds it on leaving.) The particle can, however, get from one side to the other by quantum-mechanical tunnelling. Fig. A.1B shows the situation on an energy *v.* particle-coordinate diagram.

#### A.1.1 The Hamiltonian

Let  $C_a$  be the probability amplitude for the system to be in base-state *a*, described as 'particle in box *a*', and  $C_b$  the amplitude to be in base-state *b*, described as 'particle in box *b*'. The states *a* and *b* form a complete set of base-states for this two-state system.  $C_a$  and  $C_b$  can be complex numbers. The time operator,  $i\hbar d/dt$ , and the energy operator,  $H$ , act on  $C_a$  and  $C_b$  as follows:

$$\left. \begin{aligned} i\hbar dC_a/dt &= H_{aa}C_a + H_{ab}C_b, \\ i\hbar dC_b/dt &= H_{ba}C_a + H_{bb}C_b. \end{aligned} \right\} \quad (\text{A.1})$$

The  $H$ s can be set forth in a square array:

$$\mathbf{H} = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}, \quad (\text{A.2})$$

which is called the '*Hamiltonian matrix*'. The  $H$ s are the '*matrix elements*'. They apply strictly to the base-states *a* and *b*. The matrix (A.2) is the *Hamiltonian* of the system 'in the *a, b* representation'. Another set of base-states will take a different set of matrix elements. It is seen from equations (A.1) that  $H_{aa}$  is the effect of  $C_a$  itself on  $dC_a/dt$ .  $H_{aa}$  is the energy of the system in state *a* if there were no influence on it from state *b*, that is, no possibility of the particle tunnelling from one box to the other. Likewise  $H_{bb}$  is the energy of the system in state *b* if there were no effect

from *a*;  $H_{ab}$  is the effect of  $C_b$  on  $dC_a/dt$  and  $H_{ba}$  is the effect of  $C_a$  on  $dC_b/dt$ . They represent the rate at which probability *amplitude* flows from one state to the other. If equations (A.1) were divided through by  $\hbar$  they would have the appearance of chemical rate equations with first-order rate constants ( $H/\hbar$ ), except for the presence of the imaginary root,  $i$  ( $=\sqrt{-1}$ ). In order that the energy be real it is necessary that the diagonal elements  $H_{aa}$  and  $H_{bb}$  be real and that  $H_{ab} = H_{ba}^*$ , where '\*' means 'complex conjugate'. Thus,

$$|H_{ab}| = |H_{ba}|.$$

#### A.1.2 Eigenstates and eigenvalues

(a) *Symmetrical case.* Equations (A.1) can be solved easily if the  $H$ s do not change with time. To simplify further, let  $H_{aa} = H_{bb} = E_0$ . The particle has the same energy in either box. Let, also,

$$H_{ab} = H_{ba} = -A.$$

Then if we add the equations (A.1) we get:

$$i\hbar d(C_a + C_b)/dt = (E_0 - A)(C_a + C_b). \quad (\text{A.3})$$

Subtracting the second of (A.1) from the first gives

$$i\hbar d(C_a - C_b)/dt = (E_0 + A)(C_a - C_b). \quad (\text{A.4})$$

The form of these equations allows a simpler description of the states: suppose we let  $C_1 = (C_a + C_b)/\sqrt{2}$  be the amplitude to be in a state we'll call '1' and  $C_2 = (C_a - C_b)/\sqrt{2}$  be the amplitude to be in a state called '2'. (The  $\sqrt{2}$  is necessary for proper normalization). Then equations (A.3) and (A.4) become

$$\left. \begin{aligned} i\hbar dC_1/dt &= E_1 C_1, \\ i\hbar dC_2/dt &= E_2 C_2. \end{aligned} \right\} \quad (\text{A.5})$$

where  $E_1 = E_0 - A$  and  $E_2 = E_0 + A$ .

States 1 and 2 may be taken as a new set of base-states. In this representation, equations (A.5) show that the *Hamiltonian matrix* is

$$\mathbf{H} = \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix}, \quad (\text{A.6})$$

where  $H_{11} = E_1$  and  $H_{22} = E_2$ . We have '*diagonalized*' the matrix.

The equations (A.5) are seen to be independent of each other and solutions are

$$C_1(t) = C_1(0)e^{-iE_1 t/\hbar} \text{ and } C_2(t) = C_2(0)e^{-iE_2 t/\hbar}. \quad (\text{A.7})$$

$C_1$  and  $C_2$  oscillate in the complex plane with radian frequencies  $E_1/\hbar$  and  $E_2/\hbar$  respectively.

Their probabilities,  $|C_1|^2$  and  $|C_2|^2$ , stay constant with time. States 1 and 2 are, thus, stationary states or *eigenstates*. Their energy *eigenvalues* are  $E_1$  and  $E_2$ . The *splitting* between the two energies is seen to be  $E_2 - E_1 = 2A = -2H_{ab}$ . This splitting is the result of the particle's ability to tunnel from one box to the other. It is shown in Fig. A.1 B. (Note: other phase factors than  $-1$  could have been used for  $H_{ab}$  and  $H_{ba}$  but the results would be practically the same.)

The representation is in terms of eigenstates whenever the matrix is diagonalized. On the other hand if off-diagonal elements had finite values this would indicate that the base-state amplitudes would be subject to change over a period of time and so such base-states are not stationary states.

If the particle is initially in *a*, how fast does it get into *b* and what is the future time-course of the system? This is answered by noting that from the definition of  $C_1$  and  $C_2$  if  $C_a(0) = 0$  then  $C_1(0) = C_2(0) = 1/\sqrt{2}$ . Also note, from the definition, that

$$C_a = (C_1 + C_2)/\sqrt{2} \text{ and } C_b = (C_1 - C_2)/\sqrt{2}.$$

If we substitute the solutions (A.7) for  $C_1$  and  $C_2$  into these expressions we get

$$\begin{aligned} C_a(t) &= e^{-iE_1t/\hbar} + e^{-iE_2t/\hbar} = e^{-iE_0t/\hbar} \cos(At/\hbar), \\ C_b(t) &= e^{-iE_1t/\hbar} - e^{-iE_2t/\hbar} = i e^{-iE_0t/\hbar} \sin(At/\hbar), \\ |C_a|^2 &= \cos^2(At/\hbar) = \frac{1}{2} + \left(\frac{1}{2}\right)\cos(2At/\hbar), \\ |C_b|^2 &= \sin^2(At/\hbar) = \frac{1}{2} - \left(\frac{1}{2}\right)\cos(2At/\hbar). \end{aligned} \quad (\text{A.8})$$

Equations (A.8) show that the probability of finding the particle oscillates back and forth between the two boxes with a frequency equal to the splitting ( $E_2 - E_1$ ) divided by  $\hbar$ . This is the 'resonance' phenomenon (familiar to chemists) occurring in molecules with two equivalent electronic structures. The lowering of  $E_1$  below  $E_0$  is the 'resonance lowering' of energy and it results from the ability of the particle (electron) to go back and forth between the two structures. It is always accompanied by the raising of a companion state to a higher energy. The time-course of  $|C_b|^2$  is plotted in Fig. A.2 A.

The system must be in state 1 to be in the lower energy state. How are states 1 and 2 to be described? If the system is known to be in state 1 then  $C_1 = 1$  and  $C_2 = 0$ . From the definitions we then have

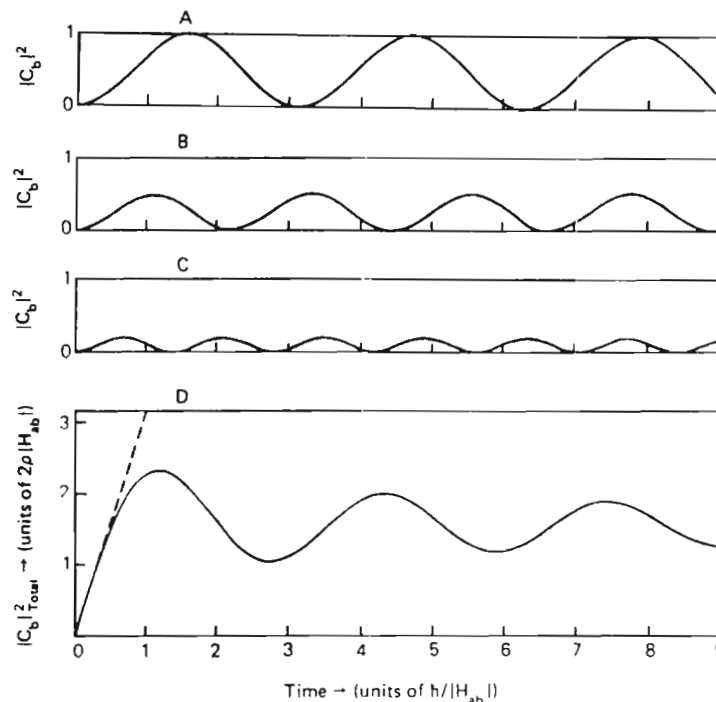
$$C_a + C_b = \sqrt{2} \text{ and } C_a - C_b = 0.$$

Thus in state 1 we have  $C_a = C_b = 1/\sqrt{2}$ . The particle has equal probability to be in both boxes ( $\frac{1}{2}$  in each). If the system is in state 2 then  $C_1 = 0$

and  $C_2 = 1$  and  $C_a + C_b = 0$  and  $C_a - C_b = \sqrt{2}$ . Thus in state 2:  $C_a = -C_b = 1/\sqrt{2}$ . Again we have equal probability ( $\frac{1}{2}$  each) to be in both *a* and *b* but the *amplitudes* to be in *a* and in *b* are *symmetrical* in state 1 and *antisymmetrical* in state 2.

Note that one cannot observe both the going back and forth and the splitting of the energy at the same time. To observe the resonance oscillation one should make observations at intervals of time considerably less than one period, which is  $\hbar/(2A)$ . The uncertainty in the time measurements must be considerably less than  $\hbar/(2A)$ . By the uncertainty principle the uncertainty in energy must then be considerably larger than  $2A$ , which is the splitting. Thus the splitting would be unobservable. To be able to tell in which of the two energy eigenstates the system is, one would have to observe it over a period of time long enough to reduce the uncertainty in energy to considerably less than  $2A$ . By the uncertainty principle the observation would require a time considerably longer than  $\hbar/(2A)$  the period of the oscillation. Therefore, if one could measure the

Fig. A.2. Time-course of  $|C_b|^2$ , the occupancy of box *b*, starting with the particle in box *a* at time 0. (A)  $H_{bb} = H_{aa}$ . (B)  $H_{bb} = H_{aa} \pm 2|H_{ab}|$ . (C)  $H_{bb} = H_{aa} \pm 4|H_{ab}|$ . (D) Distributed  $H_{bb}$ ;  $\rho$  = number of  $H_{bb}$  values per unit of energy.



energy accurately enough to know that the system is in state 1 (or in state 2) one could observe the occupancy of the boxes only as an average over a number of periods and would find simply equal probability to be in each box.

(b) *Energies different.* Next, we consider the two-box case in which the particle does not have the same energy in each box.  $H_{aa} \neq H_{bb}$ . Let  $r = (H_{aa} - H_{bb})/(2A)$  be a dimensionless representation of this energy difference where, as before,  $A = -H_{ab} = -H_{ba}$ , is considered to remain constant as  $r$  varies. Let  $E_0 = (H_{aa} + H_{bb})/2$  be the mean of the two self-energies. For constant  $H$ s the equations (A.1) can be solved with a little algebra and the energy eigenvalues are found to be

$$\left. \begin{aligned} E_1 &= E_0 - A(r^2 + 1)^{\frac{1}{2}}, \\ E_2 &= E_0 + A(r^2 + 1)^{\frac{1}{2}}. \end{aligned} \right\} \quad (\text{A.9})$$

The difference,  $E_2 - E_1$ , is now  $2A(r^2 + 1)^{\frac{1}{2}}$ . At large values of  $r$  this approaches  $H_{aa} - H_{bb}$ , indicating that any resonance effect has become small and the eigenvalues are almost the same as what the energies in the individual boxes would be if separated. The behaviour of the energies is illustrated in Fig. A.1, A-C, G.

The difference between  $E_1$  and  $H_{bb}$  or between  $E_2$  and  $H_{aa}$  at large values of  $r$  (or between  $E_1$  and  $H_{aa}$  or between  $E_2$  and  $H_{bb}$  at large negative values of  $r$ ) can be approximated from equation (A.9) with:

$$H_{bb} - E_1 \approx \frac{|H_{ab}|^2}{(H_{aa} - H_{bb})}. \quad (\text{A.10})$$

This is just the formula for the second-order perturbation of the energy level  $H_{bb}$  by  $H_{aa}$ . Thus one can think of  $H_{aa}$  perturbing  $H_{bb}$  by the amount necessary to lower it to  $E_1$  (at large value of  $r$ ). Similarly for  $E_2 - H_{aa}$  at large  $r$  or  $H_{aa} - E_1$  at large negative  $r$ , etc. The  $a, b$  representation would be diagonal if  $|H_{ab}| = 0$  as if the two boxes were moved far from each other or separated by an infinitely high barrier. Lowering the barrier or moving the boxes closer allows them to 'perturb' each other.

Let  $A_1$  be the amplitude to be in state  $a$  if the system is known to be in state 1,  $B_1$  the amplitude to be in  $b$ , given state 1,  $A_2$  and  $B_2$  the amplitudes to be in  $a$  and  $b$ , respectively, given that the system is in state 2. Although other phase factors are possible, a consistent set is:

$$\left. \begin{aligned} A_1 &= \left\{ \frac{1}{2} [1 - r/(r^2 + 1)^{\frac{1}{2}}] \right\}^{\frac{1}{2}}, \\ B_1 &= \left\{ \frac{1}{2} [1 + r/(r^2 + 1)^{\frac{1}{2}}] \right\}^{\frac{1}{2}}, \\ A_2 &= \left\{ \frac{1}{2} [1 + r/(r^2 + 1)^{\frac{1}{2}}] \right\}^{\frac{1}{2}}, \\ B_2 &= - \left\{ \frac{1}{2} [1 - r/(r^2 + 1)^{\frac{1}{2}}] \right\}^{\frac{1}{2}}. \end{aligned} \right\} \quad (\text{A.11})$$

The squares of these amplitudes are illustrated in Fig. A.1 D-F.

If at  $t = 0$  the particle is in box  $a$ , then the time-course of the probabilities to be in the two boxes become:

$$\left. \begin{aligned} |C_a|^2 &= 1 - (r^2 + 1)^{-1} (1 - \cos^2(\omega_{21} t/2)) \\ &= 1 - \frac{1}{2}(r^2 + 1)^{-1} (1 - \cos(\omega_{21} t)), \\ |C_b|^2 &= (r^2 + 1)^{-1} \sin^2(\omega_{21} t/2) \\ &= \frac{1}{2}(r^2 + 1)^{-1} (1 - \cos(\omega_{21} t)), \end{aligned} \right\} \quad (\text{A.12})$$

where  $\omega_{21} = (E_2 - E_1)/\hbar = 2A(r^2 + 1)^{\frac{1}{2}}/\hbar$ . As  $r^2$  increases the particle tends to stay more and more in the box it started from, the excursions into the other box becoming smaller in amplitude and higher in frequency. Two examples are plotted in Fig. A.2 B, C.

For large  $r$  the coefficient  $A_1$  can be approximated:

$$A_1 \approx A/(H_{aa} - H_{bb}) = H_{ab}/(H_{bb} - H_{aa}). \quad (\text{A.13})$$

This is the perturbation theory expression for the amount of state  $a$  amplitude to be mixed into the amplitude for state  $b$  (to give the state 1) because of perturbation from state  $a$  (assuming the situation corresponding to large  $r$ ).

### A.1.3 Derivation of the 'golden rule'

The tunnelling reactions discussed in this review are not seen to oscillate as in the above examples. Nor do they show a time-course

Fig. A.3. Energy levels for an ensemble of box-pairs.

