Note for Quantum Mechanics

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Contents

Chapter 1

The Principles of Quantum Mechanics by Dirac.

1.1 Superposition and Indeterminacy

1.1.1 Notes

1. The intermediate character of the state formed by superposition expresses itself through the probability of a particular result for an observation being intermediate between the corresponding probabilities for the original states, not trough the result itself being intermediate between the corresponding results for the original states.

2. Each state of a dynamical system at a particular time corresponds to a ket vector, the correspondences being such that if a state results from the superposition of certain other states, its corresponding ket vector is expressible linearly in terms of the corresponding ket vectors of the other states, and conversely.

3. If the ket vector corresponding to a state is multiplied by any complex number except 0, the resulting ket vector will correspond to the same state.[1]

1.2 Dynamical Variables and Observables

1.2.1 Definitions

Definition 1.2.1 Linear Operator *A linear operator α satisfies:*

$$\alpha\{|A\rangle + |A'\rangle\} = \alpha|A\rangle + \alpha|A'\rangle, \alpha\{c|A\rangle\} = c\alpha|A\rangle \tag{1.2.1}$$

Definition 1.2.2 Real Linear Operator *A linear operator that equals its adjoint.*

Definition 1.2.3 Observable *A real dynamical variable whose eigenstates form a complete set; any quantity that can be measured is an observable.*

Definition 1.2.4 Hilbert space *The space of bra or ket vectors when the vectors are restricted to be of finite length and to have finite scalar products.*

[1] All the states of the dynamical system are in one-one correspondence with all the possible directions for a ket vector, no distinction being made between the directions of the ket vectors $|A\rangle$ and $-|A\rangle$.

1.2.2 Notes

1. If the dynamical system is in an eigenstate of a real dynamical variable ξ, belonging to the eigenvalue ξ', then a measurement of ξ will certainly give as result the number ξ'. Conversely, if the system is in a state such that a measurement of a real dynamical variable ξ is certain to give one particular result (instead of giving one or other of several possible results according to a probability law, as is in general the case), then the state is an eigenstate of ξ and the result of the measurement is the eigenvalue of ξ to which this eigenstate belongs.

2. When we measure a real dynamical variable ξ, the disturbance involved in the act of measurement causes a jump in the state of the dynamical system.

   From physical continuity, if we make a second measurement of the same dynamical variable ξ immediately after the first, the result of the second measurement must be the same as that of the first. Thus after the first measurement has been made, there is no indeterminacy in the result of the second. Hence, after the first measurement has been made, the system is in an eigenstate of the dynamical variable ξ, the eigenvalue it belongs to being equal to the result of the first measurement. This conclusion must still hold if the second measurement is not actually made. In this way we see that a measurement always causes the system to jump into an eigenstate of the dynamical variable that is being measured, the eigenvalue this eigenstate belongs to being equal to the result of the measurement.

3. If the measurement of the observable ξ for the system in the state corresponding to $|x\rangle$ is made a large number of times, the average of all the results obtained will be $\langle x|\xi|x\rangle$, provided $|x\rangle$ is normalized.

4. $$P_a = \langle x|\delta_{\xi a}|x\rangle \tag{1.2.2}$$

5. If certain observables commute, there exist states for which they all have particular values. Thus one can give a meaning to several commuting observables having values at the same time. Further, we see that for any state one can give a meaning to the probability of particular results being obtained for simultaneous measurements of several commuting observables.

6. Any two or more commuting observables may be counted as a single observable, the result of a measurement of which consists of two or more numbers.

1.2.3 Theorems and Proofs

Theorem 1.2.1 *If ξ is a real linear operator, and*

$$\xi^m|P\rangle = 0 \tag{1.2.3}$$

for a particular ket $|P\rangle$, m being a positive integer, then

$$\xi|P\rangle = 0$$

Proof 1.2.1 *To prove this theorem, take first the case when $m = 2$. Equation 1.2.3 then gives*

$$\langle P|\xi^2|P\rangle = 0 \tag{1.2.4}$$

showing that the ket $\xi|P\rangle$ multiplied by the conjugate imaginary bra $\langle P|\xi$ is zero. Considering that

$$\langle P|\xi^2|P\rangle = \langle P|\xi\,\xi|P\rangle$$

Thus $\xi|P\rangle$ must be zero. Thus the theorem is proved for $m = 2$.
Now take $m > 2$ and put

$$\xi^{m-2}|P\rangle = |Q\rangle$$

which transforms the equation 1.2.3 into

$$\xi^2|Q\rangle = 0$$

which leads to

$$\xi|Q\rangle = 0 \Rightarrow \xi^{m-1}|P\rangle = 0$$

Thus the whole theorem is proved.

Theorem 1.2.2 *Two eigenvectors of a real dynamical varaiable belonging to different eigenvalues are orthogonal.*

Proof 1.2.2 *let $|\xi'\rangle$ and $|\xi''\rangle$ be two eigenkets of the real dynamical variable ξ, belonging to the eigenvalues ξ' and ξ'' respectively. Then we have the equations*

$$\xi|\xi'\rangle = \xi'|\xi'\rangle \tag{1.2.5}$$

$$\xi|\xi''\rangle = \xi''|\xi''\rangle \tag{1.2.6}$$

Taking the conjugate imaginary of 1.2.5, we get

$$\langle\xi'|\xi = \xi'\langle\xi'|$$

Thus

$$\langle\xi'|\xi|\xi''\rangle = \xi'\langle\xi'|\xi''\rangle$$

While 1.2.6 gives

$$\langle\xi'|\xi|\xi''\rangle = \xi''\langle\xi'|\xi''\rangle$$

Hence

$$(\xi' - \xi'')\langle\xi'|\xi''\rangle = 0 \tag{1.2.7}$$

If $\xi' \neq \xi''$, $\langle\xi'|\xi\rangle = 0$.

Theorem 1.2.3 *If a real linear operator ξ satisfies an algebraic equation*

$$\phi(\xi) = \xi^n + a_1\xi^{n-1} + a_2\xi^{n-2} + ... + a_n = 0, \tag{1.2.8}$$

the coefficients a being numbers. Let 1.2.8 be the simplest[2] algebraic equation that ξ satisfies. Then

[2]其中'simplest' 应指代为最低阶。

1. *The number of eigen values of ξ is n.*

2. *There are so many eigenkets of ξ that any ket whatever can be expressed as a sum of such eigenkets.*

Proof 1.2.3 *The algebraic form $\psi(\xi)$ can be factorized into n linear factors, the result being*

$$\psi(\xi) = (\xi - c_1)(\xi - c_2)(\xi - c_3)....(\xi - c_n) \tag{1.2.9}$$

where the c's are numbers, not assumed to be all different.

Let the quotient when $\psi\xi$ is divided by $(\xi - c_r)$ be $\chi_r(\xi)$, so that

$$\psi(\xi) = (\xi - c_r)\chi_r(\xi)(r = 1, 2, 3, ..., n)$$

Then for any ket $|P\rangle$,

$$(\xi - c_r)\chi_r(\xi)|P\rangle = \psi(\xi)|P\rangle = 0 \tag{1.2.10}$$

Now $\chi_r(\xi)|P\rangle$ cannot vanish for every ket $|P\rangle$, as otherwise $\chi_r(\xi)$ itself would vanish and we should have ξ satisfying an algebraic equation of degree $n - 1$, which would contradict the assumption that 1.2.8 is the simplest equation that ξ satisfies.

If we choose $|P\rangle$ so that $\chi_r(\xi)|P\rangle$ does not vanish, then equation 1.2.10 shows that $\chi_r(\xi)|P\rangle$ is an eigenket of ξ, belonging to the eigenvalue c_r. The argument holds for each value of r from 1 to n.

No other number can be an eigenvalue of ξ, since if ξ' is any eigenvalue, belonging to an eigenket $|\xi'\rangle$,

$$\xi\xi' = \xi'|\xi'\rangle$$

and we can deduce

$$\phi(\xi)|\xi'\rangle = \phi(\xi')|\xi'\rangle$$

considering that $\psi(\xi) = 0$, we must have $\phi(\xi') = 0$, which means that ξ' also belongs to the existing eigenvalues.

To complete the proof of the first property we must verify that the c's are all different. Suppose the c's are not all different and c_s occurs m times ($m > 1$). Then $\phi(\xi)$ is of the form

$$\phi(\xi) = (\xi - c_s)^m\theta(\xi),$$

with $\theta(\xi)$ a rational integral function of ξ. Equation 1.2.8 reveals that

$$(\xi - c_s)^m\theta(\xi)|A\rangle = 0 \tag{1.2.11}$$

for any ket $|A\rangle$. Since c_s is an eigenvalue of ξ it must be real. $\xi - c_s$ for ξ and $\theta(\xi)|A\rangle$ for $|P\rangle$. With regard of theorem 1.2.1 we can infer that

$$(\xi - c_s)\theta(\xi)|A\rangle = 0.$$

Since the ket $|A\rangle$ is arbitrary,

$$(\xi - c_s)\theta(\xi) = 0,$$

which contradicts the assumption that 1.2.8 is the simplest equation that ξ satisfies. The first property is proved.

Let $\chi_r(c_r)$ be the number obtained when c_r is substituted for ξ in the algebraic expression $\chi_r(\xi)$. Since the c's are all different, $\chi_r(c_r)$ cannot vanish. Consider now the expression

$$\sum_r \frac{\chi_r(\xi)}{\chi_r(c_r)} - 1. \tag{1.2.12}$$

If c_s is substituted for ξ here, every term in the sum vanishes except the one for which $r = s$, since $\chi_r(\xi)$ contains $(\xi - c_s)$ as a factor when $r \neq s$, and the term for which $r = s$ is unity, so the whole expression vanishes. Thus the expression 1.2.12 vanishes when ξ is put equal to any of the n numbers $c_1, c_2, ..., c_n$. Since, however, the expression is only of degree $n - 1$ in ξ, it must vanish identically. If we now apply the linear operator 1.2.12 to an arbitrary ket $|P\rangle$ and equate the result to 0, we get

$$|P\rangle = \sum_r \frac{1}{\chi_r(c_r)} \chi_r(\xi)|P\rangle. \tag{1.2.13}$$

Each term in the sum on the right here is, according to 1.2.10, an eigenket of ξ, if it does not vanish. Equation 1.2.13 thus expresses the arbitrary ket $|P\rangle$ as a sum of eigenkets of ξ, and thus the second property is proved.

Theorem 1.2.4 *The expansion of a ket $|P\rangle$ in the form of the right-hand side of 1.2.28 is unique.*

Proof 1.2.4 *Suppose that two different expansions of $|P\rangle$ are possible. Then by subtracting one from the other, we get an equation of the form*

$$0 = \int |\xi' a\rangle \, d\xi' + \sum_s |\xi^s b\rangle, \tag{1.2.14}$$

a and b being used as new labels for the eigenvectors, and the sum over s including all terms left after the subtraction of one sum from the other. If there is a term in the sum in 1.2.14 referring to an eigenvalue ξ^t not in the range, we get, by multiplying 1.2.14 on the left by $\langle \xi^t b|$ and using the orthogonality theorem 1.2.2,

$$0 = \langle \xi^t b|\xi^t b\rangle$$

which is contradictory. Again, if the integrand in 1.2.14 does not vanish for some eigenvalue ξ'' not equal to any ξ^s occuring in the sum, we get, by multiplying 1.2.14 on the left by $\langle \xi'' a|$ and using the orthogonality theorem 1.2.2,

$$0 = \int \langle \xi'' a|\xi' a\rangle \, d\xi' \tag{1.2.15}$$

which is also contradictory. Finally, if there is a term in the sum in 1.2.14 referring to an eigenvalue ξ^t in the range, we get, multiplying 1.2.14 on the left by $\langle \xi^t b|$,

$$0 = \int \langle \xi^t b|\xi' a\rangle \, d\xi' + \langle \xi^t b|\xi^t b\rangle \tag{1.2.16}$$

and multiplying 1.2.14 on the left by $\langle \xi^t a|$

$$0 = \int \langle \xi^t a|\xi' a\rangle \, d\xi' + \langle \xi^t a|\xi^t b\rangle \tag{1.2.17}$$

Now the integral in 1.2.17 is finite, so $\langle \xi^t a|\xi^t b\rangle$ *and* $\langle \xi^t b|\xi^t a\rangle$ *is finite. The integral in 1.2.16 must then be zero, so* $\langle \xi^t b|\xi^t b\rangle$ *is zero and we again have a contradiction. Thus every term in 1.2.14 must vanish and the expansion of a ket* $|P\rangle$ *in the form of the right-hand side must be unique.*

Theorem 1.2.5 *The conjugate complex of the linear operator* $f(\xi)$ *is the conjugate complex function* $\bar{f}$ *of* ξ*.*

Proof 1.2.5

$$\langle \xi'|\overline{f(\xi)} = \bar{f}(\xi')\langle \xi'| \tag{1.2.18}$$

$$\begin{aligned}\langle \xi''|\overline{f(\xi)}|P\rangle &= \bar{f}(\xi'')\langle \xi''|P\rangle \\ &= \int \bar{f}(\xi'')\langle \xi''|\xi' c\rangle\, d\xi' + \sum_r \bar{f}(\xi'')\langle \xi''|\xi^r d\rangle \\ &= \int \bar{f}(\xi'')\langle \xi''|\xi' c\rangle\, d\xi' + \bar{f}(\xi'')\langle \xi''|\xi'' d\rangle\end{aligned}$$

$$\langle \xi''|\bar{f}(\xi)|P\rangle = \iint \bar{f}(\xi'')\langle \xi''|\xi' c\rangle\, d\xi' + \bar{f}(\xi'')\langle \xi''|\xi'' d\rangle \tag{1.2.19}$$

Q.E.D

Theorem 1.2.6 *If two observables* ξ *and* η *commute there exist so many simultaneous eigenstates that they form a complete set.*

Proof 1.2.6 *Take an eigenket of* η*,* $|\eta'\rangle$ *say, belonging to the eigenvalue* η'*, and expand it in terms of eigenkets of* ξ *in the form of the right-hand side,*

$$|\eta'\rangle = \int |\xi'\eta' c\rangle\, d\xi' + \sum_r |\xi^r \eta' d\rangle \tag{1.2.20}$$

The eigenkets of ξ *and on the right-hand side here have* η' *inserted in them as an extra label, in order to remind us that they come from the expansion of a special ket vector, mainly* $|\eta'\rangle$*, and not a general one. We can now show that each of these eigenkets of* ξ *is also an eigenket of* η *belonging to the eigenvalue* η'*. We have*

$$0 = (\eta - \eta')|\eta'\rangle = |\eta'\rangle = \int (\eta - \eta')|\xi'\eta' c\rangle\, d\xi' + \sum_r (\eta - \eta')|\xi^r \eta' d\rangle \tag{1.2.21}$$

Now the ket $(\eta - \eta')|\xi^r \eta' d\rangle$ *satisfies*

$$\xi(\eta - \eta')|\xi^r \eta' d\rangle = (\eta - \eta')\xi|\xi^r \eta' d\rangle = (\eta - \eta')\xi^r|\xi^r \eta' d\rangle = \xi^r(\eta - \eta')|\xi^r \eta' d\rangle \tag{1.2.22}$$

showing that it is an eigenket of ξ *belonging to the eigenvalue* ξ^r*, and similarly the ket* $(\eta - \eta')|\xi^r \eta' c\rangle$ *is an eigenket of* ξ *belonging to the eigenvalue* ξ'*. Thus it gives an integral plus a sum of eigenkets of* ξ *equal to zero, which, as we have seen, is impossible unless the integrand and every term in the sum vanishes. Hence*

$$(\eta - \eta')|\xi^r \eta' c\rangle = (\eta - \eta')|\xi^r \eta' d\rangle = 0 \tag{1.2.23}$$

so that all the kets appearing on the right-hand side are eigen kets of η *as well as of* ξ*. Now the equation gives* $|\eta'\rangle$ *expanded in terms of simultaneous eigenkets of* ξ *and* η*. Since any ket can be expanded in terms of eigenkets* $|\eta'\rangle$ *of* η*, it follows that any ket can be expanded in terms of simultaneous eigenkets of* ξ *and* η*, and thus the simultaneous eigenstates form a complete set.*

Theorem 1.2.7 *If ξ and η are two observables such that their sumultaneous eigenstates form a complete set, then ξ and η commute.*

Proof 1.2.7 *If $|\xi'\eta'\rangle$ is a simultaneous eigenket belonging to the eigenvalues ξ' and η',*

$$(\xi\eta - \eta\xi)|\xi'\eta'\rangle = (\xi'\eta' - \eta'\xi')|\xi'\eta'\rangle = 0 \tag{1.2.24}$$

Since the simultaneous eigenstates form a complete set, an arbitrary ket $|P\rangle$ can be expanded in terms of simultaneous eigenkets $|\xi'\eta'\rangle$, for each of which 1.2.24 holds, and hence

$$(\xi\eta - \eta\xi)|P\rangle = 0 \tag{1.2.25}$$

$$\xi\eta - \eta\xi = 0 \tag{1.2.26}$$

1.2.4 Digests

Let us examine mathematically the condition for a real dynamical variable ξ to be an observable. Its eigenvalues may consist of a (finite or infinite) discrete set of numbers, or alternatively, they may consist of all numbers in a certain range, such as all numbers lying between a and b. In the former case, the condition that any state is dependent on eigenstates of ξ is that any ket can be expressed as a sum of eigenkets of ξ. In the latter case the condition needs modification, since one may have an integral instead of a sum, i.e. a ket $|P\rangle$ may be expressible as an integral of eigenkets of ξ,

$$|P\rangle = \int |\xi'\rangle \, d\xi', \tag{1.2.27}$$

$|\xi'\rangle$ being an eigenket of ξ belonging to the eigenvalue ξ' and the range of integration being the range of eigenvalues, as such a ket is dependent on eigenkets of ξ. Not every ket dependent on eigenkets of ξ can be expressed in the form of the right-hand side of 1.2.27, since one of the eigenkets itself cannot, and more generally any sum of eigenkets cannot. The condition for the eigenstates of ξ to form a complete set must thus be formulated, that any ket $|P\rangle$ can be expressed as an integral plus a sum of eigenkets of ξ, i.e.

$$|P\rangle = \int |\xi' c\rangle d\xi' + \sum_r |\xi^r d\rangle, \tag{1.2.28}$$

where the $|\xi' c\rangle$, $|\xi^r d\rangle$ are all eigenkets of ξ, the labels and d being inserted to distinguish them when the eigenvalues ξ and ξ^r are equal, and where the integral is taken over the whole range of eigenvalues and the sum is taken over any selection of them. If this condition is satisfied in the case when the eigenvalues of ξ consist of a range of numbers, then ξ is an observable.

The reciprocal of an observable exists if the observable does not have the eigenvalue zero. If the observable a does not have the eigenvalue zero, the reciprocal observable, which we call α^{-1} or $1/\alpha$, will satisfy

$$\alpha^{-1}|\alpha'\rangle = \alpha'^{-1}|\alpha'\rangle, \tag{1.2.29}$$

where $|\alpha'\rangle$ is an eigenket of α belonging to the eigenvalue α'. Hence

$$\alpha\alpha^{-1}|\alpha'\rangle = \alpha\alpha'^{-1}|\alpha'\rangle = |\alpha'\rangle \tag{1.2.30}$$

Since this holds for any eigenket $|\alpha'\rangle$, we must have

$$\alpha\alpha^{-1} = 1. \tag{1.2.31}$$

Similarly,

$$\alpha^{-1}\alpha = 1 \tag{1.2.32}$$

Either of these equations is sufficient to determine α^{-1} completely, provided α does not have the eigenvalue 0. To prove this in the case of 1.2.31, let x be any linear operator satisfying the equation

$$\alpha x = 1 \tag{1.2.33}$$

and multiply both sides on the left by the α^{-1} defined, The result is

$$\alpha^{-1}\alpha x = \alpha^{-1} \tag{1.2.34}$$

and hence $x = \alpha^{-1}$.

$$(\alpha\beta\gamma...)^{-1} = ...\gamma^{-1}\beta^{-1}\alpha^{-1} \tag{1.2.35}$$

The square root of an observable α always exists, and is real if α has no negative eigenvalues. We write it $\sqrt{\alpha}$ or $\alpha^{\frac{1}{2}}$. It satisfies

$$\sqrt{\alpha}|\alpha'\rangle = \pm\sqrt{\alpha'}|\alpha'\rangle \tag{1.2.36}$$

$$\sqrt{\alpha}\sqrt{\alpha} = \alpha \tag{1.2.37}$$

1.3 Representations

Representations are of great importance in the physical interpretation of quantum mechanics as they provide a convenient method for obtaining the probabilities of observables having given values.

1.3.1 Definitions

Definition 1.3.1 representation *The way in which the abstract quantities are to be replaced.*

Definition 1.3.2 representative *The set of numbers that replace an abstract quantity.*

Definition 1.3.3 basic bras *A complete set of bra vectors, i.e. a set such that any bra can be expressed linearly in terms of them (as a sum or an integral or possibly an integral plus a sum).*

Definition 1.3.4 orthogonal representation *The basics bras are all independent, and also satisfy the more stringent condition that any two of them are orthogonal.*

Definition 1.3.5 complete set of commuting observables *A set of observables which all commute with one another and for which there is only one simultaneous eigenstate belonging to any set of eigenvalues.*

Definition 1.3.6 the representative of a bra *the conjugate complex of the representative of the conjugate imaginary ket.*

Definition 1.3.7 weight function of the representation *the ρ' in*

$$\sum_{\xi'_1..\xi'_v} \int .. \int |\xi'_1...\xi'_u\rangle\rho' \, d\xi'_{v+1}..d\xi'_u \, \langle\xi'_1...\xi'_u| = 1 \tag{1.3.1}$$

[3]

Definition 1.3.8 probability amplitude *The numbers which form the representative of a normalized ket (or bra) for*

$$P_{\xi'_1...\xi'_u} \, d\xi'_{v+1}..d\xi'_u = |\langle\xi'_1...\xi'_u|x\rangle|^2 d\xi'_{v+1}..d\xi'_u$$

[4]

Definition 1.3.9 relative probability amplitudes *numbers $\langle\xi'_1...\xi'_u|x\rangle$ when ket x cannot be normalized.*

Definition 1.3.10 being diagonal in the representation *The requirement of the representation used in 1.3.8 that each of the ξ's shall be represented by a diagonal matrix.*

Definition 1.3.11 Transformation functions $\langle\eta'_1...\eta'_w|\xi'_1...\xi'_u\rangle$ *or* $\langle\xi'_1...\xi'_u|\eta'_1...\eta'_w\rangle$ *being the coefficients in*

$$\langle\eta'_1...\eta'_w|P\rangle = \sum_{\xi'_1...\xi'_v} \int .. \int \langle\eta'_1...\eta'_w|\xi'_1...\xi'_u\rangle \, d\xi'_{v+1}..d\xi'_u \, \langle\xi'_1...\xi'_u|P\rangle \tag{1.3.2}$$

or

$$\langle\xi'_1...\xi'_u|P\rangle = \sum_{\eta'_1...\eta'_w} \int .. \int \langle\xi'_1...\xi'_u|\eta'_1...\eta'_w\rangle \, d\eta'_{x+1}..d\eta'_w \, \langle\eta'_1...\eta'_w|P\rangle \tag{1.3.3}$$

1.3.2 Notes

1. We can similarly introduce linear operators $L_1, L_2, L_3, ..., L_u$ by multiplying $\langle\lambda_1\lambda_2...\lambda_u|a\rangle$ by the factors $\lambda_1, \lambda_2, ..., \lambda_u$ in turn and considering the resulting sets of numbers as representatives of kets. Each of these L's can be shown in the same way to have the basic bras as eigenbras and to be real and an observable. The basic bras are simultaneous eigenbras of all the L's. Since these simultaneous eigenbras form a complete set, any two of the L's commute.

[3]此处的 1 不应简单地理解为数值上的 1，而更应看待为 unit operator.

[4]THe square of the modulus of a probability amplitude is an ordinary probability, or a probability per unit range for those variables that have continuous ranges of values.

2. For labelling the basic bras in this general case, we may use the eigenvalues $\xi'_1, \xi'_2, ..., \xi'_u$ to which they belong, together with certain additional real variables $\lambda_1, \lambda_2, ..., \lambda_v$ say, which must be introduced to distinguish basic vectors belonging to the same set of eigenvalues from one another. A basic bra is then written $\langle \xi'_1 \xi'_2 ... \xi'_u \lambda_1 \lambda_2 ... \lambda_v |$. ... The basic bras are now simultaneous eigenbras of all the commuting observables $\xi'_1, \xi'_2, ..., \xi'_u, L_1, L_2, ..., L_v$.

3.
   - The basic bras of an orthogonal representation are simultaneous eigenbras of a complete set of commuting observables.
   - Given a complete commuting observables, we can set up an orthogonal representation in which the basic bras are simultaneous eigenbras of this complete set.
   - Any set of commuting observables can be made into a complete commuting set by adding certain observables to it.
   - A convenient way of labelling the basic bras of an orthogonal representation is by means of the eigenvalues of the complete set of commuting observables of which the basic bras are simultaneous eigenbras.

4. The representative of a bra is the conjugate complex of the representative of the conjugate imaginary ket.

5. The process of multiplying a function of x by $\delta(x-a)$ and integrating over all x is equivalent to the process of substituting a for x.

6. the form of $\langle \xi'_1 ... \xi'_u | \alpha | \xi''_1 ... \xi''_u \rangle$ can be expressed like:

$$\begin{pmatrix} \langle \xi^1|\alpha|\xi^1\rangle & \langle \xi^1|\alpha|\xi^2\rangle & . & . \\ \langle \xi^2|\alpha|\xi^1\rangle & \langle \xi^2|\alpha|\xi^2\rangle & . & . \\ \langle \xi^3|\alpha|\xi^1\rangle & \langle \xi^3|\alpha|\xi^2\rangle & . & . \\ ... & ... & . & . \\ ... & ... & . & . \end{pmatrix} \tag{1.3.4}$$

7. Each $\xi_m (m = 1, 2, ..., u)$ and any function of them is represented by a diagonal matrix.

8. The matrices are subject to the same algebraic relations as the linear operators.

9. The probability of the ξ's having the values ξ' is just the square of the modulus of the appropriate corrdinate of the normalized ket vector corresponding to the state concerned

10. The probability distribution of values for the ξ's is given by the square of the modulus of the representative of the normalized ket vector corresponding to the state concerned.

$$P_{\xi'_1 ... \xi'_u} \, d\xi'_{v+1} .. d\xi'_u = |\langle \xi'_1 ... \xi'_u | x \rangle|^2 d\xi'_{v+1} .. d\xi'_u \tag{1.3.5}$$

11. To introduce a representation in practice

- We look for observables which we would like to have diagonal, either because we are interested in their probabilities or for reasons of mathematical simplicity;
- We see that they all commute - anecessary condition since diagonal matrices always commute;
- We then see that they form a complete commuting set, and if not we add some more commuting observables to them to make them into a complete commuting set;
- We set up an orthogonal representation with this complete commuting set diagonal.

12. The probability of the ξ's having the values ξ' for the state for which the ξ's certainly have the values η' is equal to the probability of the η's having the values η' for the state for which the ξ's certainly have the values ξ'.

13. If the labels of a ket involve complex numbers or complex functions, the labels of the conjugate imaginary bra involve the conjugate complex numbers or functions.

14. We can construct triple products of the form $\langle f(\xi\rangle$. Such a triple product is a number, equal to $f(\xi)$ summed or integrated over the whole domain of eigenvalues for the ξ's,

$$\langle f(\xi)\rangle = \sum_{\xi'_1 \ldots \xi'_v} \int \ldots \int f(\xi')\, d\xi'_{v+1} \ldots d\xi'_u \tag{1.3.6}$$

1.3.3 Theorems and Proofs

Theorem 1.3.1 *The basic bras of the representation are sufficient to fix the representation completely.*

Proof 1.3.1 *Take any ket $|a\rangle$ and form its scalar product with each of the basic bras. The numbers so obtained constitute the representative of $|a\rangle$. They are sufficient to determine the ket $|a\rangle$ completely, since if there is a second ket, $|a_1\rangle$ say, for which these product with any basic bra vanishing, and hence its scalor product with any bra whatever will vanish and $|a\rangle - |a_1\rangle$ itself will vanish.*

Theorem 1.3.2 *If $\xi_1, \xi_2, ..., \xi_u$ are any set of commuting observables, we can set up an orthogonal representation in which the basic bras are simultaneous eigenbras of $\xi_1, \xi_2, ..., \xi_u$.*

Proof 1.3.2 *Let us suppose first that there is only one independent simultaneous eigenbra of $\xi_1, \xi_2, ..., \xi_u$ belonging to any set of eigenvalues $\xi'_1, \xi'_2, ..., \xi'_u$. Then we may take these simultaneous eigenbras, with arbitrary numerial coefficients, as our basic bras. They are all orthogonal on account of the orthogonality theorem (any two of them will have at least one eigenvalue different, which is sufficient to make them orthogonal) and there are sufficient of them to form a complete set.*

Theorem 1.3.3

$$Discrete : \sum_{\xi'} |\xi'\rangle\langle\xi'| = 1 \tag{1.3.7}$$

$$Continuous : \int |\xi'\rangle\, d\xi' \langle\xi'| = 1 \tag{1.3.8}$$

where the eigenvectors of ξ form basic vectors.

Proof 1.3.3 *We can develop the theory on closely parallel lines for the discrete and continuous cases. For the discrete case we have,*

$$\sum_{\xi'} |\xi'\rangle\langle\xi'|\xi''\rangle = \sum_{\xi'} |\xi'\rangle\delta_{\xi'\xi''} = |\xi''\rangle \tag{1.3.9}$$

the sum being taken over all eigenvalues. This equation holds for any basic ket $|\xi''\rangle$ and hence, since the basic kets form a complete set,

$$\sum_{\xi'} |\xi'\rangle\langle\xi'| = 1 \tag{1.3.10}$$

Thus

$$\sum_{\xi'} |\xi'\rangle\langle\xi'| = 1 \tag{1.3.11}$$

Similarly, for the continuous case we have,

$$\int |\xi'\rangle\, d\xi'\, \langle\xi'|\xi''\rangle = \int |\xi'\rangle\, d\xi'\, \delta(\xi' - \xi'') = |\xi''\rangle \tag{1.3.12}$$

[5]

Theorem 1.3.4 *A linear operator that commutes with an observable ξ commutes also with any function of ξ.*

Proof 1.3.4 *Let ω be the linear operator. so that we have the equation*

$$\xi\omega - \omega\xi = 0 \tag{1.3.13}$$

Let us introduce a representation in which ξ is diagonal. If ξ by itself does not form complete commuting set of observables, we must make it into a complete commuting set of observables, we must make it into a complete commuting set by adding certain observables, β say, to it, and then take the representation in which ξ and the β's are diagonal. (The case when ξ does form a complete commuting set by itself can be looked upon as a special case of the preceding one with the number of β cariables zero.) In this representation equation the former equation becomes

$$\langle\xi'\beta'|\xi\omega - \omega\xi|\xi''\beta''\rangle = 0 \tag{1.3.14}$$

which reduces to

$$\xi\langle\xi'\beta'|\omega|\xi''\beta''\rangle - \langle\xi'\beta'|\omega|\xi''\beta''\rangle\xi'' = 0 \tag{1.3.15}$$

In the case when the eigenvalues of ξ are discrete, this equation shows that all the matrix elements $\langle\xi'\beta'|\omega|\xi''\beta''\rangle$ of ω vanish except those for which $\xi' = \xi''$. In the case when the eigenvalues of ξ

Theorem 1.3.5 *A linear operator that commutes with each of a complete set of comuuting observables is a function of those observables.*

[5] enabing one to expand any bra or ket in terms of the basic vectors.

Proof 1.3.5 *Let ω be the linear operator and $\xi_1, \xi_2, ..., \xi_u$ the complete set of commuting observables, and set up a representation with these observables diagonal. Since ω commutes with each of the ξ's, the matrix representing it is diagonal with respect to each of the ξ's, by the argument we had above. This matrix is therefore a diagonal matrix and is of the form*

$$\langle \xi_1' ... \xi_u' | \omega | \xi_1'' .... \xi_u' \rangle = c' \delta_{\xi_1 \xi_1''} ... \delta_{\xi_v' \xi_v''} \delta(\xi_{v+1}' - \xi_{v+1}'') .. \delta \xi_u' - \xi_u'' \tag{1.3.16}$$

involving a number c' which is a function of the ξ''s. It thus represents the function of the ξ's that c' is of the ξ''s, and hence ω equals this function of the ξ's.

Theorem 1.3.6 *If an observable ξ and a linear operator g are such that any linear operator that commutes with ξ also commutes with g, then g is a function of ξ.*

Proof 1.3.6 *In the first place, we see that g must commute with ξ itself, and hence the representative of g must be diagonal with respect to ξ. i.e. it must be of the form*

$$\langle \xi' \beta' | g | \xi'' \beta'' \rangle = a(\xi' \beta' \beta'') \delta_{\xi' \xi''} \quad or \quad a(\xi' \beta' \beta'') \delta(\xi' - \xi'') \tag{1.3.17}$$

Now let ω be any linear operator that commutes with ξ, so that its representative is of the form

$$\langle \xi' \beta' | \omega | \xi'' \beta'' \rangle = b(\xi' \beta' \beta'') \delta_{\xi' \xi''} \quad or \quad b(\xi' \beta' \beta'') \delta(\xi' - \xi'') \tag{1.3.18}$$

By hypothesis ω must also commute with g, so that

$$\langle \xi' \beta' | g\omega - \omega g | \xi'' \beta'' \rangle = 0 \tag{1.3.19}$$

If we suppose for definiteness that the β's have discrete eigenvalues, with the help of the law of matrix multiplication, the former equation leads, with the help of the law of matrix multiplication, to

$$\sum_{\beta'''} \{ a(\xi' \beta' \beta''') b(\xi' \beta''' \beta'') - b(\xi' \beta' \beta''') a(\xi' \beta''' \beta'') \} = 0 \tag{1.3.20}$$

the left-hand sides of the two equations above different from whether multiplied by $\delta_{\xi' \xi''}$ or $\delta(\xi' \xi'')$.They should hold for all functions $b(\xi' \beta' \beta'')$. We can deduce that

$$\begin{cases} a(\xi' \beta' \beta'') = 0 \quad for \quad \beta' \neq \beta'', \\ a(\xi' \beta' \beta') = a(\xi' \beta'' \beta'') \end{cases} \tag{1.3.21}$$

The first of these results shows that the matrix representing g is diagonal and the second shows that $a(\xi' \beta' \beta')$ is a function of ξ' only. We can now infer that g is that function of ξ which $a(\xi' \beta' \beta'$ is of ξ', which proves the theorem.

1.3.4 Digests

We may suppose the basic bras to be labelled by one or more parameters, $\lambda_1, \lambda_2, ..., \lambda_u$, each of which may take on cetain numerical values. The basic bras will then be written $\langle \lambda_1 \lambda_2 ... \lambda_u |$ and the representative of $|a\rangle$ will be written $\langle \lambda_1 \lambda_2 ... \lambda_u | a \rangle$. This representative will now consist of a set of numbers, one for each set of values that $\lambda_1, \lambda_2, ..., \lambda_u$ may have in their respective domains. Such a set of numbers just forms a function of the

variables $\lambda_1, \lambda_2, ..., \lambda_u$. Thus the representative of a ket may be looked upon either as a set of numbers or as a function of the variables used to label the basic bras.

If the number of independent states of our dynamical system is finite, equal to n say, it is sufficient to take n basic bras, which may be labelled by a single parameter λ taking on the values $1, 2, 3, ..., n$. The representative of any ket $|a\rangle$ now consists of the set of n numbers $\langle 1|a\rangle$,$\langle 2|a\rangle$,$\langle 3|a\rangle$,...,$\langle n|a\rangle$, which are precisely the coordinates of the vector $|a\rangle$ referred to a system of coordinates in the usual way.

The most important property of $\delta(x)$ is exemplified by the following equation,

$$\int_{-\infty}^{\infty} f(x)\delta(x)\,dx = f(0) \tag{1.3.22}$$

where $f(x)$ is any continuous function of x. By making a change of origin, we can deduce the formula

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a) \tag{1.3.23}$$

where a is any real number. The range of integration in both equations need not be from $-\infty$ to ∞, but may be over any domain surrounding the critical point at which the δ function does not vanish.

An alternative way of defining the δ function is as the differential coefficient $\epsilon'(x)$ of the function $\epsilon(x)$ given by

$$\begin{aligned}\epsilon(x) &= 0\,(x<0)\\ &= 1\,(x>0)\end{aligned}$$

We may verify that this is equivalent to the previous definition by sustituting $\epsilon'(x)$ for $\delta(x)$ in the left-hand side and integrating by parts, We find, for g_1 and g_2 two positive numbers,

$$\begin{aligned}\int_{-g_2}^{g_1} f(x)\epsilon'(x)\,dx &= [f(x)\epsilon(x)]_{-g_2}^{g_1} - \int_{-g_2}^{g1} f'(x)\epsilon(x)\,dx\\ &= f(g_1) - \int_0^{g_1} f'(x)\,dx\\ &= 0\end{aligned}$$

$$\delta(-x) = \delta(x) \tag{1.3.24}$$

$$x\delta(x) = 0 \tag{1.3.25}$$

$$\delta(ax) = a^{-1}\delta(x) \tag{1.3.26}$$

$$\delta(x^2-a^2) = \frac{1}{2}a^{-1}\delta(x-a) + \delta(x+a) \quad (a>0) \tag{1.3.27}$$

$$\int \delta(a-x)\,dx\,\delta(x-b) = \delta(a-b) \tag{1.3.28}$$

$$f(x)\delta(x-a) = f(a)\delta(x-a) \tag{1.3.29}$$

$$\int f(x)x\delta(x)\,dx = 0 \tag{1.3.30}$$

$$\frac{d}{dx}\,logx = \frac{1}{x} \tag{1.3.31}$$

In order to make the reciprocal function $1/x$ well defined in the neighborhood of $x = 0$ we must impose on it an extra condition, such as that its integral from $-\epsilon$ to ϵ vanishes. With this extra condition, the integral of the right-hand side of 1.3.31 from $-\epsilon$ to ϵ vanishes. while that of the left-hand side of 1.3.31 equals $log(-1)$, so that 1.3.31 is not a correct equation. To correct it, we must remember that, taking principal values, log x has a pure imaginary term $i\pi$ for negative values of x. As x passes through the value zero this pure imaginary term vanishes discontinuously. The differentiation of this pure imaginary term gives us the result $-i\pi\delta(x)$, so that 1.3.31 should read

$$\frac{d}{dx}\,logx = \frac{1}{x} - i\pi\delta(x) \tag{1.3.32}$$

In the case when the eigenvalues of ξ are continuous we cannot normalize the basic vectors. If we now consider the quantity $\langle\xi'|\xi''\rangle$ with ξ' fixed and ξ'' varying,.... this quantity $\xi'' \neq \xi'$ and that its integral over a range of ξ'' extending through the value ξ' is finite, equal to c say. Thus

$$\langle\xi'|\xi''\rangle = c\delta(\xi' - \xi'') \tag{1.3.33}$$

c has been proved to be a positive number. It may vary with ξ' so we should write it $c(\xi')$ or c' for brevity, and thus

$$\langle\xi|\xi''\rangle = c'\delta(\xi' - \xi'') \tag{1.3.34}$$

Alternatively,

$$\langle\xi|\xi''\rangle = c''\delta(\xi' - \xi'') \tag{1.3.35}$$

where c'' is short for $c(\xi'')$.

$$|P\rangle = \sum_{\xi'} |\xi'\rangle\langle\xi'|P\rangle \quad (discrete) \tag{1.3.36}$$

$$= \int |\xi'\rangle\, d\xi'\, \langle\xi'|P\rangle \quad (continuous) \tag{1.3.37}$$

$$\langle Q|P\rangle = \sum_{\xi'} \langle Q|\xi'\rangle\langle\xi'|P\rangle \quad (discrete) \tag{1.3.38}$$

$$= \int \langle Q|\xi'\rangle\, d\xi'\, \langle\xi'|P\rangle \quad (continuous) \tag{1.3.39}$$

Let us now pass to the general case when we have several commuting observables $\xi_1, \xi_2, ..., \xi_u$ forming a complete commuting set and set up an orthogonal representation in which the basic vectors are simultaneous eigenvectors of all of them, and are written $\langle\xi'_1, ..., \xi'_u|, |\xi'_1, ..., \xi'_u\rangle$. Let us suppose $\xi_1, \xi_2, ..., \xi_v (v \leqslant u)$ have discrete eigenvalues and $\xi_{v+1}, ..., \xi_u$ have continuous eigenvalues.

Consider the quantity $\langle\xi'_1..\xi'_v\xi'_{v+1}..\xi'_u|\xi'_1..\xi'_v\xi'_{v+1}..\xi'_u\rangle$. From the orthogonality theorem, it must vanish unless each $\xi''_s = \xi'_s$ for $s = v + 1, ..., u$. The $(u - v)$-fold integral of this quantity with respect to each $\xi'')s$ over a range extending through the value ξ'_s is a

finite positive number, Calling this number c', the $'$ denoting that it is a function of $\xi'_1..\xi'_v\xi'_{v+1}..\xi'_u$, we can express our results by the equation

$$\langle\xi'_1..\xi'_v\xi'_{v+1}..\xi'_u|\xi''_1..\xi''_v\xi''_{v+1}..\xi''_u\rangle = c'\delta(\xi'_{v+1}-\xi''_{v+1})..\delta(\xi'_u-\xi''_u) \tag{1.3.40}$$

with one δ factor on the right-hand side for each value of s from $v+1$ to u. We know change the lengths of our basic vectors so as to make c' unity. By a further use of the orthogonality theorem, we get finally

$$\langle\xi'_1..\xi'_v\xi'_{v+1}..\xi'_u|\xi''_1..\xi''_v\xi''_{v+1}..\xi''_u\rangle = \delta_{\xi'_1\xi''_1}..\delta_{\xi'_v\xi''_v}\delta(\xi'_{v+1}-\xi''_{v+1})..\delta(\xi'_u-\xi''_u) \tag{1.3.41}$$

with a two-suffix δ symbol on the right-hand side for each ξ with discrete eigenvalues and a δ function for each ξ with continuous eigenvalues.

$$\sum_{\xi'_1..\xi'_v}\int..\int|\xi'_1...\xi'_u\rangle\,d\xi'_{v+1}..d\xi'_u\,\langle\xi'_1...\xi'_u| = 1 \tag{1.3.42}$$

There are some problems in which it is convenient not to make the c' equal unity, but to make it equal to some definite function of the ξ''s instead. Calling this function of the ξ''s ρ'^{-1} we then have,

$$\langle\xi'_1...\xi''_u|\xi''_1...\xi''_u\rangle = \rho'^{-1}\delta_{\xi'_1\xi''_1}..\delta_{\xi'_v}\xi''_v\delta(\xi'_{v+1}-\xi''_{v+1})..\delta(\xi'_u-\xi''_u) \tag{1.3.43}$$

and we get

$$\sum_{\xi'_1..\xi'_v}\int..\int|\xi'_1...\xi'_u\rangle\rho'\,d\xi'_{v+1}..d\xi'_u\,\langle\xi'_1...\xi'_u| = 1 \tag{1.3.44}$$

ρ' is called the weight function of the representation, $\rho'\,d\xi'_{v+1}..d\xi'_u$ begin the 'weight' attached to a small volume element of the space of the variables $\xi'_{v+1},..,\xi'_u$.

An example of a useful representation with non-unit weight function occurs when one has two ξ's which are the polar and azimuthal angles θ and ϕ giving a direction in three-dimensional space and one takes $\rho' = \sin\theta'$. One then has the element of solid angle $\sin\theta'\,d\theta'd\phi'$.

The probability of each ξ_r having the value ξ'_r for the sate corresponding to the normalized ket vector $|x\rangle$ is

$$P_{\xi'_1...\xi'_u} = \langle x|\delta_{\xi_1\xi'_1}\delta_{\xi_2\xi'_2}...\delta_{\xi_u\xi'_u}|x\rangle \tag{1.3.45}$$

If the ξ's all have discrete eigenvalues, we can use 1.3.42 with $v=u$ and no integrals, and get

$$\begin{aligned}P_{\xi'_1...\xi'_u} &= \sum_{\xi''_1...\xi''_u}\langle x|\delta_{\xi_1\xi'_1}\delta_{\xi_2\xi'_2}...\delta_{\xi_u\xi'_u}|\xi''_1...\xi''u\rangle\langle\xi''_1...\xi''_u|x\rangle\\ &= \sum_{\xi''_1...\xi''_u}\langle x|\delta_{\xi''_1\xi'_1}\delta_{\xi''_2\xi'_2}...\delta_{\xi''_u\xi'_u}|\xi''_1...\xi''u\rangle\langle\xi''_1...\xi''_u|x\rangle\\ &= \langle x|\xi'_1...\xi'_u\rangle\langle\xi'_1...\xi'_u|x\rangle = |\langle\xi'_1..\xi'_u|x\rangle|^2\end{aligned}$$

If the ξ's do not all have discrete eigenvalues, but if, say, $\xi_1,...,\xi_v$ have dicrete eigenvalues and $\xi_{v+1},..,\xi_u$ have continuous eigenvalues, then to get something physically significant we must obtain the probability of each $\xi_r(r=1,...,v)$ having a specified value

ξ'_r and each $\xi_s (s = v+1, ..., u$ lying in a specified small range ξ'_s to $\xi'_s + d\xi'_s$. For this purpose we must replace each factor $\delta_{\xi_s \xi'_s}$ in

$$P_{\xi'_1 \ldots \xi'_u} = \langle x | \delta_{\xi_1 \xi'_1} \delta_{\xi_2 \xi'_2} \ldots \delta_{\xi_u \xi'_u} | x \rangle$$

by a factor χ_s, which is that function of the observable ξ_s which is equal to unity for ξ_s within the range ξ'_s to $\xi' s + d\xi'_s$ and zero otherwise. Proceeding as before, we obtin for this probability

$$P_{\xi'_1 \ldots \xi'_u} \, d\xi'_{v+1} .. d\xi'_u = |\langle \xi'_1 \ldots \xi'_u | x \rangle|^2 d\xi'_{v+1} .. d\xi'_u \tag{1.3.46}$$

In a representation in which the complete set of commuting observables $\xi_1, ..., \xi_u$ are dagonal any ket $|P\rangle$ will have a representative $\langle \xi'_1 \ldots \xi'_u | P \rangle$,or$\langle \xi' | P \rangle$ for brevity. This representativce is a definite function of the variables ξ', say $\psi(\xi')$. The fucnction ψ then determines the ket $|P\rangle$ completely, so it may be used to label this ket, to replace the arbitrary label P. In synbols,

$$\begin{cases} \text{if} \quad \langle \xi' | P \rangle = \psi(\xi') \\ \text{then} \quad |P\rangle = |\psi(\xi)\rangle \end{cases} \tag{1.3.47}$$

We mut put $|P\rangle$ to $|\psi(\xi)\rangle$ and not $|\psi(\xi')\rangle$, since it does not depend on a particular set of eigenvalues for the ξ's, but only on the form of the function ψ.

With $f(\xi)$ any function of the observables $\xi_1, ..., \xi_u$, $f(\xi)|P\rangle$ will have as its representative

$$\langle \xi' | f(\xi) | P \rangle = f(\xi') \psi(\xi') \tag{1.3.48}$$

Thus it is defined

$$f(\xi)|P\rangle = |f(\xi)\psi(\xi)\rangle \tag{1.3.49}$$

It is also defined

$$\begin{cases} \langle \xi' | P \rangle = \psi(\xi') \\ |P\rangle = \psi(\xi)\rangle \end{cases} \tag{1.3.50}$$

We may further shorten $\psi(\xi')\rangle$ to $\psi\rangle$.

The ket $\psi(\xi)\rangle$ may be considered as the product of the linear operator $\psi(\xi)$ with a ket which is denoted simply by $\rangle$ without a label. We call the ket $\rangle$ the *standard ket*. Any ket whatever can be expressed as a function of the ξ's multiplied into the standard ket.

Suppose we have a dynamical system describable in terms of dynamical variables wich can all be divided into two sets, set A and set B say, such that any number of set A commutes with any member of set B. A general dynamical variable must be expressible as a function of the A-varables and B-variables together.[6]

Let us take any ket $|a\rangle$ for the A-system and any ket $|b\rangle$ for the B-system. We assume that they have a product $|a\rangle|b\rangle$ for which the commutative and distributive axioms of multiplication hold, i.e.

$$\begin{cases} |a\rangle|b\rangle = |b\rangle|a\rangle \\ \{c_1|a_1\rangle + c_2|a_2\rangle\}|b\rangle = c_1|a_1\rangle|b\rangle + c_2|a_2\rangle|b\rangle \\ |a\rangle\{c_1|b_1\rangle + c_2|b_2\rangle\} = c_1|a\rangle|b_1\rangle + c_2|a\rangle|b_2\rangle \end{cases} \tag{1.3.51}$$

[6]这里面确实 A 系统和 B 系统算符之间相互对易，能够存在共同的完备基组，但这是在一个总的 Hilbert 空间下成立，如果所要求的自由度不一样则是在两个 Hilbert 子空间，而这两个子空间的直积才是总的 Hilbert 空间

the c's being numbers. We can give a meaning to any A-variable operating on the product $|a\rangle|b\rangle$ by assuming that it operates only on the $|a\rangle$ factor and commutes with the $|b\rangle$ factor, similarly for the B-variable system.

Then

$$|a\rangle|b\rangle = |b\rangle|a\rangle = |ab\rangle \tag{1.3.52}$$

The standard ket and bra are defined with respect to a representation.If we carried through the above work with a different representation in which the complete set of commuting observables η are diagonal, or if we merely changed the phase factors in the representation with the ξ's diagonal, we should get a different standard ket and bra.

The representative of $|ab\rangle$ equals the product of the representatives of $|a\rangle$ and of $|b\rangle$ in their respective representations, namely

$$\langle\xi'_A|a\rangle\langle\xi'_B|b\rangle = \langle\xi'_A\xi'_B|ab\rangle \tag{1.3.53}$$

We can introduce the representation with the ξ_A's diagonal, and also with respect to the standard ket, $\rangle_A$ say,for the A-system and $\rangle_B$ for the B-system, both with respect to the representation with the two variable-systems diagonal. Their product $\rangle_A\rangle_B$ is the nthe standard ket for the original system. Any ket for the oprignal system may be expressed as

$$\psi(\xi_A\xi_B)\rangle_A\rangle_B \tag{1.3.54}$$

It may be that in a certain calculation we wish to use a particular representation for the B-system, say the above representation with the ξ_B's diagonal, but do not wish to introduce any particular representation for the A-system. Under these circumstances we could write any ket for the original system as

$$|\xi_B\rangle\rangle_B \tag{1.3.55}$$

in which $|\xi_B\rangle$ is a ket for the A-system and is also a function of the ξ_B's. We can also have

$$|\xi_B\rangle = \psi(\xi_A\xi_B)\rangle_A \tag{1.3.56}$$

Thus it is clear that

$$|a\rangle|b\rangle|c\rangle... = |abc...\rangle \tag{1.3.57}$$

1.4 The Quantum Conditions

1.4.1 Notes

1. The main properties of Poisson Brackets, which follow at once from the definition:

$$[u, v] = \sum_r \left\{ \frac{\partial u}{\partial q_r}\frac{\partial v}{\partial p_r} - \frac{\partial u}{\partial p_r}\frac{\partial v}{\partial q_r} \right\} \tag{1.4.1}$$

are:

$$[u, v] = -[v, u] \tag{1.4.2}$$
$$[u, constant] = 0 \tag{1.4.3}$$
$$\begin{cases} [u_1 + u_2, v] = [u_1, v] + [u_2, v] \\ [u, v_1 + v_2] = [u, v_1] + [u, v_2] \end{cases} \tag{1.4.4}$$
$$[u_1 u_2, v] = [u_1, v]v_2 + u_1[u_2, v] \tag{1.4.5}$$
$$[u, v_1 v_2] = [u, v_1]v_2 + v_1[u, v_2] \tag{1.4.6}$$
$$[u, [v, w]] + [v, [w, u]] + [w, [u, v]] \tag{1.4.7}$$

2. We want to introduce a quantum P.B, which shall be the analogue of the classical one. We assume the quantum P.B. to satisfy all the conditions listed above. We can deduce that

$$\begin{aligned} [u_1 u_2, v_1 v_2] &= [u_1, v_1 v_2]u_2 + u_1[u_2, v_1 v_2] \\ &= [u_1 u_2, v_1]v_2 + v_1[u_1 u_2, v_2] \end{aligned}$$

after expansion, we obtain

$$[u_1, v_1](u_2 v_2 - v_2 u_2) = (u_1 v_1 - v_1 u_1)[u_2, v_2] \tag{1.4.8}$$

Since this condition holds with u_1 and v_1 quite independent of u_2 and v_2, we get

$$uv - vu = i\hbar[u, v] \tag{1.4.9}$$

the coefficient $i\hbar$ being added to agree with the experimentary results.

And we assume the fundamental quantum conditions

$$\begin{cases} [q_r, q_s] = 0 \\ [p_r, p_s] = 0 \\ [q_r, p_s] = i\hbar\delta_{rs} \end{cases} \tag{1.4.10}$$

which indicates that dynamical variables referring to different degrees of freedom commute.

3. We construct the quantum conditions to make it analogous to the classical mechanics, which guarantees that classic mechanics may be regarded as the limiting case of quantum mechanics when $\hbar$ tends to zero.

4. It can be deduced that

$$\langle \phi \frac{d}{dq} = -\langle \frac{d\phi}{dq} \tag{1.4.11}$$

To get the representative of d/dq we note that

$$|q''\rangle = \delta(q - q'')\rangle \tag{1.4.12}$$

so that

$$\langle q'| \frac{d}{dq} |q''\rangle = \frac{d}{dq'}\delta(q' - q'') \tag{1.4.13}$$

and we deduce that

$$\frac{d}{dq}q\psi\rangle = \frac{dq\psi}{dq}\rangle = q\frac{d}{dq}\psi\rangle + \psi\rangle \tag{1.4.14}$$

Thus

$$\frac{d}{dq}q - q\frac{q}{dq} = 1 \tag{1.4.15}$$

Thus $-i\hbar d/dq$ *satisfies the same commutation relation with* q *and* p *does.*

5. It can also be achieved that

$$\begin{cases} \frac{\partial}{\partial q_r}q_s - q_s\frac{\partial}{\partial q_r} = \delta_{rs} \\ \frac{\partial}{\partial q_r}\frac{\partial}{\partial q_s} = \frac{\partial}{\partial q_s}\frac{\partial}{\partial q_r} \end{cases} \tag{1.4.16}$$

6. It would be possible to take

$$p_r = -i\hbar\partial/\partial q_r + f_r(q) \tag{1.4.17}$$

Then for an arbitrary real function f of the q's we have

$$[f, p_r] = \partial f/\partial q_r \tag{1.4.18}$$

utilization of the commuting property of $\partial/\partial q_r$ and $\partial/\partial q_s$ we obtain

$$(p_r - f_r)(p_s f_s) = (p_s - f_s)(p_r - f_r) \tag{1.4.19}$$

then

$$[p_r, f_s] = [p_s, f_r] \tag{1.4.20}$$

thus

$$\partial f_s/\partial q_r = \partial f_r/\partial q_s \tag{1.4.21}$$

showing that the functions f_r are all of the form

$$f_r = \partial f_r/\partial q_s \tag{1.4.22}$$

then

$$p_r = -i\hbar\partial/\partial q_r + \partial F/\partial q_r \tag{1.4.23}$$

7. $\partial F/\partial q_r$ can be eliminated by adding a phase factor. Using stars to distinguish quantities referring to the new representation with the new phase factors,

$$\langle q'...q'^*_n| = e^{i\gamma'}\langle q'...q'_n| \tag{1.4.24}$$

where $\gamma' = \gamma(q')$ is a real function of the q''s. Then

$$\rangle^* = e^{-i\gamma}\rangle \tag{1.4.25}$$

then

$$\left(\frac{\partial}{\partial q_r}\right)^* \psi\rangle^* = \frac{\partial\psi}{\partial q_r}^* = e^{-i\gamma}\frac{\partial\psi}{\partial q_r}\rangle = e^{-i\gamma}\frac{\partial}{\partial q_r}e^{i\gamma}\psi\rangle^* \tag{1.4.26}$$

thus

$$\left(\frac{\partial}{\partial q_r}\right)^* = e^{-i\gamma}\frac{\partial}{\partial q_r}e^{i\gamma} \tag{1.4.27}$$

with utilization of $[f, p_r] = \partial f/\partial q_r$,

$$\left(\frac{\partial}{\partial q_r}\right)^* = \frac{\partial}{\partial q_r} + i\frac{\partial \gamma}{\partial q_r} \tag{1.4.28}$$

By choosing γ so that

$$F = \hbar\gamma + constant \tag{1.4.29}$$

then

$$p_r = -i\hbar(\partial/\partial q_r)^* \tag{1.4.30}$$

8. The momentum representation utilizes

$$p'\langle q'|p'\rangle = \langle q'|p|p'\rangle = -i\hbar\frac{d}{dq'}\langle q'|p'\rangle \tag{1.4.31}$$

whose solution is

$$\langle q'|p'\rangle = c'e^{ip'q'/\hbar} \tag{1.4.32}$$

We need

$$\begin{cases} \int_{-\infty}^{\infty} e^{iax}\,dx = 2\pi\delta(a) \\ \int_{-\infty}^{\infty} f(a)\,da \int_{-g}^{g} e^{-iax}\,dx = 2\pi f(0) \end{cases} \tag{1.4.33}$$

and we get

$$\langle p'|p''\rangle = |c'|^2 h\delta(p' - p'') \tag{1.4.34}$$

showing the analogy between q and p. Thus

$$q = i\hbar d/dp \tag{1.4.35}$$

and

$$\langle q'|p'\rangle = h^{-1/2}e^{ip'q'/\hbar} \tag{1.4.36}$$

9. it is assumed that the superposition relationship holds when D is acted on the ket vectors, which indicates that D is an unitary operator, or

$$D^\dagger D = 1 \tag{1.4.37}$$

10. for a displaced dynamical variable v_d,

$$v_d = DvD^{-1} \tag{1.4.38}$$

11. From physical continuity we should expact a displaced ket $|Pd\rangle$ to tend to the original $|P\rangle$ and we may further expect the limit

$$\lim_{\delta x\to 0}\frac{|Pd\rangle - |P\rangle}{\delta x} = \lim_{\delta x->0}\frac{D-1}{\delta x}|P\rangle \tag{1.4.39}$$

to exist. This requires that the limit

$$\lim_{\delta x\to 0}(D-1)/\delta x \tag{1.4.40}$$

shall exist. This limit is a linear operator which we shall call the *displacement operator* for the x-direction and denote by d_x. The arbitrary numerical factor $e^{i\gamma}$

with γ real which we may multiply into D must be made to tend to unity as $\delta x \to 0$ and then introduces an arbitrariness in d_x, namely, d_x may be replaced by

$$\lim_{\delta x \to 0}(De^{i\gamma} - 1)/\delta x = \lim_{\delta x \to 0}(D - 1 + i\gamma)/\delta x = d_x + ia_x \tag{1.4.41}$$

where a_x is the limit of $\gamma/\delta x$. Thus d_x contains an arbitrary additive pure imaginary number.

For δx small

$$D = 1 + \delta x d_x \tag{1.4.42}$$

Considering that D is a unitary oprerator,

$$(1 + \delta x \bar{d_x})(1 + \delta x d_x) = 1 \tag{1.4.43}$$

thus

$$\delta x(\bar{d_x} + d_x) = 0 \tag{1.4.44}$$

Thus d_x is a pure imaginary linear operator. Then

$$v_d = (1 + \delta x d_x)v(1 - \delta x \bar{d_x}) = v + \delta x(d_x v - v d_x) \tag{1.4.45}$$

showing that

$$\lim_{\delta x \to 0}(v_d - v)/\delta x = d_x v - v d_x \tag{1.4.46}$$

If we suppose a piece of apparatus which has been set up to measure x, to be displaced a distance δx in the direction of the x-axis, it will measure $x - \delta x$, hence

$$x_d = x - \delta x \tag{1.4.47}$$

Thus

$$d_x x - x d_x = -1 \tag{1.4.48}$$

Then

$$p_x = i\hbar d_x \tag{1.4.49}$$

1.5 The Equations of Motion

1.5.1 Definitions

Definition 1.5.1 Constant of the motion *We call v_t or v a constant of the motion if*

$$v_t = v_{t_0} = v \tag{1.5.1}$$

Definition 1.5.2 Heisenberg representation *A representation in which all the basic vectors are eigenvectors of the energy and so correspond to stationary states in the Heisenberg picture.*

1.5.2 Notes

1. It is assumed that a superposition relation holds through out time. $\Rightarrow T$ is a linear operator independent of P and depending only on t and t_0:

$$\Rightarrow \begin{cases} |Pt\rangle = T|Pt_0\rangle \\ |Pt\rangle = |Pt^a\rangle + |Pt^b\rangle = T(|Pt_0^a\rangle + |Pt_0^b\rangle) \end{cases} \tag{1.5.2}$$

2. It is assumed that $|Pt\rangle$ has the same length as the corresponding $|Pt_0\rangle$. $\Rightarrow T$ is a unitary transformation:

$$\bar{T}T = 1 \tag{1.5.3}$$

3. There exists a limit

$$\frac{d|Pt_0\rangle}{dt_0} = \left\{ \lim_{t\to t_0} \frac{T-1}{t-t_0} \right\} |Pt_0\rangle \tag{1.5.4}$$

4. Schrödinger's form for the equations of motion:

$$i\hbar \frac{d|Pt\rangle}{dt} = H(t)|Pt\rangle \tag{1.5.5}$$

5. Using T, we get

$$i\hbar \frac{dT}{dt}|Pt_0\rangle = H(t)T|Pt_0\rangle \tag{1.5.6}$$

It holds for any ket, thus

$$i\hbar \frac{dT}{dt} = H(t)T \tag{1.5.7}$$

6. Introducing a representation with a complete set of commuting observables ξ diagonal and putting $\langle \xi'|Pt\rangle$ equal to $\psi(\xi' t)$, we have, passing to the standard ket notation,

$$|Pt\rangle = \psi(\xi t)\rangle$$

Schrödinger's equation becomes

$$i\hbar \frac{\partial}{\partial t}\psi(\xi t)\rangle = H\psi(\xi t)\rangle \tag{1.5.8}$$

7. In Heisenberg's picture,

$$v_t = T^{-1} v T \tag{1.5.9}$$

Differentiating with respect to t, we get

$$\frac{dT}{dt}v_t + T\frac{dv_t}{dt} = v\frac{dT}{dt} \tag{1.5.10}$$

Using relation between H and T,

$$i\hbar \frac{dv_t}{dt} = v_t H_t - H_t v_t \tag{1.5.11}$$

Thus

$$\frac{dv_i}{dt} = [v_t, H_t] \tag{1.5.12}$$

8. The laws of conservation of energy, momentum, and angular momentum hold for an isolated system in the Heisenberg picture in quantum mechanics, as they hold in classic mechanics.

9. It can be Integrated
$$T = e^{-iH(t-t_0)/\hbar} \tag{1.5.13}$$
with the help of the initial condition that $T = 1$ for $t = t_0$. The time-dependent wave function $\psi(\xi t)$ representing a stationary state of energy H' will vary with time according to the law
$$\psi(\xi t) = \psi_0(\xi)e^{-iH't/\hbar} \tag{1.5.14}$$
and Schrödinger's wave equation reduces to
$$H\psi_0\rangle = H'\psi_0\rangle \tag{1.5.15}$$

1.5.3 Digests

Free Particle:

$$i\hbar\dot{x}_t = i\hbar\frac{dx_t}{dt} = x_t c(m^2c^2 + \sum p_k^2)^{1/2} - c(m^2c^2 + \sum p_k^2)^{1/2}x_t \tag{1.5.16}$$

$$q_r f - f q_r = i\hbar\partial f/\partial p_r \tag{1.5.17}$$

$$\dot{x}_t = \frac{\partial}{\partial p_x}c(m^2c^2 + \sum p_k^2)^{1/2} = \frac{c^2 p_x}{H} \tag{1.5.18}$$

$$v_t = (\sum \dot{x}_{t,k}^2)^{1/2} = c^2(\sum p_k^2)^{1/2}/H \tag{1.5.19}$$

Let us consider a state that is an eigenstate of the momenta, belonging to the eigenvalues p'_x, p'_y, p'_z. This state must be an eigenstate of the Hamiltonian, belonging to the eigenvalue
$$H' = c(m^2c^2 + \sum p_k'^2)^{1/2} \tag{1.5.20}$$
and must therefore be a stationary state. The possible values for H' are all numbers from mc^2 to ∞, as in the classical theory. The wave function $\psi(xyz)$ representing this state at any time in Schrödinger's representation must satisfy
$$p'_x\psi(xyz)\rangle = p_x\psi(xyz)\rangle = -i\hbar\frac{\partial\psi(xyz)}{\partial x}\rangle \tag{1.5.21}$$
with similar equations for p_y and p_z.

Thus
$$\psi(xyzt) = a_0 e^{i(\sum p'_k k - H't)\hbar} \tag{1.5.22}$$
which describes plane waves in space-time.

$$\begin{cases} \nu = H'/h \\ \lambda = h/(\sum p_k'^2)^{1/2} = h/P' \\ \lambda\nu = H'/P' = c^2/v' \end{cases} \tag{1.5.23}$$

The group velocity of the waves, is

$$\frac{d\nu}{d(1/\lambda)} \tag{1.5.24}$$

which gives,

$$\frac{dH'}{dP'} = c\frac{d}{dP'}(m^2c^2 + P'^2)^{1/2} = \frac{c^2P'}{H'} = v' \tag{1.5.25}$$

The motion of wave packets

$$\psi(qt) = Ae^{iS/\hbar} \tag{1.5.26}$$

where A and S are real functions of the q's and t which do not vary very rapidly with their arguments. Then Schrödinger's wave equation gives

$$i\hbar\frac{\partial}{\partial t}Ae^{iS/\hbar}\rangle = H(q_r, p_r)Ae^{iS/\hbar}\rangle \tag{1.5.27}$$

or

$$\left\{i\hbar\frac{\partial A}{\partial t} - A\frac{\partial S}{\partial t}\right\}\rangle = e^{-iS/\hbar}H(q_r, p_r)Ae^{iS/\hbar}\rangle \tag{1.5.28}$$

Now $e^{-iS/\hbar}$ is evidently a unitary linear operator and may be used for U to give us a unitary transformation. The q's remain unchanged by this transformation, each p_r goes over into

$$e^{-iS/\hbar}H(q_r, p_r)e^{iS/\hbar} = H(q_r, p_r + \partial S/\partial q_r) \tag{1.5.29}$$

since algebraic relations are preserved by the transformation. Thus it becomes

$$\left\{i\hbar\frac{\partial A}{\partial t} - A\frac{\partial S}{\partial t}\right\}\rangle = H\left(q_r, p_r + \frac{\partial S}{\partial q_r}\right)A\rangle \tag{1.5.30}$$

If we neglect the $\hbar$ and equating p_r with $-i\hbar\partial/\partial q_r$, we get

$$-\frac{\partial S}{\partial t} = H_c\left(q_r, \frac{\partial S}{\partial q_r}\right) \tag{1.5.31}$$

The equation is determined by the classical Hamiltonian function H_c and is known as the *Hamilton-Jacobi equation.*

Multiplying $\langle Af$ on the left, we get

$$\langle Af\left\{i\hbar\frac{\partial A}{\partial t} - A\frac{\partial S}{\partial t}\right\}\rangle = \langle AfH\left(q_r, p_r + \frac{\partial S}{\partial q_r}\right)A\rangle \tag{1.5.32}$$

Having it subtracted by its conjugate complex, we obtain

$$2\langle Af\frac{\partial A}{\partial t} = \langle A\left[f, H(q_r, p_r + \frac{\partial S}{\partial q_r}\right]A\rangle \tag{1.5.33}$$

We now have to evaluate the P.B.

$$[f, H(q_r, p_r + \partial S/\partial q_r)] \tag{1.5.34}$$

One assumption that $\hbar$ can be counted as small enables us to expand $H(q_r, p_r + \partial S/\partial q_r)$ as a power series in the p's. The terms of zero degree will contribute nothing to the

P.B. The terms of the first degree in the p's give a contribution to the P.B. which can be evaluated most easily with the help of the classical formula[7]. The amount of this contribution is

$$\sum_s \frac{\partial f}{\partial q_s}\left[\frac{\partial H(q_r,p_r)}{\partial p_s}\right]_{p_r=\partial S/\partial q_r} \tag{1.5.35}$$

The terms of higher degree in the p's give contributions to the P.B. which vanish when $\hbar \to 0$. Thus, with neglect of terms involving $\hbar$,

$$\langle f\frac{\partial A^2}{\partial t}\rangle = \langle A^2 \sum_s \frac{\partial f}{\partial q_s}\left[\frac{\partial H_c(q_r,p_r)}{\partial p_s}\right]_{p_r=\partial S/\partial q_r}\rangle \tag{1.5.36}$$

Now if $a(q)$ and $b(q)$ are any two functions of the q's, there is

$$\langle a(q)b(q)\rangle = \int a(q')dq'b(q') \tag{1.5.37}$$

and so

$$\langle a(q)\frac{\partial b(q)}{\partial q_r}\rangle = -\langle \frac{\partial a(q)}{\partial q_r}b(q)\rangle \tag{1.5.38}$$

provided $a(q)$ and $b(q)$ satisfy suitable boundary conditions. Then

$$\langle f\frac{parital A^2}{\partial t}\rangle = -\langle f\sum_s \frac{\partial}{\partial q_s}\left\{A^2\left[\frac{\partial H_c(q_r,p_r)}{\partial p_s}\right]_{p_r=\partial S/\partial q_r}\right\}\rangle \tag{1.5.39}$$

Since this holds for an arbitrary real function f, we must have

$$\frac{\partial A^2}{\partial t} = -\sum_s \frac{\partial}{\partial q_s}\left\{A^2\left[\frac{\partial H_c(q_r,p_r)}{\partial p_s}\right]_{p_r=\partial S/\partial q_r}\right\} \tag{1.5.40}$$

This is the equation for the amplitude A of the wave function.

1.6 Elementary Applications

1.6.1 digests

The harmonic oscillator

$$H = \frac{1}{2m}(p^2 + m^2\omega^2 q^2) \tag{1.6.1}$$

using Heisenberg equations of motion,

$$\begin{cases}\dot{q}_t = [q_t, H] = p_t/m \\ \dot{p}_t = [p_t, H] = -m\omega^2 q_t\end{cases} \tag{1.6.2}$$

construct an operator

$$\eta = \frac{1}{\sqrt{2m\hbar\omega}}(p + im\omega q) \tag{1.6.3}$$

[7]This formula being valid also in the quantum theory if u is independent of the p's and v is linear in the p's.

and it is easily deduced that

$$\dot{\eta}_t = (2m\hbar\omega)^{-1/2}(-m\omega^2 q_t + i\omega p_t) = i\omega\eta_t \tag{1.6.4}$$

Having it integrated,[8]

$$\eta_t = \eta_0 e^{i\omega t} \tag{1.6.5}$$

where η_0 is a linear operator independent of t, and is equal to the value of η_t at time $t = 0$. The above equations are all as in the classical theory.

Then

$$\hbar\omega\eta\bar{\eta} = (2m)^{-1}(p + im\omega q)(p - im\omega q) = H - \frac{1}{2}\hbar\omega \tag{1.6.6}$$

and similarly

$$\hbar\omega\bar{\eta}\eta = H + \frac{1}{2}\hbar\omega \tag{1.6.7}$$

Thus

$$\bar{\eta}\eta - \eta\bar{\eta} = 1 \tag{1.6.8}$$

Then

$$\bar{\eta}\eta^n - \eta^n\bar{\eta} = n\eta^{n-1} \tag{1.6.9}$$

Also

$$\begin{cases} \hbar\omega\bar{\eta}\eta\bar{\eta} = \bar{\eta}H - \frac{1}{2}\hbar\omega\bar{\eta} \\ \hbar\omega\bar{\eta}\eta\bar{\eta} = H\bar{\eta} + \frac{1}{2}\hbar\omega\bar{\eta} \end{cases} \tag{1.6.10}$$

Thus

$$\bar{\eta}H - H\bar{\eta} = \hbar\omega\bar{\eta} \tag{1.6.11}$$

[8]海森堡表象的一大好处在于算符运算'is analogous to the classic theory'，所以是可以按照经典的方式进行算符的处理——虽然算符的互换性并不能被保证。

Chapter 2

Introduction to Quantum Mechanics by David J. Griffiths

2.1 Fundamental Equations

- Schrödingerequation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{2.1.1}$$

- Time-independent Schrödingerequation:

$$H\psi = E\psi, \qquad \Psi = \psi e^{-iEt/\hbar} \tag{2.1.2}$$

- Hamiltonian operator:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V \tag{2.1.3}$$

- Momentum operator:

$$\mathbf{p} = -i\hbar\nabla \tag{2.1.4}$$

- Time dependence of an expectation value:

$$\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\langle[H,Q]\rangle + \langle\frac{\partial Q}{\partial t}\rangle \tag{2.1.5}$$

- Generalized uncertainty principle:

$$\sigma_A\sigma_B \geqslant |\frac{1}{2i}\langle[A,B]\rangle| \tag{2.1.6}$$

- Canonical commutator:

$$[x,p] = i\hbar \tag{2.1.7}$$

- Angular momentum:

$$[L_x,L_y] = i\hbar L_z, \qquad [L_y,L_z] = i\hbar L_x, \qquad [L_z,L_x] = i\hbar L_y \tag{2.1.8}$$

- Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.1.9}$$

2.2 Fundamental Constants

Planck's constant:	$\hbar$	=	$1.05457 \times 10^{-34}\,\mathrm{J\,s}$
Speed of light:	c	=	$2.99792 \times 10^{8}\,\mathrm{m/s}$
Mass of electron:	m_e	=	$9.10939 \times 10^{-31}\,\mathrm{kg}$
Mass of proton:	m_p	=	$1.67262 \times 10^{-27}\,\mathrm{kg}$
Charge of electron:	e	=	$1.60218 \times 10^{-27}\,\mathrm{C}$
Permittivity of space:	ϵ_0	=	$8.85419 \times 10^{-12}\,\mathrm{C^2/Jm}$
Boltzmann constant:	k_B	=	$1.38066 \times 10^{-23}\mathrm{J/K}$

Fine structure constant:	α	=	$e^2/4\pi\epsilon_0\hbar c$	=	$1/137.036$
Bohr radius:	a	=	$4\pi\epsilon_0\hbar^2/m_e e^2 = \hbar/\alpha m_e c$	=	$5.29177 \times 10^{-11}\mathrm{m}$
Bohr energies:	E_n	=	$E_1/n^2 (n = 1, 2, 3, ...)$		
Ground state energy:	$-E_1$	=	$m_e e^4/2(4\pi\epsilon_0)^2\hbar^2 = \alpha^2 m_e c^2/2$	=	13.6057 eV
Wave function:	ψ_0	=	$\frac{1}{\sqrt{\pi a^3}} e^{-r/a}$		
Rydberg formula:	$\frac{1}{\lambda}$	=	$R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$		
Rydberg constant:	R	=	$-E_1/2\pi\hbar c$	=	$1.09737 \times 10^{7}\mathrm{m}$

Chapter 3

高等物理化学——量子化学课程笔记

3.1 Linux 具体操作

1. 通过 SSH 连接所需服务器；
2. 常用操作、后缀列表：

cd 进入输入目录的文件夹；'cd amusphere/' P.S : 'cd ..' 返回上一级文件夹

ls 列出所在文件夹的子文件夹；

vi 打开文件查看内容；
P.S : 输入不存在的文件可直接创立该文件；

pwd 显示所在文件夹；

mkdir 在所在目录下建立文件夹：'mkdir levest' 表示建立名字为 'levest' 的文件夹

Ins/i 修改文件；'esc' 退出修改，':wq!' 保存文件并退出;':q!' 不保存退出。

***.log** 输出文件；

***.com** 输入文件 / 文本文件；

cp 复制文件至某个目录 'cp einfield.com slot' 表示将 'einfield.com' 在 'slot' 文件夹下进行粘贴

mv 重命名文件/文件夹（后缀还是要加好）；

rm remove; 'rm file.com' 表示删除该文件；'rm -r rescot' 表示删除该文件夹；

Shift+G 移至最后一行;

gg 似乎是回到开头；

tail 打开文件并至最后一行；

/'Zero' 搜索文件含 'Zero' 的地方；

formchk 将 chk 二进制文件转化;

3.2 调教 Gaussian 步骤

1. 运行 GaussView，画出苯甲酸分子；

2. 点击 Calculate ⇒ Gaussian Calculation Setup;
3. 调教各种参数;
4. 若在 windows 内部运行，选择后缀为 *.gif 保存；若在 Linux 系统，选择后缀为 *.com;
5. 在 windows 内部运行 Gaussian 时直接运行；若在 Linux 系统，
   - 修改.com 文件中内容：%chk=benzoicacid.chk
   - 将脚本文件 PBS_Script 拷贝到输入文件所在文件夹
   - 输入命令 qsub PBS_script
   - 等待。

3.3 理论课笔记

3.3.1 量子的化学

1. 算符对易子:
$$[A, B] = AB - BA \tag{3.3.1}$$
2. 算符对易常用公式:
$$[A, BC] = [A, B]C - B[A, C] \tag{3.3.2}$$
$$[AB, C] = [A, C]B + A[B, C] \tag{3.3.3}$$
3. x 与 p 的对易关系:
$$[x, p]\psi = (xp - px)\psi = -i\hbar[x\frac{\partial}{\partial x}\psi - \frac{\partial}{\partial x}(x\psi)] = i\hbar\psi \tag{3.3.4}$$
4. 波函数是量子态在基组中的投影:
$$\psi(x) = \langle x|\psi\rangle \quad \psi(p) = \langle p|\psi\rangle \tag{3.3.5}$$

3.3.2 量子与经典

1. 一维简谐振子的哈密顿量求解:
$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2} \\ &= h\omega\frac{m\omega}{2h}(\hat{x}^2 + \frac{1}{m^2\omega^2}\hat{p}^2) \\ &= h\omega\{\sqrt{\frac{m\omega}{2h}}(\hat{x} - \frac{1}{m\omega}\hat{p}) \cdot \sqrt{\frac{m\omega}{2h}}(\hat{x} + \frac{1}{m\omega}\hat{p}) - \frac{m\omega}{2h}\frac{i}{m\omega}[\hat{x}, \hat{p}]\} \\ &= h\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})\end{aligned}$$

其中，

$$\hat{a}^\dagger = \sqrt{m\omega}2h(\hat{x} - \frac{i}{m\omega}\hat{p}) \tag{3.3.6}$$

$$\hat{a} = \sqrt{m\omega}2h(\hat{x} + \frac{i}{m\omega}\hat{p}) \tag{3.3.7}$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \tag{3.3.8}$$

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \tag{3.3.9}$$

$$\hat{a}^\dagger\hat{a}|n\rangle = n|n\rangle \tag{3.3.10}$$

$$\tag{3.3.11}$$

2.

$$\begin{aligned}\hat{O} &= \sum_i |\phi_i\rangle\langle\phi_i|\hat{O}\sum_j |\phi_j\rangle\langle\phi_j| \\ &= \sum_{ij} |\phi_i\rangle\langle\phi_i|\hat{O}|\phi_j\rangle\langle\phi_j| \\ &= \sum_{ij} \langle\phi_i|\hat{O}|\phi_j\rangle|\phi_i\rangle\langle\phi_j| \\ &= \sum_{ij} O_{ij}|\phi_i\rangle\langle\phi_j|\end{aligned}$$

3. 描述体系状态的本质上是 $|\psi\rangle$, 波函数只是 $|\psi\rangle$ 在实空间上的投影。

Theorem 3.3.1 *Ehrenfest Theorem:*

$$\langle \boldsymbol{p}\rangle = m\frac{d\langle \boldsymbol{x}\rangle}{dt} \tag{3.3.12}$$

$$\langle \boldsymbol{F}\rangle = \frac{d\langle \boldsymbol{p}\rangle}{dt} \tag{3.3.13}$$

Proof 3.3.1 充分考虑到

$$\frac{d|\phi\rangle}{dt} = \frac{1}{i\hbar}[\frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x})]|\phi\rangle \tag{3.3.14}$$

$$\begin{aligned}\frac{d\langle \boldsymbol{x}\rangle}{dt} &= \frac{d\langle\psi|\boldsymbol{x}|\psi\rangle}{dt} \\ &= \frac{d\langle\psi|}{dt}\boldsymbol{x}|\psi\rangle + \langle\psi|\boldsymbol{x}\frac{d|\psi\rangle}{dt} \\ &= -\frac{1}{i\hbar}\langle\psi|[\frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x})]\boldsymbol{x}|\psi\rangle + \langle\psi|\boldsymbol{x}\frac{1}{i\hbar}[\frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x})]|\psi\rangle \\ &= -\frac{1}{i\hbar}(\frac{\boldsymbol{p}^2}{2m}\boldsymbol{x} - \boldsymbol{x}\frac{\boldsymbol{p}^2}{2m})|\psi\rangle \\ &= -\frac{1}{2mi\hbar}\langle\psi|[\boldsymbol{p}^2, \boldsymbol{x}]|\psi\rangle \\ &= -\frac{1}{2mi\hbar}\langle\psi|2\boldsymbol{p}[\boldsymbol{p}, \boldsymbol{x}]|\psi\rangle \\ &= \frac{1}{m}\langle\phi|\boldsymbol{p}|\phi\rangle \\ &= \langle \boldsymbol{p}\rangle\end{aligned}$$

$$\begin{aligned}\frac{d\langle \boldsymbol{p}\rangle}{dt} &= \frac{d\langle\psi|\boldsymbol{p}|\psi\rangle}{dt}\\ &= \frac{d\langle\psi|}{dt}\boldsymbol{p}|\psi\rangle + \langle\psi|\boldsymbol{p}\frac{d|\psi\rangle}{dt}\\ &= -\frac{1}{i\hbar}\langle\psi|[\frac{\boldsymbol{p}^2}{2m}+V(\boldsymbol{x})]\boldsymbol{p}|\psi\rangle + \langle\psi|\boldsymbol{p}\frac{1}{i\hbar}[\frac{\boldsymbol{p}^2}{2m}+V(\boldsymbol{x})]|\psi\rangle\\ &= -\frac{1}{i\hbar}\langle\psi|[V(\boldsymbol{x}),\boldsymbol{p}]|\phi\rangle\\ &= -\frac{1}{i\hbar}\langle\phi|i\hbar\frac{\partial V(\boldsymbol{x})}{\partial \boldsymbol{x}}|\phi\rangle\\ &= \langle\phi|[-\frac{\partial V(\boldsymbol{x})}{\partial \boldsymbol{x}}]|\phi\rangle\\ &= \langle \boldsymbol{F}\rangle\end{aligned}$$

$$\begin{aligned}[V(\boldsymbol{x}),\boldsymbol{p}]|\psi\rangle &= [V(x),-i\hbar\frac{\partial}{\partial \boldsymbol{x}}]|\psi\rangle\\ &= -i\hbar V(x)\frac{\partial}{\partial \boldsymbol{x}} + i\hbar\frac{\partial}{\partial \boldsymbol{x}}[V(\boldsymbol{x})|\psi\rangle]\\ &= -i\hbar V(x)\frac{\partial}{\partial \boldsymbol{x}} + i\hbar\frac{\partial V(\boldsymbol{x})}{\partial \boldsymbol{x}}|\psi\rangle + i\hbar V(\boldsymbol{x})\frac{\partial|\psi\rangle}{\partial \boldsymbol{x}}\\ &= i\hbar\frac{\partial V(\boldsymbol{x})}{\partial \boldsymbol{x}}|\psi\rangle\end{aligned}$$

3.3.3 量子精确解

1. 拉普拉斯算符极坐标变换：

$$\hat{\nabla}^2 = \frac{1}{r^2}[\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}] \tag{3.3.15}$$

2. 分离变量：

$$\begin{cases}[-\frac{1}{2r^2}\frac{d}{dr}(r^2\frac{d}{dr}) - \frac{Z}{r} - E]|\psi_R\rangle = -\frac{\beta}{2r^2}|\psi_R\rangle\\ [-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]|\psi_Y\rangle = \beta|\psi_Y\rangle\\ \\ \Rightarrow \begin{cases}\frac{d^2}{d\phi^2}|\psi_\Phi\rangle = -\alpha\\ \beta\sin^2\theta + \frac{\sin\theta}{|\psi_\Theta\rangle}\frac{d}{d\theta}(\sin\theta\frac{d|\psi_\Theta\rangle}{d\theta}) = \alpha\end{cases}\end{cases} \tag{3.3.16}$$

3. 球谐函数：

$$Y_{lm}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}P_l^{|m|}(\cos\theta)e^{im\phi}} \quad \begin{cases}l = 0,1,2,...,n\\ m = 0,\pm1,\pm2,...,\pm l\end{cases} \tag{3.3.17}$$

4. 轨道角动量算符：

$$\hat{L}^2 = -h^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}] \tag{3.3.18}$$

$$\hat{L}^2 Y_{lm} = l(l+1)h^2 Y_{lm} \tag{3.3.19}$$

$$\hat{L}_z Y_{lm} = mh Y_{lm} \tag{3.3.20}$$

5. 径向波函数：

$$R_{nl}(r) = \sqrt{(\frac{2Z}{n})^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-Zr/n} (\frac{2Zr}{n})^l L_{n-l-1}^{2l+1}(\frac{2Zr}{n}) \tag{3.3.21}$$

$$L_n^\alpha(x) = x^{-\alpha}\frac{1}{n!}(\frac{d}{dx}-1)^n x^{n+\alpha} \tag{3.3.22}$$

6. 类氢原子轨道为理解其他原子电子结构基础，但并非本征，这是由于未考虑电子之间的相互作用，然而完备基使原子轨道的线性组合能够描述分子轨道。

7. 动能算符的近似描述：

$$\hat{T}\psi(x) = -\frac{h^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) \approx \frac{h^2}{2m\Delta x^2}[2\psi(x) - \psi(x+\Delta x) - \psi(x-\Delta x)] \tag{3.3.23}$$

$$T_{ij} = \frac{h^2}{2m\Delta x^2} \times \begin{cases} 2, & i = j \\ -1, & |i-j| = 1 \\ 0, & others \end{cases} \tag{3.3.24}$$

8. 离散变量表象 (DVR)，优点：形式简单，图像清晰，方法普适。缺点：基组巨大，不适合大量自由度的计算。

$$V_{ij} = V(x_i)\delta_{ij} \tag{3.3.25}$$

$$T_{ij} = \frac{h^2}{2m\Delta x^2} \times \begin{cases} \frac{\pi^2}{3}, & i = j \\ \frac{2(-1)^{i-j}}{(i-j)^2}, & i \neq j \end{cases} \tag{3.3.26}$$

3.4 量子近似解

变分法 在有限空间中寻找最优解；任意波函数对应的能量期望值都不小于最低本征态能量

Theorem 3.4.1 *The eigenstate of the system has the minimum energy compared to all other states.*

Proof 3.4.1

$$\begin{cases} H|\psi_i\rangle = E_i|\psi_i\rangle \\ |\psi\rangle = \sum_i c_i|\psi_i\rangle \end{cases} \tag{3.4.1}$$

$$\Rightarrow \langle\psi|H|\psi\rangle = \sum_i c_i^* \langle\psi_i|H\sum_j c_j|\psi_j\rangle \tag{3.4.2}$$

$$= \sum_{ij} c_i^* c_j E_j \delta_{ij} = \sum_i c_i^* c_i E_i \geq \sum_i c_i^* c_i E_0 = E_0 \tag{3.4.3}$$

微扰法 尽可能利用简单体系的精确解描述复杂问题

$$H|\psi_i\rangle = E_i|\psi_i\rangle \quad H = H^{(0)} + \lambda H^{(1)} \tag{3.4.4}$$

$$\begin{cases} |\psi_i\rangle = |\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle \\ E_i = E_i^{(0)} + \lambda E_i^{(1)} \end{cases}$$
$$\Rightarrow (H^{(0)} + \lambda H^{(1)})(|\psi_i^{(0)}\rangle + \lambda|\psi_i^{(0)}\rangle) = (E_i^{(0)} + \lambda E_i^{(1)})(|\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle)$$
$$\Rightarrow \begin{cases} (H^{(0)} - E_i^{(0)})|\psi_i^{(0)}\rangle = 0 \\ (H^{(0)} - E_i^{(0)})|\psi_i^{(1)}\rangle + (H^{(1)} - E_i^{(1)})|\psi_i^{(0)}\rangle = 0 \end{cases}$$
$$\Rightarrow \langle\psi_j^{(0)}|H^{(0)} - E_i^{(0)}|\psi_i^{(1)}\rangle = \langle\psi_j^{(0)}|(E_i^{(1)} - H^{(1)})|\psi_i^{(0)}\rangle$$
$$\Rightarrow (E_j^{(0)} - E_i^{(0)})\langle\psi_j^{(0)}|\psi_i^{(1)}\rangle = E_i^{(1)}\delta_{ij} - \langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle$$
$$\Rightarrow \begin{cases} E_i^{(1)} = \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle & i = j \\ |\psi_i^{(1)}\rangle = \sum_{j\neq i} \frac{\langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} & i \neq j \end{cases}$$

二阶微扰先略。

微扰应用：

$$T = \frac{p^2}{2m} - \frac{p^4}{8c^2m^3} + ... \tag{3.4.5}$$

非谐性：对势能项做微扰

$$V = V(0) + \frac{k}{2}x^2 + \frac{\alpha}{6}x^3 + \frac{\beta}{24}x^4 + ... \tag{3.4.6}$$

Stark 效应：对外场做微扰

$$H = H_0 - \mu \cdot F \tag{3.4.7}$$

全同性原理 量子世界的全同粒子不可区分，任何两个粒子交换不影响体系的状态；

交换算符

$$\mathbf{P}_{12}[f(q_1, q_2, ..., q_n)] = f(p_2, p_1, ..., p_n) \tag{3.4.8}$$
$$P_{12}[1s(1)\alpha(1)3s(2)\beta(2)] = 1s(2)\alpha(2)3s(1)\beta(1) \tag{3.4.9}$$

交换算符的本征值

$$\mathbf{P}_{12}[\mathbf{P}_{12}[f(q_1, q_2, ..., q_n)]] = f(q_1, q_2, ..., q_n) \Rightarrow P_{12}^2 = 1 \tag{3.4.10}$$

Thus

$$c_i = \pm 1 \tag{3.4.11}$$

交换算符的本征值为实数，只能为 ± 1，对应波函数分别称为对称和反对称。不具备对称性的波函数无法用于描述全同粒子。

玻色子和费米子 波函数反对称的粒子为费米子，而波函数对称的粒子为玻色子

反对称粒子的泡利不相容原理

$$f(q_1,q_1,....,q_n)=-f(q_1,q_1,....,q_n)\Rightarrow f(q_1,q_1,....,q_n)=0 \tag{3.4.12}$$

自旋统计 Pauli 使用量子场论证明了自旋统计理论，指出费米子（电子和质子等）拥有半整数自旋，而玻色子（光子和声子等）具有整数自旋，电子具有 $\frac{1}{2}$ 的自旋。

相对论量子化学 自旋角动量很自然地以内禀方式蕴含在相对论性狄拉克方程中。作为最低阶非相对论近似，薛定谔方程人为地丢弃了自旋这种相对论效应。

Slater 行列式

$$|\Psi(p_1,p_2,...,p_n)|=\frac{1}{\sqrt{N!}}\begin{vmatrix}|\phi_1(q_1)\rangle & |\phi_2(q_1)\rangle & ... & |\phi_n(q_1)\rangle\\ |\phi_2(q_2)\rangle & |\phi_2(q_2)\rangle & ... & |\phi_n(q_2)\rangle\\ ... & ... & ... & ...\\ |\phi_1(q_n)\rangle & |\phi_2(q_n)\rangle & ... & |\phi_n(q_n)\rangle\end{vmatrix} \tag{3.4.13}$$

双电子自旋

$$\alpha(1)\alpha(2),\beta(1)\beta(2),\alpha(1)\beta(2),\beta(1)\alpha(2)\begin{cases}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]\\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\end{cases} \tag{3.4.14}$$

$$\begin{aligned}
E&=\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\\
&=\frac{(\sum_i c_i^*\langle\phi_i|)\hat{H}(\sum_j c_j|\phi_j\rangle)}{\sum_i c_i^*\langle\phi_i|(\sum_j c_j|\phi_j\rangle)}\\
&=\frac{\sum_{ij}c_i^*c_j\langle\phi_i|\hat{H}|\phi_j\rangle}{\sum_{ij}c_i^*c_j\langle\phi_i|\phi_j\rangle}\\
&=\frac{\sum_{ij}c_i^*H_{ij}c_j}{\sum_{ij}c_i^*S_{ij}c_j}\\
&=\frac{C^*HC}{C^*SC}\\
&\Rightarrow EC^*SC=C^*HC\\
&\Rightarrow \partial_{c_k}(EC^*SC)=\partial_{c_k}(C^*HC)\\
&\Rightarrow (\partial_{c_k}E)C^*SC+E(\partial_{c_k}C^*)SC+EC^*S\partial_{c_k}C=(\partial_{c_k}C^*)HC+C^*H\partial_{c_k}C\\
&\Rightarrow \partial_{c_k}E=\frac{\partial_{c_k}(HC-ESC)+(C^*H-EC^*S)\partial_{c_k}C}{C^*SC}
\end{aligned}$$

$$\begin{aligned}
&\frac{\partial E}{\partial c_k}=0\\
&\Rightarrow\begin{cases}HC-ESC=0\\ C^*H-EC^*S=0\end{cases}\\
&\Rightarrow HC=ESC
\end{aligned}$$

$$\begin{cases} |\phi_{1s}^{(1)}\rangle = \frac{1}{\sqrt{\pi}} e^{-r_1}; \\ |\phi_{1s}^{(1)}\rangle = \frac{1}{\sqrt{\pi}} e^{-r_2}; \end{cases} \tag{3.4.15}$$

$$\Rightarrow S = \langle \phi_{1s}^{1} | \phi_{1s}^{(2)} \rangle = (1 + R + \frac{R^2}{3}) e^{-R} \tag{3.4.16}$$

$$\begin{aligned} \langle \phi_{1s}^{(1)} | \hat{H} | \phi_{1s}^{(1)} \rangle &= \langle \phi_{1s}^{(1)} | (-\frac{\nabla_e^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}) | \phi_{1s}^{(1)} \rangle \\ &= \langle \phi_{1s}^{(1)} | -\frac{\nabla_e^2}{2} - \frac{1}{r_1} | \phi_{1s}^{(1)} \rangle - \langle \phi_{1s}^{(1)} | \frac{1}{r_2} | \phi_{1s}^{(1)} \rangle + \frac{1}{R} \\ E_{1s} - \langle \phi_{1s}^{(1)} | \frac{1}{r_2} | \phi_{1s}^{(1)} \rangle &= E_{1s} + J \end{aligned}$$

$$\langle \phi_{1s}^{(2)} | \hat{H} | \phi_{1s}^{(2)} \rangle = E_1 s + J$$

库伦积分法

$$\begin{cases} |\phi_{1s}^{(1)}\rangle = \frac{1}{\sqrt{\pi}} e^{-r_1} \\ |\phi_{1s}^{(2)}\rangle \frac{1}{\sqrt{\pi}} e^{-r_2} \end{cases} \quad \Rightarrow J = (1 + \frac{1}{R}) e^{-2R} \tag{3.4.17}$$

交换积分

$$\begin{cases} |\phi_{1s}^{(1)}\rangle = \frac{1}{\sqrt{\pi}} e^{-r_1} \\ |\phi_{1s}^{(2)}\rangle \frac{1}{\sqrt{\pi}} e^{-r_2} \end{cases} \quad \Rightarrow K = (\frac{1}{R} - \frac{2R}{3}) e^{-R} \tag{3.4.18}$$

它在分子成键中起到了非常关键的作用，是量子效应。

$$\begin{aligned} & |\psi(c_1, c_2)\rangle = c_1 |\psi_{1s}^{(1)}\rangle + c_2 |\psi_{1s}^{(2)}\rangle \\ \Rightarrow & E(c_1, c_2) = \frac{\langle \psi_(c_1, c_2) | \hat{H} | \psi(c_1, c_2) \rangle}{\langle \psi(c_1, c_2) | \psi(c_1, c_2) \rangle} \\ = & \frac{(c_1^2 + c_2^2)(E_{1s} + J) + (c_1^* c_2 + c_1 c_2^*)(S E_{1s} + K)}{(c_1^2 + c_2^2) + (c_1^* c_2 + c_1 c_2^*) S} \\ = & (E_{1s} + J) + \frac{(c_1^* c_2 + c_1 c_2^*)(K - SJ)}{(c_1^2 + c_2^2) + (c_1^* c_2 + c_1 c_2^*) S} \\ = & (E_{1s} + J) + \frac{K - SJ}{\frac{c_1^2 + c_2^2}{c_1^* c_2 + c_1 c_2^*} + S} \end{aligned}$$

平均场近似 忽略电子动态关联，多电子问题转化为单电子问题，多电子波函数简化为单电子波函数的乘积，使用自洽场得到单电子波函数

Koopmans 定理 假设离子轨道与中性分子轨道相同，可计算分子的电离能喝亲和势，改变电子数会引起单电子轨道重排和弛豫，与电子关联量级相似，但符号相反

$$
\begin{aligned}
&\langle \hat{H} \rangle_{Hartree} \\
=&\langle \Psi(\{r_i\}) | \hat{H} | \Psi(\{r_i\}) \rangle \\
=&(\prod_i \langle \phi_i(r_i) |)(\sum_k \hat{h}_k + \frac{1}{2}\sum_{k\neq l} \frac{1}{\hat{r}_k l})(\prod_j |\phi_j(r_j)\rangle) \\
=&\sum_k \langle \phi_k(r_k) | \hat{h}_k | \phi_k(r_k) \rangle (\prod_{i\neq k} \langle \phi_i(r_i) |)(\prod_{j\neq k} |\phi_j(r_j)\rangle) \\
&+ \frac{1}{2}\sum_{k\neq l} \langle \phi_k(r_k)\phi_l(r_l) | \frac{1}{\hat{r}_{kl}} \phi_k(r_k)\phi_l(r_l) | \langle \rangle \prod_{i\neq\{k,l\}} \langle \phi_i(r_i) |)(\prod_{i\neq\{k,l\}} |\phi_j(r_j)\rangle) \\
=&\sum_k \langle \phi_k(r_k) | \hat{h}_k | \phi_k(r_k) \rangle + \frac{1}{2}\sum_{k\neq l} \langle \phi_k(r_k)\phi_l(r_l) | \frac{1}{\hat{r}_{kl}} | \phi_k(r_k)\phi_l(r_l) \rangle
\end{aligned}
$$

变分法与基组 Hartree-Fock 变分法中，波函数的形式原则上是任意的，但是波函数的随意变化数字处理起来非常麻烦，使用基组对波函数进行线性展开，对量子化学中的所有电子结构计算都至关重要。

原子轨道基组 完备的基组在量子化学是很难实现的，从计算量的角度需要尽可能地减少基组的数目。氢原子的电子结构可解析求解，为理解更复杂原子和分子的电子结构打开了大门。使用氢原子和类氢离子的原子轨道作为基组，是解决复杂化学问题的通用做法，有着重要的意义。

原子轨道

$$\psi(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \tag{3.4.19}$$

Slater 基组和 Gaussian 基组

$$\chi(r) \sim e^{-\xi r} \qquad g(r) \sim e^{-\alpha r^2} \tag{3.4.20}$$

从基组数目角度看，STO 比 GTO 好；

从波函数积分计算效率角度看，GTO 比 STO 好。

高斯函数线性组合

$$e^{-\xi r} = \frac{\xi}{2\sqrt{\pi}} \int_0^\infty \alpha^{-3/2} e^{-\xi^2/4\alpha} e^{-\alpha r^2}\, d\alpha \tag{3.4.21}$$

$$\Rightarrow \xi_\mu(r - R_A) \approx \sum_P c_{p\mu} g_p(\alpha_{p\mu}, r - R_p) \tag{3.4.22}$$

$$\begin{cases} g_{1s}(\alpha, r) = (8\alpha^3/\pi^3)^{1/4} e^{-\alpha r^2}; \\ (\alpha, r) = (128\alpha^5/\pi^3)^{1/4} x e^{-\alpha r^2}; \\ g_{3dxy}(\alpha, r) = (2048\alpha^7/\pi^3)^{1/4} xy e^{-\alpha^2} \end{cases} \tag{3.4.23}$$

Dunning 原子轨道基组 如 aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z...

aug: 弥散, cc: correlation consistent; p: polarized; V: Valence bonds; DZ: double zeta.

赝势原子轨道基组 当原子中的电子很多事，内层电子通常对原子性质的影响很小，但是其对应的全电子基组很复杂，为了减少计算量，其贡献可通过有效势能来描述，而且可以包含相对论效应的修正。

赝势基组 赝势基组包括赝势和基组两部分，内部电子的贡献采用赝势描述，直接放在哈密顿量里，外层价电子采用一般的基组。

LANL1 只考虑加电子，LANL2 系列除了加电子外，还考虑次外层电子，因为他们与价层的能查不明显，而且对成键有贡献。

LanL2DZ：对 H-Ne 使用 D95V 全电子基组，对 Na-Bi 使用赝势基组，也就是 LANL 有效核势加上 DZ 基组；LanL2DZ 是常用基组，适合过渡金属等中等质量的金属元素。

总能量 变分法保证基组越大，HF 能量越小，越接近于精确值。

Hessian 矩阵

$$F_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \tag{3.4.24}$$

振动频率

$$\sum_{j-1}^{N} (F_{ij} - \delta_{ij}\lambda_k) l_{jk} \Rightarrow det(F_{ij} - \delta_{ij}\lambda_k) = 0 \tag{3.4.25}$$

电子关联 Hartree-Fock 理论中采用平均场处理电子-电子相互作用，缺乏电子关联，直接用多电子基组展开多电子波函数计算量巨大，很难实现。

如何有效加入电子关联 以 Hartree-Fock 得到的单 Slater 行列式为基础，考虑多电子关联的主要方法有 CI(Configurate Interaction)、MCSCF(Multi-Configured Self-Consistent Field)、MPn、CC(Couple Cluster) 等。

HF 方法的计算量与电子数的四次方成正比，MP2 为五次方，CISD 和 CCS 为六次方，CCSD（T）为七次方，CISDT 和 CCSDT 为八次方，随着电子数增加而迅速增加。

多电子组态 在 Hartree-Fock 分子轨道的基础上，组态相当于多电子组态，用之可展开多电子波函数，对角化多电子哈密顿量，得到基态和激发态性质。

若有 K 个分子轨道，每个轨道最多占据两个电子，总电子书数 N，则 n 激发组态数为

$$C_N^n C_{2K-N} = \frac{N!}{n!(N-n)!} \frac{(2K-N)!}{n!(2K-N-n)!} \tag{3.4.26}$$

每个组态都可以用 Slater 行列式表示。

多电子波函数的组态线性组合

$$\begin{aligned} |\Phi\rangle &= c_0|\psi_0\rangle + \sum_{ra} c_a^r |\psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \sum_{a<b<c,r<s<t} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle + ... \\ &= c_0|\psi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + ... \end{aligned}$$

Full CI（FCI）包括所有可能的激发，可以给出多电子问题的精确解，

实际上即使我们只考虑有限个单电子基组，所有可能的 N-电子基组数目也非常庞大。

通常需要对组态进行阶段，只处理有限个 N-电子基组。如只考虑单激发，成为 CIS；截断到双激发，成为 CISD。

组态相互作用关系 单激发对基态能量没有直接贡献，双激发对基态能量的修正起首要作用，Hartree Fock 的本征值问题等价于确保组态与单激发不直接混合，相差两个激发的组态之间没有直接相互作用。

Brillouin 定理

$$\langle\psi_0|\hat{H}|\psi_a^r\rangle = \langle a|\hat{h}|r\rangle + \sum_b \langle ab||rb\rangle = \langle\phi_a|\hat{f}|\phi_r\rangle = 0 \tag{3.4.27}$$

$$\begin{aligned}\langle\psi_0|\hat{H}|\psi_a^r\rangle &= (\prod_i \langle\phi_i|)O_1(\prod_j |\phi_j\rangle) \\ &= \sum_k (\prod_i \langle\psi\phi_i|)h_k(\prod_l |\phi_j\rangle) \\ &= \sum_k \langle\phi_k|h_k|\phi_k\rangle * \prod_{i\neq k}\langle\phi_i| \prod_{j\neq k}\langle\phi_j| \\ &- \sum_k \langle\phi_k|h_k|\phi_k\rangle\end{aligned}$$

Thomas-Fermi 理论 是现代密度泛函理论的雏形，能量期望值完全形成电子密度的泛函，使得电子结构处理变得非常简单。

当时其精度有限，因为动能项通过简单的近似得到，而且没有考虑交换和关联对总能量的贡献。

Hohenberg-Kohn 定理

- 所有客观测量的期望值原则上都是基态电子密度的泛函。

电子密度分布 $\rho(r)$ 决定了总电子数 N，从而哈密顿量 $H = T_e + U_{ee} + V_{ext}$ 总只有最后一项可能是不确定的。如果 $\rho(r)$ 是两个不同哈密顿量 H 和 H' 的基态电子密度，而两者的基态波函数分别为 $|\Psi\rangle$ 和 $|\Psi'\rangle$，基态能量分别为 E_0 和 E_0', 基态在不兼并的情况下有

$$\begin{cases} E_0 &= \langle\Psi|H|\Psi\rangle \\ &< \langle\Psi'|H|\Psi'\rangle \\ &= \langle\Psi'|H'|\Psi'\rangle + \langle\Psi'|(H-H')|\Psi'\rangle \\ &= E_0' + \int \rho(r)(V_{ext} - V_{ext}')\,dr \\ E_0' &= \langle\Psi'|H'|\Psi'\rangle \\ &< \langle\Psi|H'|\Psi\rangle \\ &= \langle\Psi|H|\Psi\rangle + \langle\Psi|(H'-H)|\Psi\rangle \\ &= E_0 - \int \rho(r)(V_{ext} - V_{ext}')\,dr \end{cases} \tag{3.4.28}$$

Then

$$E_0 + E_0' < E_0 + E_0' \tag{3.4.29}$$

矛盾，故电子密度与唯一的哈密顿量对应。反过来，哈密顿量有唯一的基态电子密度。[1]因此，所有可观测量的期望值都是基态电子密度的泛函，特别地，基态总能量是电子密度的泛函：

$$E[\rho] = T_e[\rho] + V_{ext}[\rho] + U_{ee}[\rho] \tag{3.4.30}$$

[1]在这里，需要指出的是此定理在基态不兼并的情况下成立。

- 基态电子密度原则上可以通过变分法严格得到。

Kohn-Sham 密度泛函理论 哈密顿量中的动能项难以用密度泛函直接表达，而波函数可以更容易地计算动能，为此 1965 年 Kohn 和 Sham 提出了融合波函数和密度的现代 DFT 理论，使密度泛函理论成为实际可行的理论方法。

- 动能

$$T_0[\rho] = \sum_i \langle\phi_i| - \frac{1}{2}\nabla^2|\phi_i\rangle \tag{3.4.31}$$

- 库伦势

$$U_{cl}[\rho] = \frac{1}{2}\iint \frac{\rho(r')\rho(r)}{|r'-r|}\,drdr' \tag{3.4.32}$$

$$\begin{aligned}
&H|\phi_i\rangle = E_i|\phi_i\rangle \\
&|\phi(t=0)\rangle \sum_i c_i(0)|\phi_i\rangle \\
\Rightarrow &\frac{\partial|\phi(t)\rangle}{\partial t} = \frac{1}{i\hbar}H|\phi(t)\rangle \\
\Rightarrow &c_i|\phi_i\rangle = \frac{1}{i\hbar}\sum_i \langle H|\phi_i\rangle \\
\Rightarrow &\langle\phi_j|\sum_i c_i|\phi_i\rangle = \frac{1}{i\hbar}\sum_i c_i E_i\langle\phi_j|\phi_i\rangle \\
\Rightarrow &c_j^* = \frac{1}{i\hbar}c_j E_j \\
\Rightarrow &c_j(t) = c_j(0)e^{\frac{e_j}{i\hbar}t} \\
\Rightarrow &|\phi(t)\rangle = \sum_i c_j|\phi_j\rangle
\end{aligned}$$

HK 定理 体系的基态电子密度与外势一一对应；

RG 定理 但体系的初态确定时，任何时刻电子密度都与外势一一对应；

正定理 哈密顿量

$$H(r,t) = T_e(r) + U_{ee}(r) + V_{ext}(r,t) \tag{3.4.33}$$

其中，动能项 $T_e = -\sum \frac{\nabla_i^2}{2}$，电子相互作用项 $U_{ee} = \frac{1}{2}\sum_{i\neq j}\frac{1}{r_i - r_j}$ 当外势项 $V_{ext}(r,t) = \sum_i v(r,t)$ 已知时，含时哈密顿量确定。

外势有唯一的含时电子密度与之对应 薛定谔方程 $i\frac{\partial}{\partial t}|\psi(r,t)\rangle = H(r,t)$

逆定理 假设

电流密度

$$j(r) = \frac{1}{2i}\sum_{i=1}^{N}[\nabla_i\delta(r-r_i) + \delta(r-r_i)\nabla_i] \quad f(r,t) = \langle\psi(t)|j(r)|\psi(t)\rangle \tag{3.4.34}$$

海森堡方程

$$\frac{\partial}{\partial t}j(r,t) = -i\langle\psi(r,t)|[j(r)H(r,t)]|\psi(r,t)\rangle \tag{3.4.35}$$

分子存在振动能级，其能级差正好落于红外光波段。外界电磁波对体系的影响可通过哈密顿量的一阶微扰进行处理:

$$\hat{H} = \hat{H}_0 + \hat{W} \tag{3.4.36}$$

$|\phi_n\rangle$ 定义为基态哈密顿量, 即 $\hat{H}_0$ 的特征向量。由于 $\hat{H}_0$ 是一个可观测量，其特征向量能够形成完备基组，故针对 3.4.36的特征向量 $|\psi(t)\rangle$ 可进行线性展开:

$$\psi(t) = \sum_n c_n(t) \exp(-\frac{i}{\hbar} E_n t) \, |\phi_n\rangle \tag{3.4.37}$$

其中 E_n 为 $|\phi_n\rangle$ 对应的特征根。并且拥有初始条件

$$c_n(t=0) = \delta_{n,i} \tag{3.4.38}$$

其中，i 表示 $t=0$ 状态下体系所处的状态。当体系经过 t 时间后，体系被观测为处于 f 的状态的概率为

$$w_{i\to f}(t) = |c_f(t)|^2 \tag{3.4.39}$$

为计算 c_n 对 3.4.37式对时间进行求导, 并结合 Schrödinger's equation, 得到

$$i\hbar \sum_n (\frac{dc_n}{dt} - \frac{i}{\hbar} E_n c_n) \exp(-\frac{i}{\hbar} E_n t) |\phi_n\rangle = \sum_n c_n \exp(-\frac{i}{\hbar} E_n t)(E_n + \hat{W}) |\phi_n\rangle \tag{3.4.40}$$

化简并左乘 $\langle\phi_m|$，得到

$$i\hbar \frac{dc_m}{dt} = \sum_n W_{mn} c_n \exp[\frac{i}{\hbar}(E_m - E_n)t] \tag{3.4.41}$$

并定义

$$W_{mn} = \langle\phi_m|\hat{W}|\phi_n\rangle \tag{3.4.42}$$

对公式进行积分，可得到

$$c_m(t) = c_m(0) + \frac{1}{i\hbar} \int_0^t dt' \sum_n W_{mn} \exp[\frac{i}{\hbar}(E_m - E_n)t'] c_n(t') \tag{3.4.43}$$

针对微扰的一阶项,$c_m(t)$ 由下式给出:

$$c_m(t) = c_m(0) + \frac{1}{i\hbar} \int_0^t dt' \sum_n W_{mn} \exp[\frac{i}{\hbar}(E_m - E_n)t'] c_n(0) \tag{3.4.44}$$

代入状态 i 及 f 的初始条件，得到

$$c_f(t) = \frac{1}{i\hbar} \int_0^t dt' W_{fi} \exp[\frac{i}{\hbar}(E_f - E_i)t'] \tag{3.4.45}$$

并假设 W_{fi} 并不随时间发生改变，从而直接积分得到

$$|c_f(t)|^2 = w_{i\to f}(t) = |W_{fi}|^2 \frac{\sin^2[(E_f - E_i)t/(2\hbar)]}{[(E_f - E_i)/2]^2} \tag{3.4.46}$$

若对一个较大的 t, 有

$$w_{i\to f}(t) \approx |W_{fi}|^2 \frac{2\pi}{\hbar} t\delta(E_f - E_i) \tag{3.4.47}$$

即每一个元时间发生跃迁的概率为

$$P_{i\to f} = \frac{1}{t} w_{i\to f}(t) = \frac{2\pi}{\hbar} |W_{fi}|^2 \delta(E_f - E_i) \tag{3.4.48}$$

从而推导得到 Fermi's Golden Rule.

$$P_{i\to f} = \frac{2\pi}{\hbar} |\langle \phi_f | \hat{W} | \phi_i \rangle|^2 \rho(E_f = E_i) \tag{3.4.49}$$

其中 $\rho(E_f = E_i)$ 表达了其态密度。
在偶极近似中，与电磁波的作用可表示为

$$\hat{V}(t) = \hat{V}_{el}(t) + \hat{V}_{mag}(t) \begin{cases} \hat{V}_{el}(t) = -\overrightarrow{\mu}_{el} \cdot \overrightarrow{E} \\ \hat{V}_{mag}(t) = -\overrightarrow{\mu}_{mag} \cdot \overrightarrow{E} \end{cases} \tag{3.4.50}$$

在低磁场环境下电场相互作用占主导，从而推导得到吸收峰

$$G_{fi} = \frac{8\pi^3 h}{3h^2(4\pi\varepsilon_0)c} |\langle f | \overrightarrow{\mu} | i \rangle|^2 \tag{3.4.51}$$

从而可得到 G_{fi} 与偶极矩大小成正相关，若一个键的振动带来大的偶极矩变化，其吸收峰会较大；而若不产生偶极矩，则 $|\langle f | \overrightarrow{\mu} | i \rangle|$ 一项为零，故不发生吸收。

3.5 组会笔记

离散空间连续化 可以理解为给一大堆的 δ 函数赋予一定的宽度，或者将一堆离散的点进行拟合；

连续空间离散化 将函数用许多高斯函数进行分离，然后将高斯函数转化为 δ 函数；

Charging Patching Method 假设一些部分体系之间的相互作用是有限的，从而能够将一些大体系划分为几个小体系计算电子密度（个人猜测其内涵）

> It is assumed that the charge density at a given point depends only on the local atomic environment around the point. As a relsult, charging density motifs for all the atoms can be calculated from prototype system, and can then be used to reassemble the charge density of a large system.

$$m_{l_\alpha}(\mathbf{r}-\mathbf{R}_\alpha)=\rho_{LDA}(\mathbf{r})\frac{w_\alpha(|\mathbf{r}-\mathbf{R}_\alpha|)}{\sum_{\mathbf{R}_{\alpha'}} w_{\alpha'}(|\mathbf{r}-\mathbf{R}_{\alpha'}|)} \tag{3.5.1}$$

R_α: an atomic site of atom typed α

$m_{l_\alpha}(\mathbf{r}-\mathbf{R}_\alpha)$: charge-density motif belonging to this atomic site;

$\rho_{LDA}(\mathbf{r})$: the self-consistently calculated charge density of a prototype system

$w_\alpha(\mathbf{r})$: exponential decay function

$$\rho_{\text{patch}}(\mathbf{r})=\sum_{\mathbf{R}_\alpha} m_{l_\alpha}(\mathbf{r}-\mathbf{R}_\alpha) \tag{3.5.2}$$

min-cost problem Minimum-cost flow problem, is an optimization and decision problem to find the cheapest possible way of sending a certain amount of flow through a flow network. A typical application of this problem involves finding the best delivery route from a factory to a warehouse where the road network has some capacity and cost associated.

The minimum cost flow problem is one of the most fundamental among all flow and circulation problems because most other such problems can be cast as a minimum cost flow problem and also that it can be solved very efficiently using the network simplex algorithm.

A flow network is a directed graph $G=(V,E)$ with a source vertex $s\in V$ and a sink vertex $t\in V$, where each edge $(u,v)\in E$ has capacity $c(u,v)>0$, flow $f(u,v)\geq 0$ and cost $a(u,v)$, with most minimum-cost flow algorithms supporting edges with negative costs. The cost of sending this flow along an edge (u,v) is $f(u,v)\cdot a(u,v)$. The problem requires an ammount of flow d to be sent from source s to sink t.

The definition of the problem is to minimize the **total cost** of the flow over all edges:

$$\sum_{(u,v)\in E} a(u,v)\cdot f(u,v) \tag{3.5.3}$$

with the constraints

$$\begin{aligned}
\textbf{Capacity constraints:} & f(u,v) \geq c(u,v) \\
\textbf{Skew symmetry:} & f(u,v) = -f(v,u) \\
\textbf{Flow conservation:} & \sum_{w \in V} f(u,w) = 0 \,\text{for all}\, u \neq s,t \\
\textbf{Required flow:} & \sum_{w \in V} f(s,w) = d \,\text{and}\, \sum_{w \in V} f(w,t) = d
\end{aligned}$$

Network simplex algorithm In mathematical optimization, the network simplex algorithm is a graph theorestic specialization of the simplex algorithm.

The algorithm is usually formulated in terms of a standard problem, minimum-cost flow problem and can be efficiently solved in polynomial time.

FSSH 方法 简单高效的处理核-电子耦合非绝热动力学模型，有如下缺点：

- 轨迹之间独立，天生不存在 decoherence 效应，需要额外算法
- 每个轨迹演化过程需满足能量守恒，速度校正能量不够时，就会出现 frustrated hopping

SCH（Consensus Surface Hopping） 利用多轨迹系综模拟体系的密度矩阵的演化，每个轨迹的跃迁由体系的密度矩阵来决定。

- 每个轨迹不需保证能量守恒，跃迁前后速度矫正被舍弃；
- 轨道势能面跃迁前后不校正栋梁，理由：
  - 集体代表密度演化的轨迹不需要各自满足能量守恒
  - 速度校正违背了耦合刘维尔方程的局域性质；跃迁前后不应改变核的相空间的位置。
- 不额外加入 decoherence 算法，能够包括退相干效应；
- 判断是否跃迁时，比较的是 $\Delta\sigma_k$ 和随机数 η

量子刘维尔定理

$$i\hbar\frac{\partial\rho}{\partial t} = [\mathbf{H},\rho] \tag{3.5.4}$$

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \partial_t|\psi\rangle\langle\psi| \\
&= \partial_t|\psi\rangle\langle\psi| + |\psi\rangle\partial_t\langle\psi| \\
i\hbar\partial_t(|\psi\rangle\langle\psi|) &= \mathbf{H}|\psi\rangle\langle\psi|
\end{aligned}$$

$$\rho = |\psi\rangle\langle\psi| = \sum_{i,j} c_i|\psi_i\rangle c_j^*\langle\psi_j| = \sum_{i,j} c_{ij}|\psi_i\rangle\langle\psi_j| \tag{3.5.5}$$

$$\frac{1}{i\hbar}[\mathbf{H},\rho] = \{\{\mathbf{H},\rho\}\} = \{\mathbf{H},\rho\} + O(\hbar^2) \tag{3.5.6}$$

Charge transfer mechanism

- The competition between coherent tunneling and incoherent hopping
- For small V, the population tends to localize to form polarons, and incoherent hopping dominates the transfer processes.
- For large V, the population tends to be delocalized for a few hundred femtoseconds and coherent tunneling dominates transfer processes through delocalized states.
- The effect of coherent tunneling becomes weaker along a linear chain because of the uphill site energies and localization.
- With increasing site numbers, a hange of the charge transfer mechanism from tunneling to hopping occurs, and this process is strongly dependent on the tunneling parameter V.

Charge separation in photo voltaic systems:

Exciton dissociation occurs within a few hundred femtoseconds when the delocalized states are first reached. After that, polaron formation can localize the electronic states; holes and electrons will move via incoherent hopping within these localized states. The transfer mechanism of this separation from tunneling to hopping.

最少面间跳跃 John Tully 的最少面间跳跃，面间跳跃的轨迹平均是把每条轨迹铵概率而非概率幅叠加。

- 电子必须用量子力学描述
- 原子核质量比电子大得多，往往可近似认为服从经典力学
- 经典的原子核在与量子的电子构成的势能面间跳跃
- 非绝热过程中原子核的量子力学效应事实上较为明显

Chapter 4

文献摘要

4.1 *On the Quantum Correction For Thermodynamics* by E. Wigner

1. The mean value of any physcial quantity is, (apart from a normalizing constant depending only on temperature), the sum of the diagonal elements of the matrix

$$Qe^{-\beta H} \tag{4.1.1}$$

where Q is the matrix(operator) of the quantity under consideration and H is the Hamiltonian of the system.

2. If a wave function $\psi(x_1 \cdots x_n)$ is given one may build the following expression

$$P(x_i; p_i) = \left(\frac{1}{h\pi}\right)^n \int_{-\infty}^{\infty} dy_i \, \psi(x_i + y_i)^* \psi(x_i - y_i) e^{2i \sum p_i y_i / h} \tag{4.1.2}$$

and call it the probability-function of the simultaneous values of $x_1 \cdots x_n$ for the coordinates and p_i for the momenta.[1]

3. 上式恒为实数但不恒为正数。当对 p 进行积分时能够给出一般熟知的实空间下的概率分布函数，即 $|\psi(x_i)|^2$，对 x_i 积分可得到关于 p_i 的概率分布函数

$$\left| \int dx_i e^{i \sum_l p_l x_l / h} \right|^2 \tag{4.1.3}$$

分别由 Fourier Integral 和 $u_i = x_i + y_i, v_i = x_i - y_i$ 进行坐标变换得到。

4. 有

$$\int dx_i \int dp_i [f(p_i) + g(x_i)] P(x_i; p_i) = \int dx_i \psi(x_i)^* [f\left(-ih\frac{\partial}{\partial x_i}\right) + g(x_i)] \psi(x_i) \tag{4.1.4}$$

或使用 Dirac 记号，

$$\langle x'p' | (f(p_i) + g(x_i)) P | x'p' \rangle = \langle \psi | f\left(-ih\frac{\partial}{\partial x_i}\right) + g(x_i) | \psi \rangle_{x'} \tag{4.1.5}$$

[1] 在整篇文章用 h 来代表约化普朗克常数，即 $\hbar$.

简而言之，相空间下的动量、坐标算符的线性组合可直接等效于 Schrödinger's representation 下的算符写法，而只需要对 p 进行变换。用 $\langle\rangle_{x'}$ 表示 Schrödinger's representation.

5. 根据 Schrödinger's equation,

$$(-\sum_i p_i^2/2m + V(x_i))|\psi\rangle_{x',t'} = ih\frac{\partial}{\partial t}|\psi\rangle_{x',t'} \tag{4.1.6}$$

the change of $P(x_i; p_i)$ is given by

$$\frac{\partial P}{\partial t} = -\sum \frac{p_i}{m_i}\frac{\partial P}{\partial x_i} + \sum \frac{\partial^{\sum\lambda_i} V}{\Pi \partial x_i^{\lambda_i}} \frac{-(ih/2)^{(\sum\lambda_i)-\lambda_n}}{\Pi\lambda_i!} \sum \frac{\partial^{\sum\lambda_i} P}{\Pi \partial p_i^{\lambda_i}} \tag{4.1.7}$$

where the last summation has to be extended over all positive integer values of λ_i for which the sum $\sum_{i=1}^n \lambda_i$ is odd.[2]

6. 利用 (4.1.2) 及 Schrödinger's equation,

$$\begin{aligned}\frac{\partial P}{\partial t} = \frac{1}{h\pi^n}\int dy_i e^{2i\sum p_i y_i/h} \\ \cdot\{\sum_k \frac{ih}{2m_k}\left[-\frac{\partial^2\psi(x_i+y_i)^*}{\partial x_k^2}\psi(x_i-y_i) + \psi(x_i+y_i)\frac{\partial^2\psi(x_i-y_i)}{\partial x_k^2}\right] \\ + \frac{i}{h}[V(x_i+y_i) - V(x_i-y_i)]\psi(x_i+y_i)^*\psi(x_i-y_i)\}\end{aligned}$$

Here one can replace the differentiations with respect to x_k by differentiations with respect to y_k and perform in the first two terms one partial integration with respect to y_k. In the last term we can develop $V(x_i + y_i)$ in a Taylor series with respect to the y and get

$$\begin{aligned}\frac{\partial P}{\partial t} = \frac{1}{h\pi^n}\int dy_i e^{2i\sum p_i y_i/h} \\ \cdot\{\sum_k \frac{p_k}{m_k}\left[-\frac{\partial\psi(x_i+y_i)^*}{\partial y_k}\psi(x_i-y_i) + \psi(x_i+y_i)\frac{\partial\psi(x_i-y_i)}{\partial y_k}\right] \\ + \frac{i}{h}\sum_\lambda \frac{\partial^{\sum\lambda_l} V}{\prod x_l^{\lambda_l}}\frac{\prod y_l^{\lambda_l}}{\prod\lambda_l!}\psi(x_i+y_i)^*\psi(x_i-y_i)\}\end{aligned}$$

which is identical with (4.1.7) if one replaces now the differentiations with respect to y_k by differentiations with respect to x_k. Of course, it is legitimate only if it is possible to develop the potential energy V in a Taylor series.

It also shows the close analogy between the probability function of the classical mechanics and our P, indeed the equation of continuity

$$\frac{\partial P}{\partial t} = -\sum_k \frac{p_k}{m_k}\frac{\partial P}{\partial x_k} + \sum_k \frac{\partial V}{\partial x_k}\frac{\partial P}{\partial p_k} \tag{4.1.8}$$

differs from (4.1.7) only in terms of at least the second power of h and at least the third derivative of V. Expression (4.1.7) is even identical with the classical when V has no third and higher derivatives as, e.g., in a system of oscillators.

[2] 突然意识到下标的 i 与虚数 i 冲突……嘛谅解谅解。

7. Alternative form for $\partial P/\partial t$[3]:

$$\frac{\partial P}{\partial t} = -\sum_k \frac{p_k}{m_k}\frac{\partial P}{\partial x_k} + \int dj_l P(x_l; p_l + j_l) J(x_l; j_l) \tag{4.1.9}$$

wherer $J(x_l; j_l)$ can be interpreted as the probability of a jump in the momenta with the amounts j_l for the configuration x_l. The probability of this jump is given by

$$J(x_l; j_l) = \frac{i}{\pi^n h^{n+1}} \int dy_l [V(x_l + y_l) - V(x_l - y_l)] e^{-2i\sum y_l j_l/h} \tag{4.1.10}$$

that is, by the Fourier expansion coefficients of the potential $V(x_l)$. This form clearly shows the quantum mechanical nature of our P: the momenta change discontinuously by amounts which would be half the momenta of light quanta if the potential were composed of light.

8. 若多个态线性组合，For a system in statistical equilibrium at the temperature $T = 1/k\beta$ the relative probability of a statonary state ψ_λ is $e^{-\beta E_\lambda}$ where E_λ is the energy of ψ_λ. Therefore the probability function is a part from a constant

$$P = \sum_\lambda \int dy_k \psi_\lambda \psi(x_k + y_k)^* e^{-\beta E_\lambda} \psi(x_k - y_k) e^{2i\sum p_k y_k/h} \tag{4.1.11}$$

Now

$$\sum_\lambda \langle u_i \psi_\lambda | f(H_\lambda) | \psi_\lambda \rangle_{v_i} \tag{4.1.12}$$

represents the operator $f(H)$, Thus[4]

$$P = \int dy_k e^{i\sum (x_k + y_k) p_k/h} [e^{-\beta H}]_{x_k + y_k; x_k - y_k} e^{-i\sum (x_k - y_k) p_k/h} \tag{4.1.13}$$

[3]然而在原文中多重积分里的 P 是用 $P(x_l; P_l + j_l)$ 来描述，这显得有些奇怪——至少量纲会崩盘。
[4]也就是将波函数整合进 $e^{-\beta H}$，然后左右拆分为关于 $x_k - y_k$,$x_k + y_k$ 两项。

Chapter 5

非绝热动力学中的量子力学效应研究 *by* 沈一帆

5.1 绪论摘要

1. 在更多的化学问题中，电子会发生跃迁，Born-Oppenheimer 近似失效，比如光催化反应，光电材料中的电荷传输，无辐射跃迁，生命活动中的光合作用，呼吸作用等，必须使用更普适的非绝热动力学研究。

2. 非绝热动力学的思想分为两派：追求严格，将电子与原子核做量子化处理；追求效率，将原子核作经典处理。需要在拥有量子效应的基础上保证计算效率。David Manolopoulos 提出的环聚合物方法（ring polimer）是一种可能，并已被 John Tully 和 Frank Huo 等人与面间跳跃方法相结合。而该方法只能处理热力学平衡态，但很多化学过程发生在非平衡态。Oleg Prezhdo 提出的量子哈密顿动力学（QHD）是另一种可能。

3. QHD 从经典描述出发，逐级添加量子效应修正，添加无穷阶修正即可达到全量子严格解。

4. QHD 用 Hilbert 空间描述，以一系列算符的期望值作为变量组来描述粒子的运动过程。由于经典力学中确定粒子的运动状态只需要坐标和动量，因此 HS-QHD 的一阶变量直接对应于经典力学，而高阶变量选择坐标算符和动量算符高阶数的乘积。由于坐标算符和动量算符的不对易，它们的乘积并非 Hermite 算符，而只有 Hermite 算符的期望值才是实验可观察的实数值，因此 Weyl 对称化被引入来保证变量组纯实。

5. Hilbert 空间中任意算符 $\hat{A}$ 期望值随时间的演化遵循 Ehrenfest 定理：

$$\frac{d}{dt}\langle\hat{A}\rangle = \langle\frac{\partial}{\partial t}\hat{A}\rangle + \langle\frac{1}{i\hbar}\left[\hat{A},\hat{H}\right]\rangle \tag{5.1.1}$$

6. HS-QHD 的演化方程具有级联方程组形式，即低阶量的含时演化依赖于高阶量的值。我们计算的动力学只能采用有限阶，为使方程组完备只能在计算的有限阶的基础上去近似表达未知的高阶量，从而完成方程组截断，求得参数，通行的近似方法是将高阶中心矩近似为各种可能的低阶中心矩在保持变量的总数及总阶数不

变时乘积的叠加，以三阶和四阶为例：

$$\begin{aligned}&\langle(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)(\hat{C}-\langle\hat{C}\rangle)\rangle\\ \sim&\sum_{\text{轮换求和}}\langle(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)\rangle\langle(\hat{C}-\langle\hat{C}\rangle)\rangle\\ =&0\end{aligned}$$

$$\begin{aligned}&\langle(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)(\hat{C}-\langle\hat{C}\rangle)(\hat{D}-\langle\hat{D}\rangle)\rangle\\ \sim&\sum_{\text{轮换求和}}\langle(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)\rangle\langle(\hat{C}-\langle\hat{C}\rangle)(\hat{D}-\langle\hat{D}\rangle)\rangle\end{aligned}$$

[1]

问题：

(a) 算符乘法不可交换，存在算子序

(b) 近似只对中心矩有效，需要转换回变量组，而变量组是对称化的原点矩，导致这一转换复杂冗长，难以卸除通用公式

(c) 不显式地保证高阶收敛性，即不保证睡着中心矩阶数的上升截断误差不断减小直至在无穷阶极限收敛到零。

7. 量子力学等价表述形式：
   - Hilbert 空间及其关联的波函数、密度矩阵和力学量算符
   - 相空间极其关联的 Wigner 分布函数和力学量函数
8. 相空间表象在研究混合量子经典问题更有优势，在 $\hbar\to 0$ 的经典极限可直接转换到经典相空间，在 $\hbar$ 越来越重要时量子效应项按照依赖 $\hbar$ 的阶数逐渐发挥作用，符合从经典向量子过度并按精度选择合适描述的思想。自然保证变量组纯实，因为 Wigner 函数和力学函数都是实函数，故坐标函数和动量函数的乘积仍为实函数，期望值为实数。
9. 高阶变量除去对应阶的标准差来避免由分布宽度引起的不必要数字膨胀，采用
$$\langle\frac{1}{m!n!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^m\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^n\rangle \tag{5.1.2}$$
10. 相空间乘法可交换，在采用通行的级联方程组截断方案时将不会遇到算子序问题。由于变量组采用相空间无量纲中心矩，不存在转换回原点矩及对称化问题，对不同变量有共通形式。无穷阶收敛性问题则仍然存在，在采用合适的阶段方案后才能得到解决。

5.2 正文摘要

5.2.1 相空间 Ehrenfest 定理

1. 相空间 Ehrenfest 定理：
$$\frac{d}{dt}\langle A\rangle=\langle\frac{\partial}{\partial t}A\rangle+\langle\{\{A,H\}\}\rangle=\langle\frac{\partial}{\partial t}A\rangle+\langle\left\{\{A,\frac{p^2}{2m}+V\}\right\}\rangle \tag{5.2.1}$$

[1] 最后求和展开每一个系数为 1，虽然这看起来有点奇怪。

2. $\{\{*,*\}\}$ 为 Moyal 括号，定义为

$$\{\{A,H\}\} \equiv \frac{2}{\hbar} A \sin\left[\frac{\hbar}{2}(\overleftarrow{\partial_x}\overrightarrow{\partial_p} - \overleftarrow{\partial_p}\overrightarrow{\partial_x})\right] H \tag{5.2.2}$$

$$= \{A,H\} + \sum_{j=1}^{\infty} \frac{(-1)^j}{(2j+1)!}\left(\frac{\hbar}{2}\right)^{2j} A(\overleftarrow{\partial_x}\overrightarrow{\partial_p} - \overleftarrow{\partial_p}\overrightarrow{\partial_x})^{2j+1} H \tag{5.2.3}$$

偏导数符号的左右箭头代表该偏导数向左或向右作用，$\{*,*\}$ 为 Poisson 括号。

3. 将 A 替换为变量组，得到演化方程，可以看到，前二阶量的演化中不会出现 $\hbar$，是纯经典及准经典项：

$$\begin{cases} \frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle p\rangle \\ \frac{d}{dt}\langle p\rangle = -\langle \nabla V\rangle \\ \frac{d}{dt}\sigma_x = \frac{1}{m}\rho\sigma_p \\ \frac{d}{dt}\rho = \frac{1}{m}\frac{\sigma_p}{\sigma_x} - \frac{1}{\sigma_p}\langle(\nabla V - \langle\nabla V\rangle)\left(\frac{x-\langle x\rangle}{\sigma_x}\right)\rangle - \left(\frac{1}{\sigma_x}\right) \\ \frac{d}{dt}\sigma_p = -\langle(\nabla V - \langle\nabla V\rangle)\left(\frac{p-\langle p\rangle}{\sigma_p}\right)\rangle \end{cases} \tag{5.2.4}$$

高阶项的 $\hbar$ 依赖性与 A 对 p 和 ∇V 对 x 的非零偏导数有关：[2]

$$\begin{aligned} &\frac{d}{dt}\langle\frac{1}{m!n!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^m\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^n\rangle \\ &= \frac{n+1}{M}\frac{\sigma_p}{\sigma_x}\langle\frac{1}{(m-1)!(n+1)!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^{m-1}\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^{n+1}\rangle \\ &\quad - \frac{1}{\sigma_p m!}\langle\frac{1}{(n-1)!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^m\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^{n-1}(V'-\langle V'\rangle)\rangle \\ &\quad + \sum_{j=1}^{Floor(\frac{n-1}{2})}\frac{(-1)^{j+1}}{(2j+1)!\sigma_p^{2j+1}}\left(\frac{\hbar}{2}\right)^{2j}\frac{1}{m!}\langle\frac{1}{[n-(2j+1)]!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^m\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^{n-2j-1}V^{2j+1}\rangle \\ &\quad - \left(\frac{m}{\sigma_x}\frac{d\sigma_x}{dt} + \frac{n}{\sigma_p}\frac{d\sigma_p}{dt}\right)\langle\frac{1}{m!n!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^m\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^n\rangle \end{aligned}$$

5.2.2 相空间分布函数

1. 为实现方程组截断，采用类似变分的手段得到相空间分布函数。原则上，相空间分布函数形式可以有多种选择，这里我们选择与我们的变量组形成线性映射的函数空间：

$$P(x,p) = G(x,p)\sum_{0\le i+j\le N} c_{ij} f_{ij}(x,p) \tag{5.2.5}$$

其中 $P(x,p)$ 是相空间分布函数，$G(x,p)$ 是任意光滑函数，$f_{ij}(x,p)$ 是任意保证无穷阶完备性的基函数，N 是我们计算的最高阶 PS-QHD 变量的阶数，c_{ij} 是待

[2]在这里面为了和指数里面的 m 区分使用 M 来代表质量。

定参数。待定参数的个数为 $1+N(N+3)/2$，与前 N 阶变量总数加归一化所得的条件个数相同。我们可以通过一个线性方程来求解这些待定参数：

$$\sum_{0\le i+j\le N}\left[\frac{1}{k!l!}\int G(x,p)c_{ij}f_{ij}(x,p)\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^k\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^l dxdp\right]$$
$$=\langle\frac{1}{k!l!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^k\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^l\rangle$$

而后

$$\langle A\rangle=\int A(x,p)P(x,p)\,dxdp \tag{5.2.6}$$

如果 $G(x,p)$ 为高斯函数而 $f_{ij}(x,p)$ 为 Hermite 多项式，其低阶运动方程与通行的 HS-QHD 近似截断方法一致：

$$\begin{cases}G(x,p)=\frac{1}{2\pi\sigma_x\sigma_p\sqrt{1-\rho^2}}e^{-\frac{1}{2(1-\rho^2)}\left[\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^2-2\rho\left(\frac{x-\langle x\rangle}{\sigma_x}\right)\left(\frac{p-\langle p\rangle}{\sigma_p}\right)+\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^2\right]}\\ \sum_{0\le i+j\le N}c_{ij}f_{ij}(x,p)=\sum_{0\le i+j\le N}\frac{c_{ij}}{i!j!}\left(\frac{x-\langle x\rangle}{\sigma_x}\right)^k\left(\frac{p-\langle p\rangle}{\sigma_p}\right)^l\end{cases} \tag{5.2.7}$$

5.3 自己研究出的一些垃圾

- 指数函数展开：

  若针对 $x\to\infty$ 有 $f(x)\to 0$ 且满足

  $$f(x)=\sum a_n e^{-n_(x-x_0)} \tag{5.3.1}$$

  则有

  $$\sum_{n=0}^{\infty}(-n)^k e^{-nx_0}=f^{(k)}(x_0) \tag{5.3.2}$$

  其一致收敛性暂未证明。

- 高斯函数积分：

$$\int_{\mathrm{R^n}}dX\,f(X)\,e^{-\frac{1}{2}X^TAX+B^TX}=\sqrt{\frac{(2\pi)^n}{\det A}}e^{\frac{1}{2}B^TA^{-1}B}\exp\left(\frac{1}{2}(A^{-1})_{ij}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\right)f(X+B) \tag{5.3.3}$$

实现代码为

```
GaussianIntegrate[variableList_, A_, B_, function_, end_] :=
 Module[{inverse, b, modifiedfunction},
  inverse = Inverse[A];
  b = inverse.B;
  Evaluate[
   Sqrt[(2 Pi)^Length[variableList]/Det[A]]*Exp[0.5*B.inverse.B]*

    ParallelSum[
```

```
    1/n!*Nest[
      Function[a,
       0.5*Flatten[
          inverse].(D[a, ##] & @@@
           Tuples[variableList, 2])], (function /.
        Rule @@@ Transpose[{variableList, variableList + b}]),
      n], {n, 0, end}]

  ] /.
 Rule @@@ Transpose[{variableList, Table[0, Length[variableList]]}
   ]
];
```