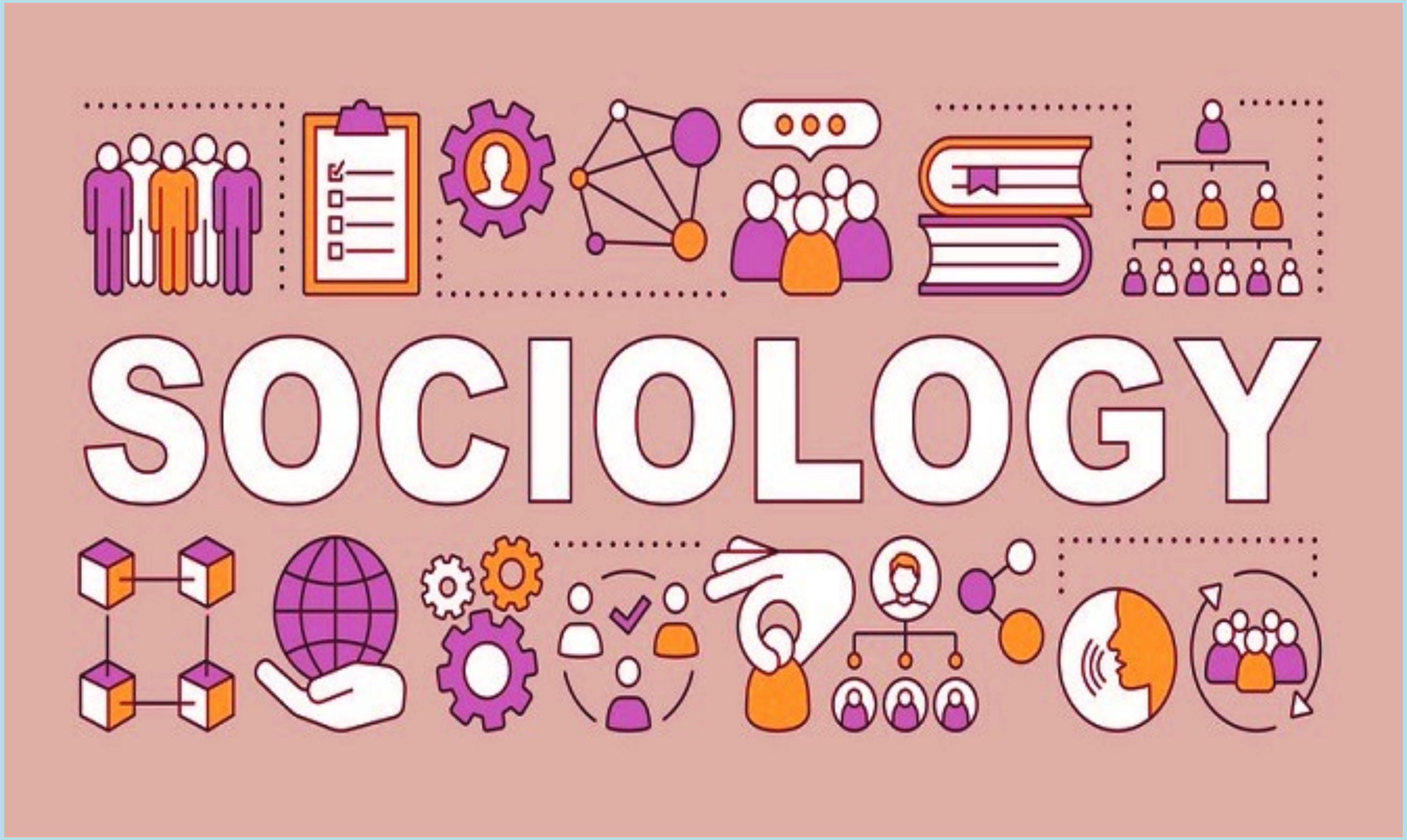
電子的社會學

Identical Particles 全同粒子

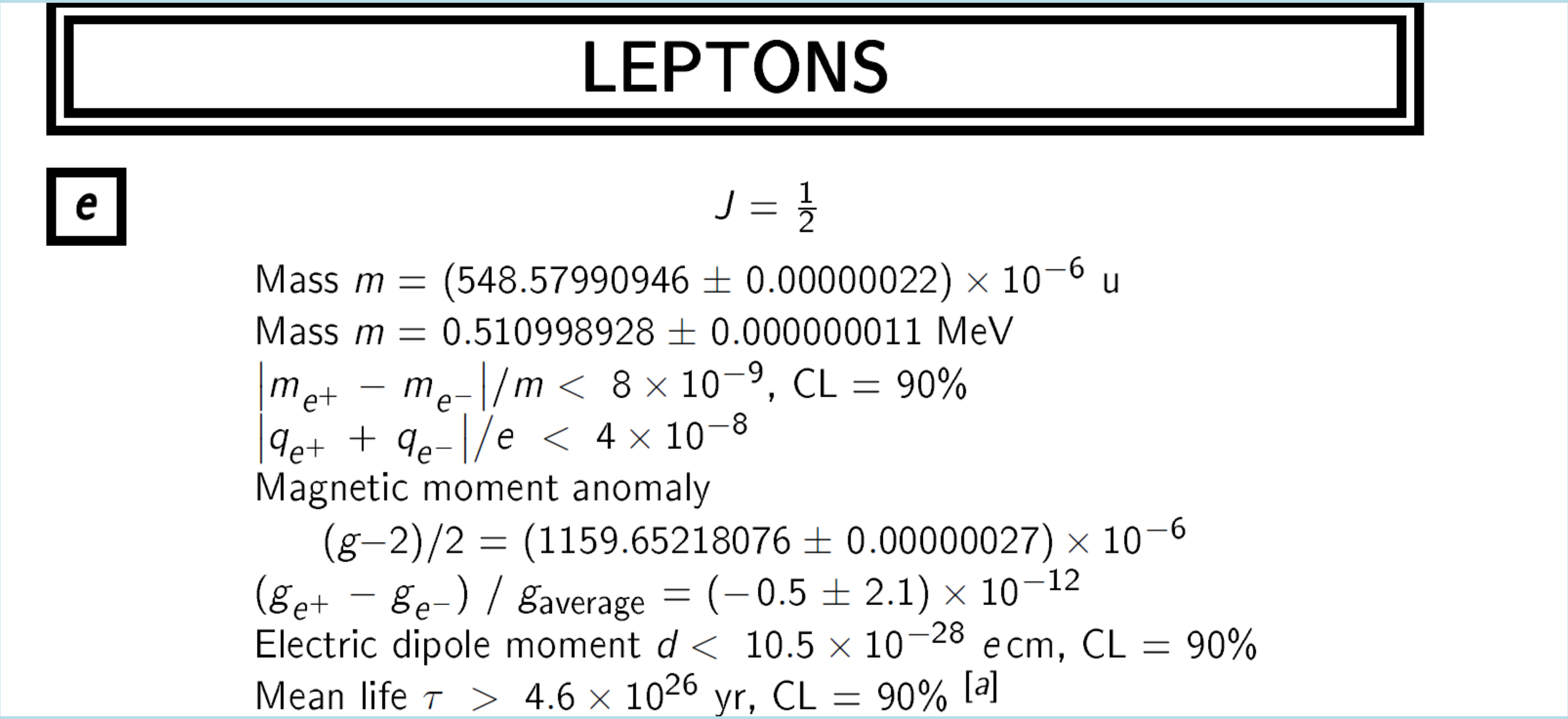


電子1

電子2

Could you tell the difference?你能分辨嗎？

顯然所有的電子，實驗測量的性質都一樣！



LEPTONS

e

$J = \frac{1}{2}$

Mass $m = (548.57990946 \pm 0.00000022) \times 10^{-6}$ u

Mass $m = 0.510998928 \pm 0.000000011$ MeV

$\left| m_{e+} - m_{e-} \right| / m < 8 \times 10^{-9}$, CL = 90%

$\left| q_{e+} + q_{e-} \right| / e < 4 \times 10^{-8}$

Magnetic moment anomaly

$(g-2)/2 = (1159.65218076 \pm 0.00000027) \times 10^{-6}$

$(g_{e+} - g_{e-}) / g_{\text{average}} = (-0.5 \pm 2.1) \times 10^{-12}$

Electric dipole moment $d < 10.5 \times 10^{-28}$ e cm, CL = 90%

Mean life $\tau > 4.6 \times 10^{26}$ yr, CL = 90% [a]

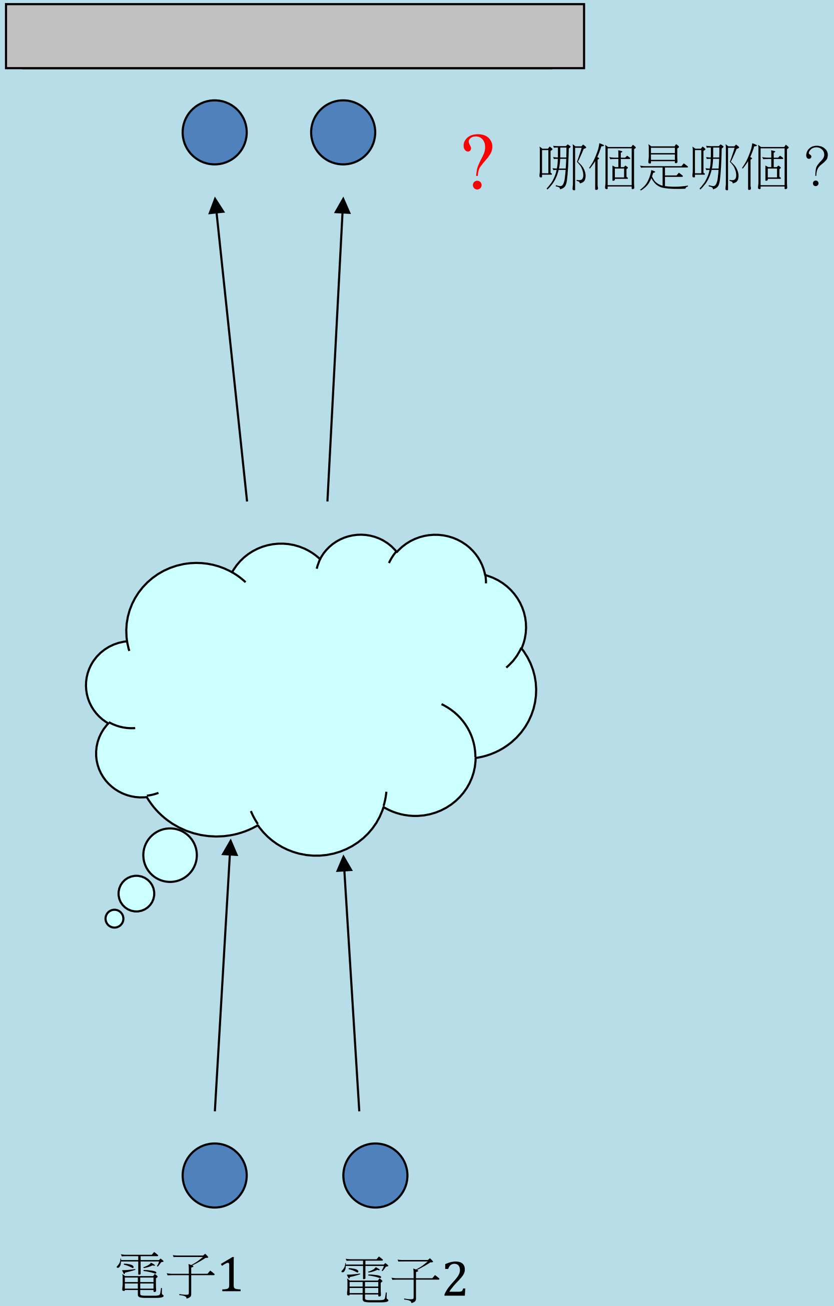
因為是基本粒子，電子並沒有太多的性質，

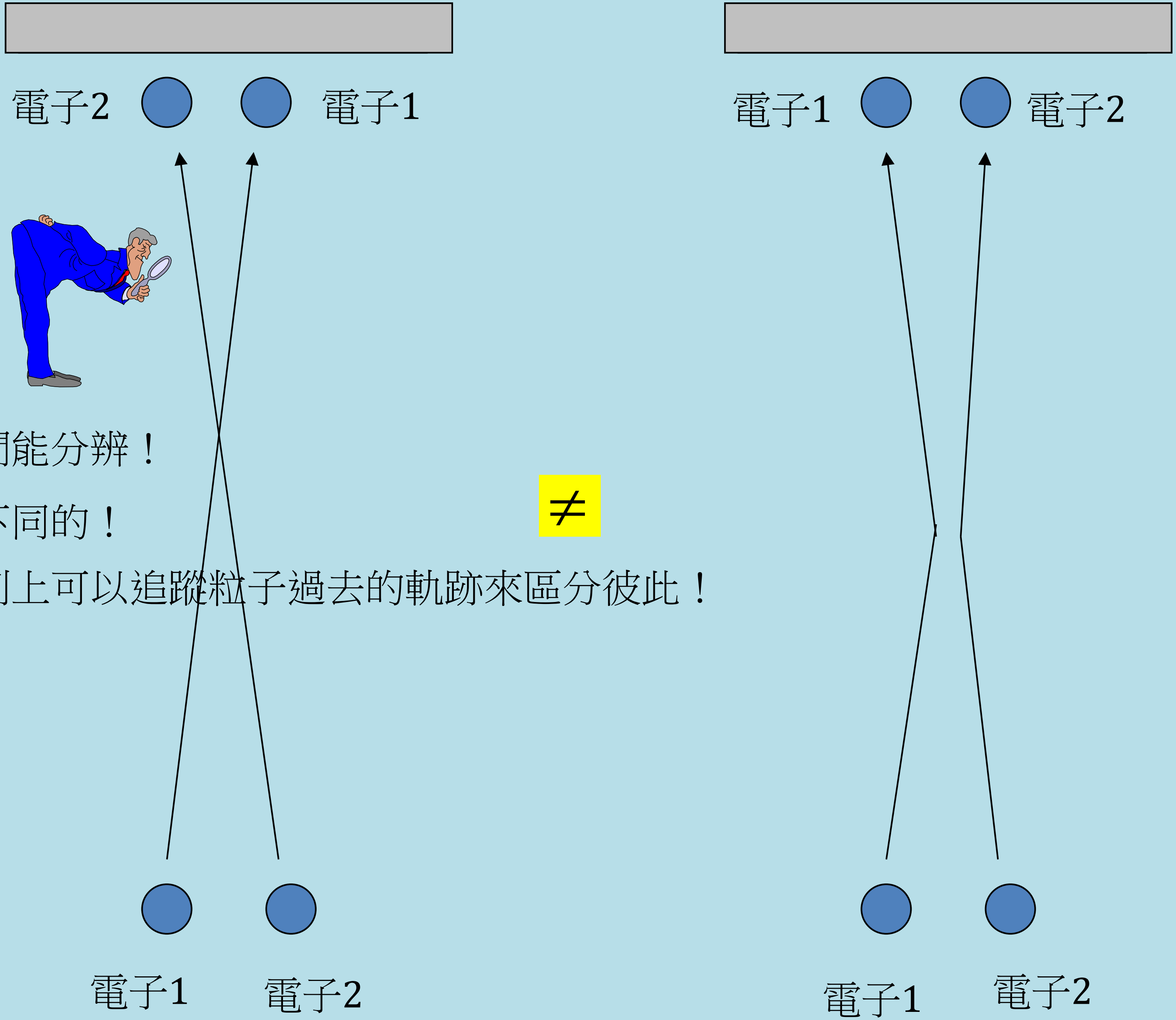
所有電子的質量、磁偶極矩都一樣！因此兩顆電子完全無法分辨彼此。

考慮兩顆電子的交互作用：

在實驗前將電子編號，

作用後測量時我們能分辨嗎？



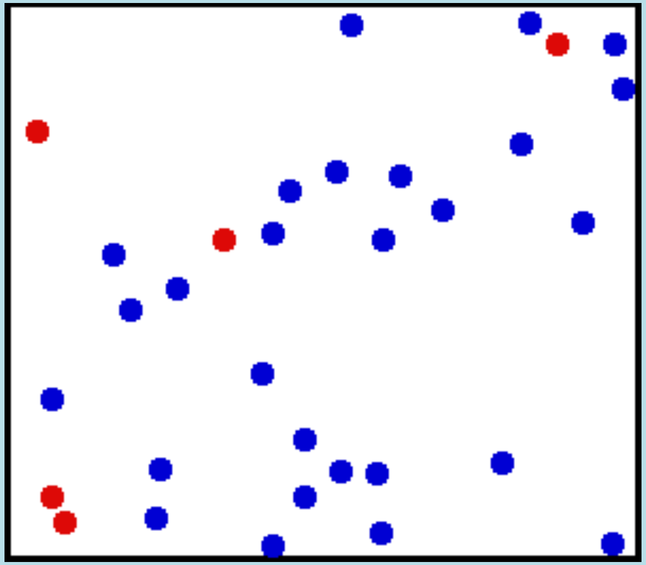


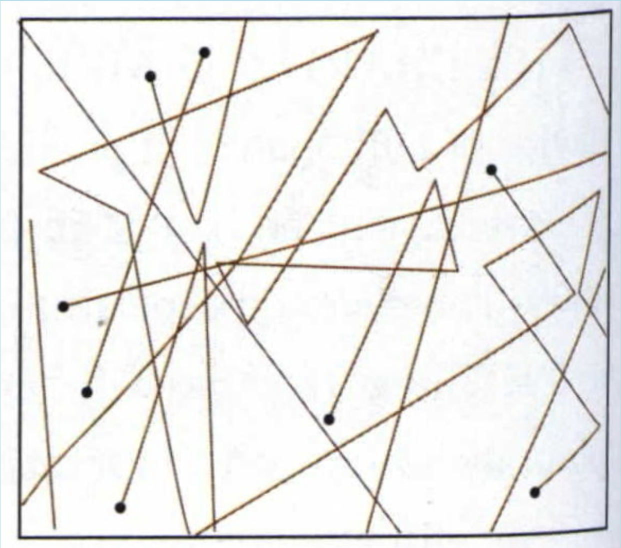
若是古典粒子，我們能分辨！

因為左圖與右圖是不同的！

在古典物理中，原則上可以追蹤粒子過去的軌跡來區分彼此！

理想氣體模型就是！



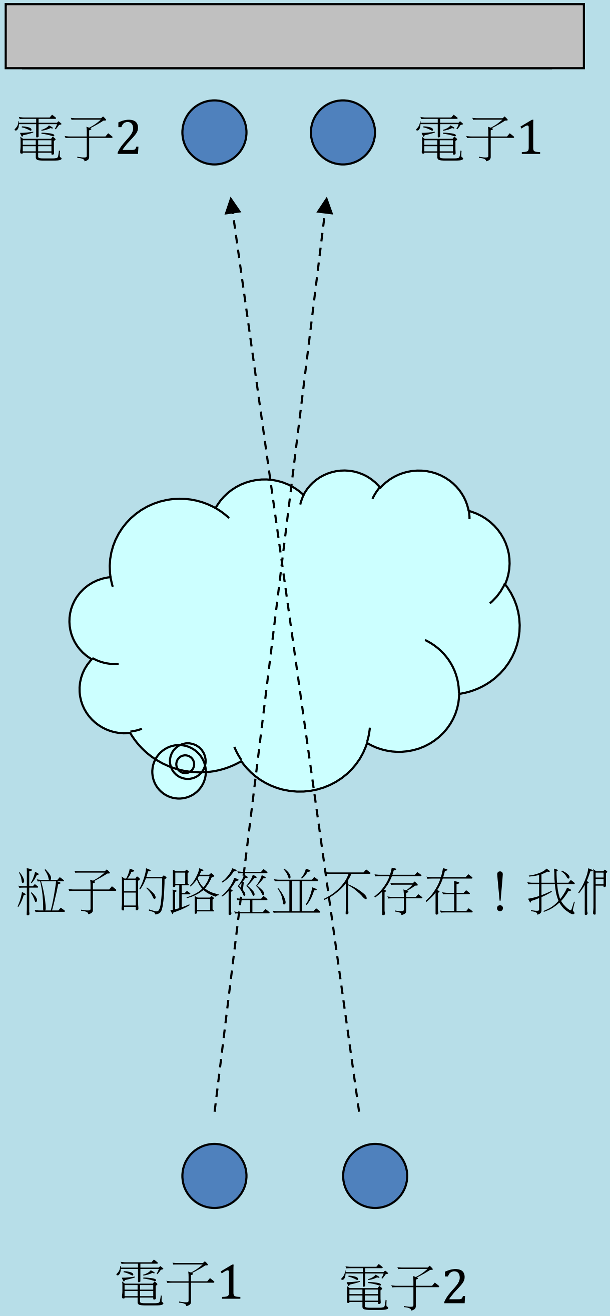


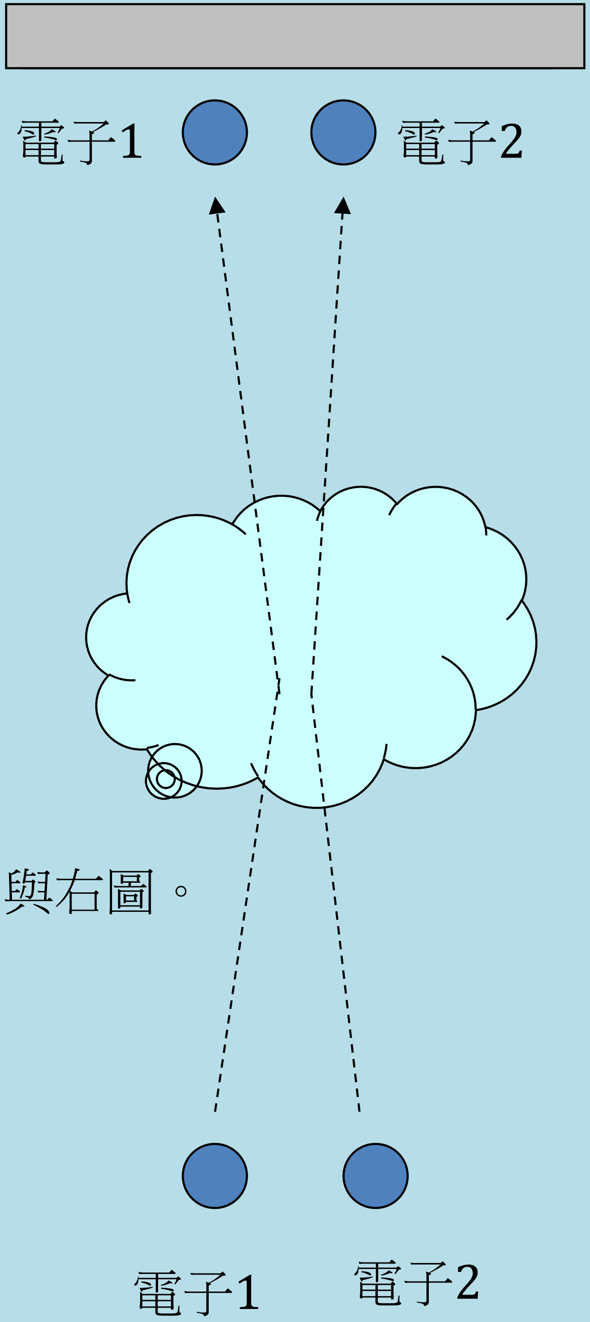
氣體就是一羣不斷運動碰撞的牛頓粒子！

技術上就是一個質點系統，基本上粒子是有編號i的！

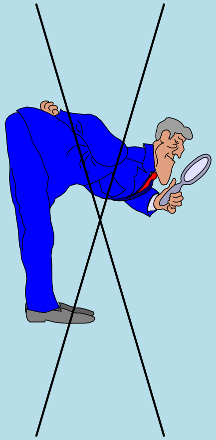
要描述一個質點系統，需要所有個別粒子的位置與速度。

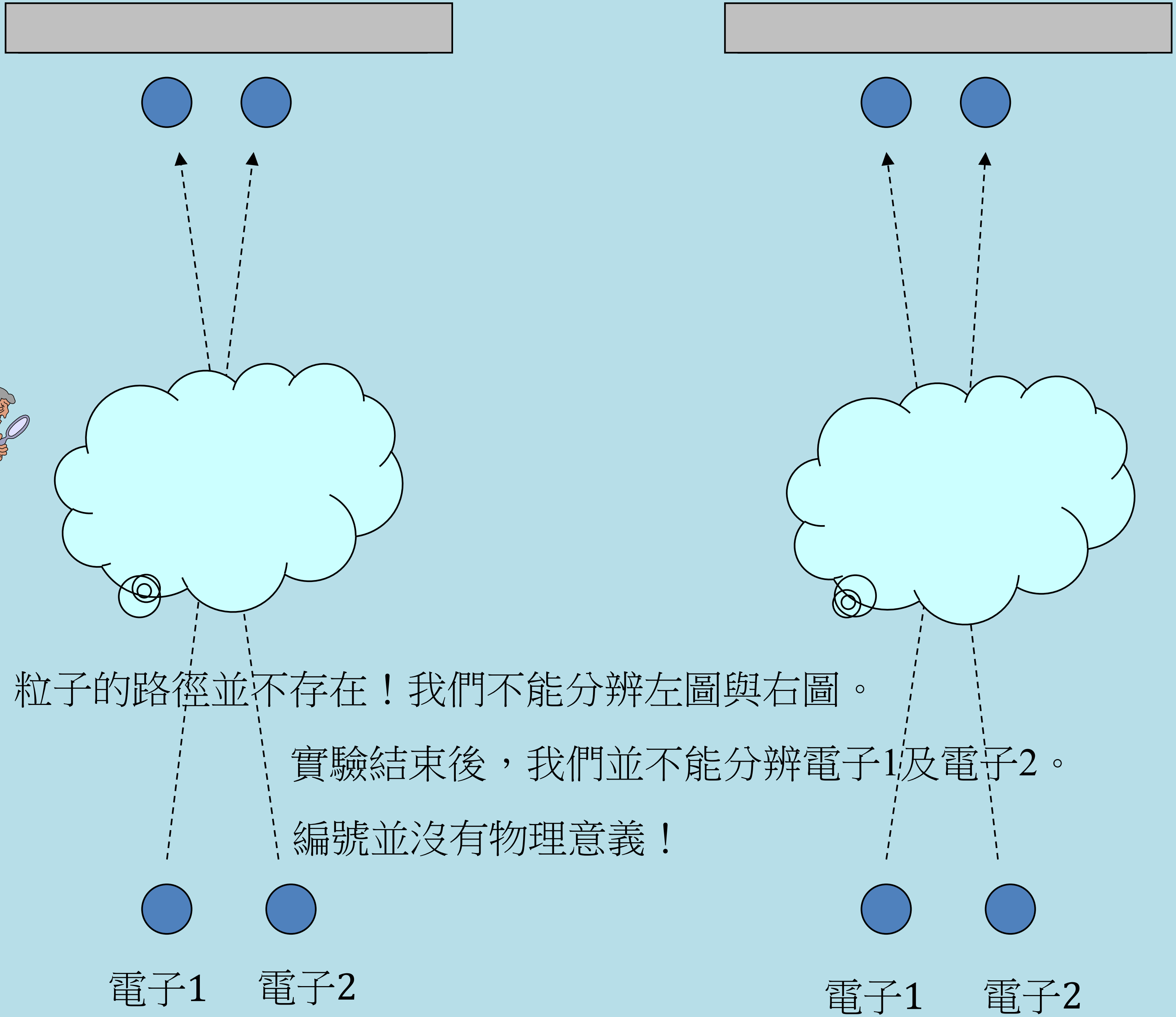
$$\vec{r}_i, \vec{v}_i \quad i = 1 \cdots N$$





但在量子力學中，粒子的路徑並不存在！我們不能分辨左圖與右圖。





但在量子力學中，粒子的路徑並不存在！我們不能分辨左圖與右圖。

實驗結束後，我們並不能分辨電子1及電子2。

編號並沒有物理意義！

我們可以考慮兩顆電子，它們都靜止，因此只需考慮自旋。

觀察發現有一顆自旋向上、一顆自旋向下。

將這個狀態記為：|↓↑⟩或 $\left|m_{s1}=\frac{\hbar}{2}, m_{s2}=-\frac{\hbar}{2}\right\rangle$ 。

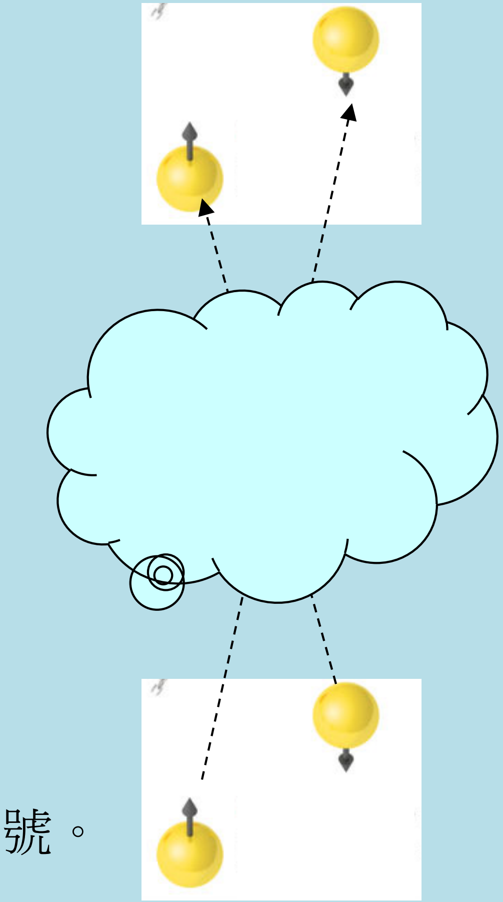
自旋向上的電子編為1號，自旋向上的電子編為2號。

過了一陣子再來觀察，

依舊發現有一顆自旋向上、一顆自旋向下。

但我並不能確定這個狀態是原來的|↓↑⟩，

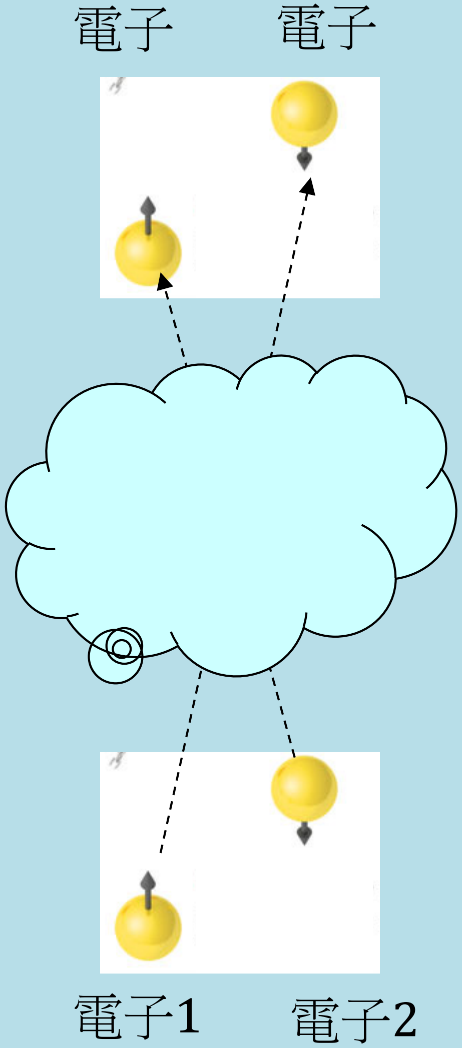
還是兩個電子的自旋都翻轉了的：|↑↓⟩。

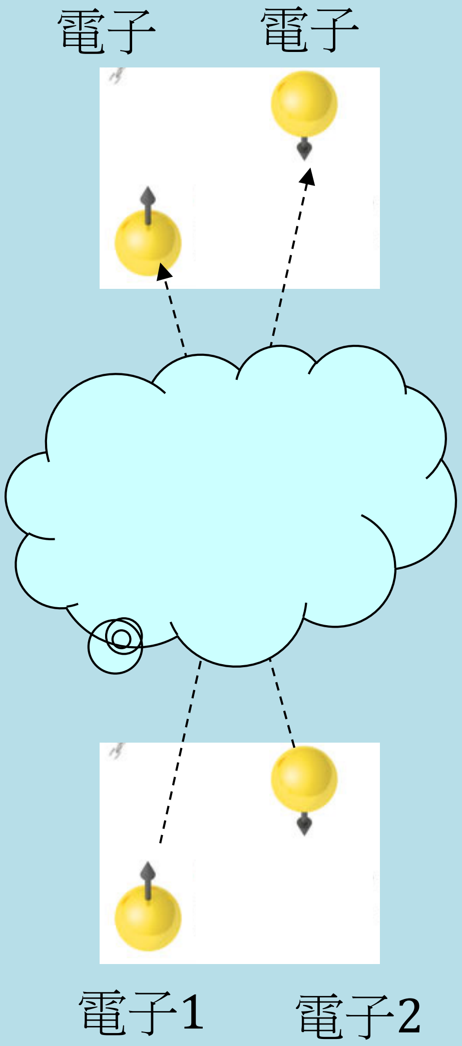


實驗上無法分辨那一個電子是一號，那一個電子是二號。

要不，末狀態不能編號，

但那就不會計算了！

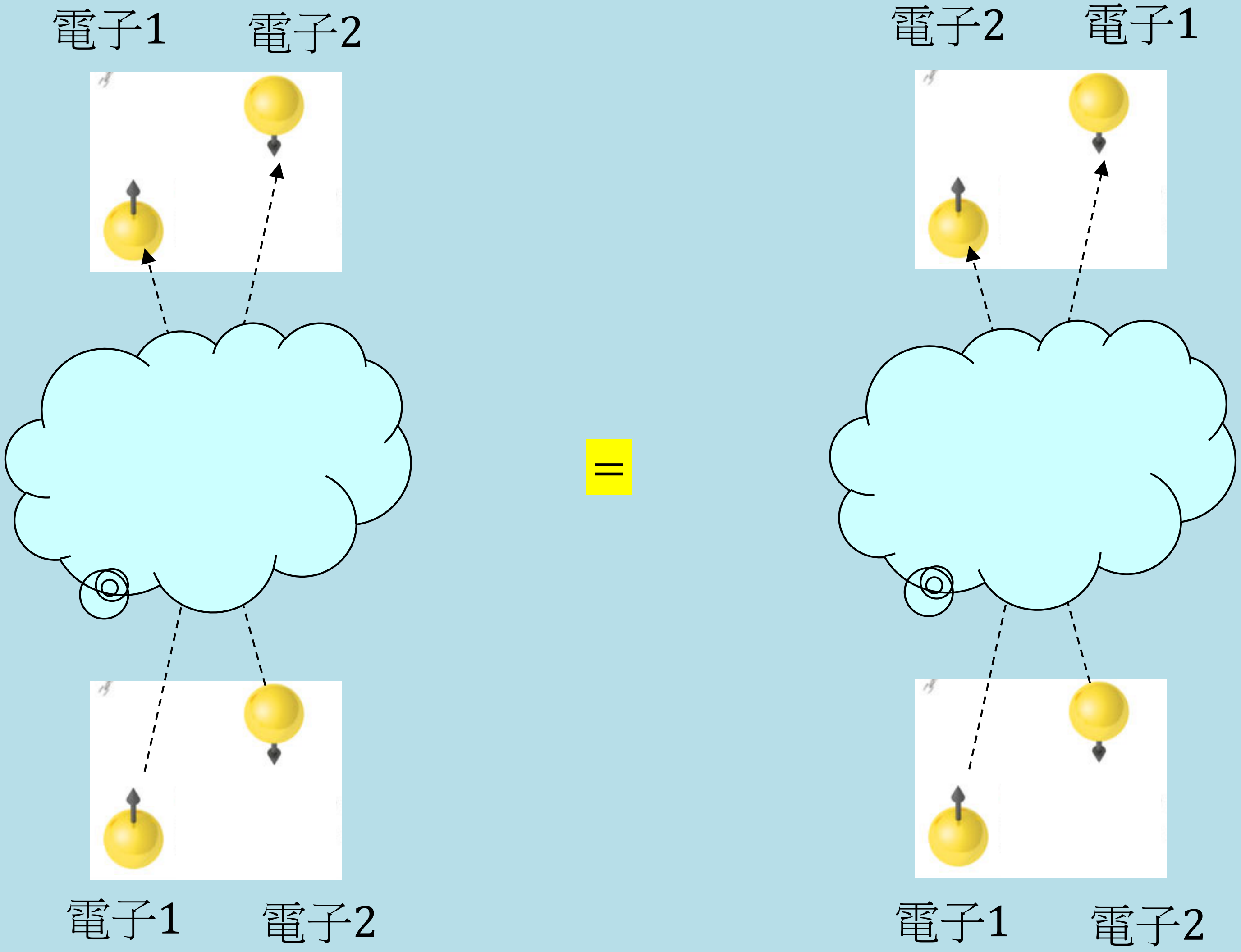




不然，編號必須沒有觀察上的意義！

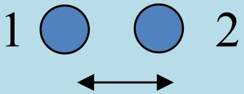
意思是實驗結果與如何編號無關！

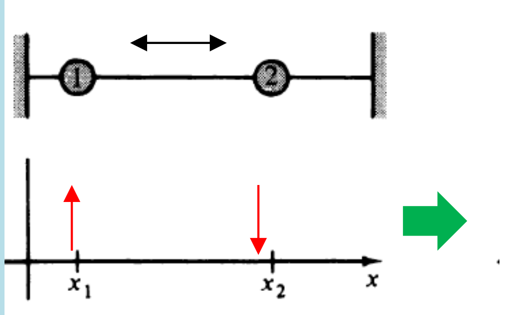
如此的話，實驗結果發生的機率在兩個電子互換後必須不變！



兩粒子狀態以波函數$\psi(x_1,x_2,m_{s1},m_{s2})$描述：

$m_{s1,2}\hbar$是$S_{z1,2}$的本徵值：$\pm\frac{\hbar}{2}$。





兩個粒子互換，等同將兩個位置及自旋數值互換： $x_1 \leftrightarrow x_2$ $m_{s1} \leftrightarrow m_{s2}$

例如現在一號粒子位置數值是x_2，自旋數值為m_{s2}。

代入$\psi(x_1,x_2,m_{s1},m_{s2})$的$x_1,m_{s1}$，就得到交換後波函數$\psi(x_2,x_1,m_{s2},m_{s1})$，

若是全同粒子，以上兩個圖是完全無法分辨的！標籤是人工加上去的。

有關的測量，在交換後與交換前結果必須相同！

如此則機率、也就是波函數的絕對值，在粒子數值交換後必須永遠等於交換前。

$$|\psi(x_1,x_2,m_{s1},m_{s2})|^2 = |\psi(x_2,x_1,m_{s2},m_{s1})|^2$$

因此全同粒子能存在的狀態的波函數，必須加上上述這個額外條件，理論才合理。

不滿足此條件的波函數，不能採用！

$$|\psi(x_1,x_2,m_{s1},m_{s2})|^2=|\psi(x_2,x_1,m_{s2},m_{s1})|^2$$

要滿足這個條件，有兩種可能，這已為實驗所證實：

Symmetric $$\psi_S(x_1,x_2,m_{s1},m_{s2})=\psi_S(x_2,x_1,m_{s2},m_{s1})$$

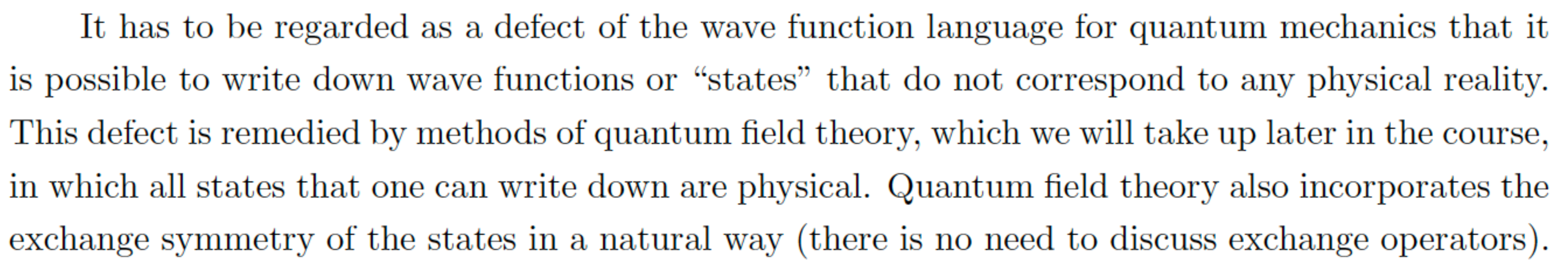
波函數不變，此粒子稱為波色子。

Anti-Symmetric $$\psi_A(x_1,x_2,m_{s1},m_{s2})=-\psi_A(x_2,x_1,m_{s2},m_{s1})$$

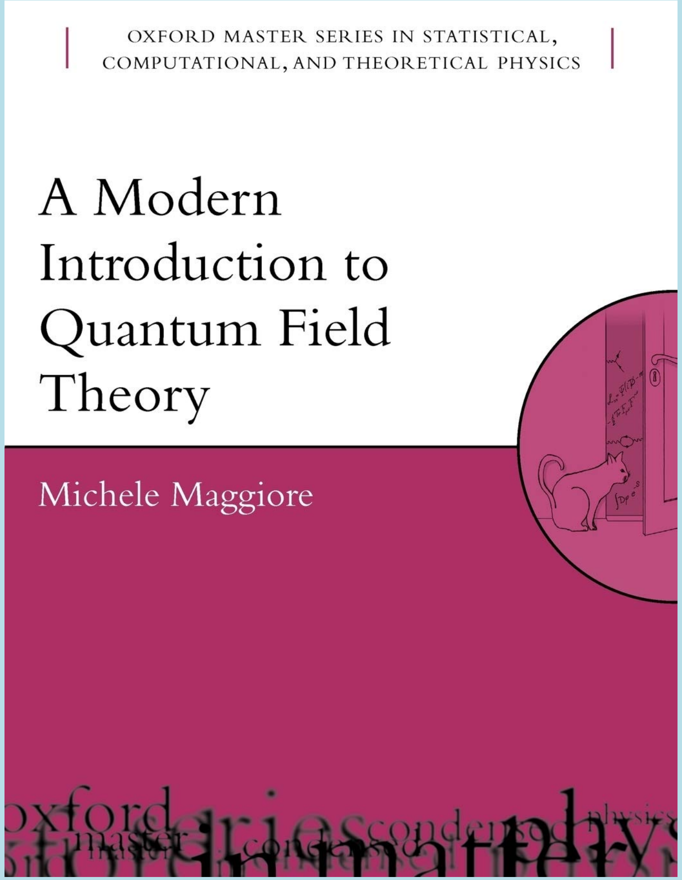
波函數多一個負號，稱為反對稱，注意機率依舊不變，此粒子稱為費米子。

這稱為對稱性原則。

若多粒子的波函數一定滿足以上條件，實驗結果自然就與粒子的標籤無關了。
能寫下其他不對應於現實的波函數，必須視為波函數語言的先天缺憾，
條件必須外加，才能使波函數對應於現實。不滿足的不對應於現實。



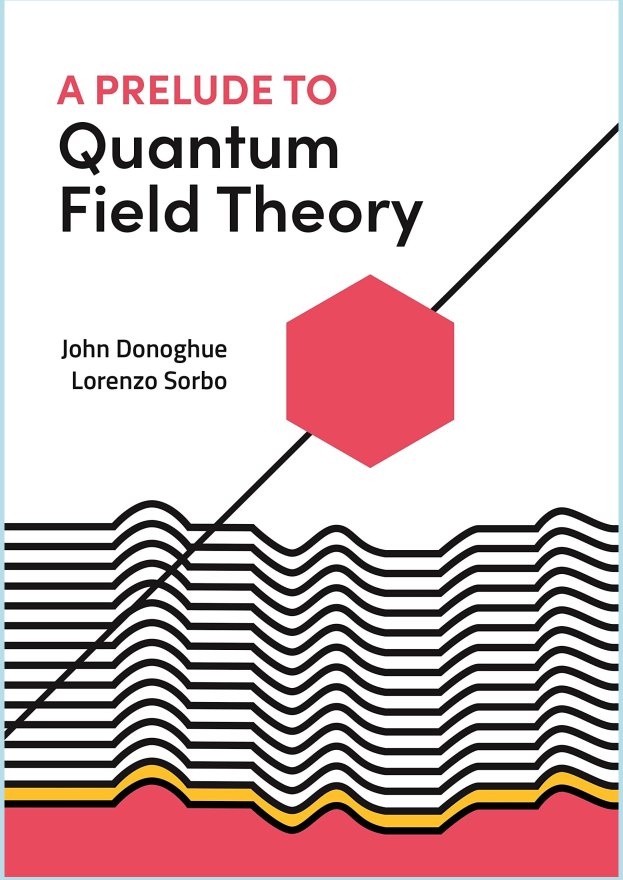
It has to be regarded as a defect of the wave function language for quantum mechanics that it is possible to write down wave functions or “states” that do not correspond to any physical reality. This defect is remedied by methods of quantum field theory, which we will take up later in the course, in which all states that one can write down are physical. Quantum field theory also incorporates the exchange symmetry of the states in a natural way (there is no need to discuss exchange operators).



OXFORD MASTER SERIES IN STATISTICAL, COMPUTATIONAL, AND THEORETICAL PHYSICS

A Modern Introduction to Quantum Field Theory

Michele Maggiore



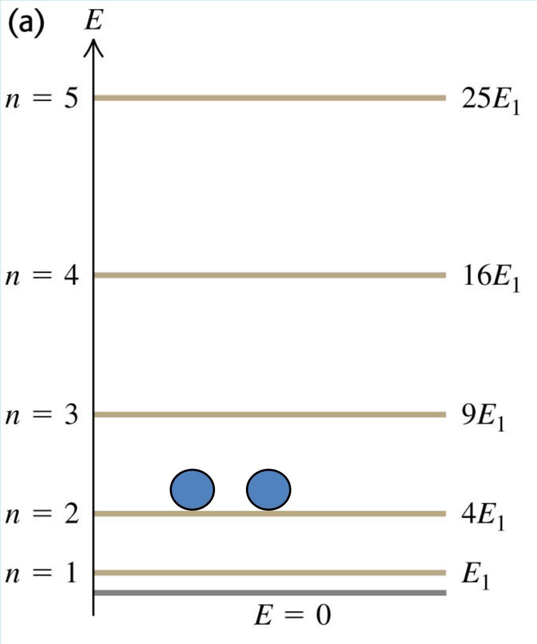
A PRELUDE TO
Quantum Field Theory

John Donoghue
Lorenzo Sorbo

基本粒子物理的量子場論可以證明自旋是整數的粒子是波色子。

自旋是半整數的粒子是費米子。電子是費米子！

這可以說是相對論原則加上量子力學原則後，理論必須的結果！



電子是費米子，將兩個電子位置數值互換時，多一負號。

$$\psi_A(x_1,x_2)=-\psi_A(x_2,x_1)$$

若兩電子存於同一狀態ϕ，波函數可分解為個別ϕ的乘積：

$$c\phi(x_1)\phi(x_2)$$

$$\psi_A(x_1,x_2)=c\phi(x_1)\phi(x_2)=-\psi_A(x_2,x_1)=-c\phi(x_2)\phi(x_1)$$

$c=-c=0$ 因此波函數必須為零。

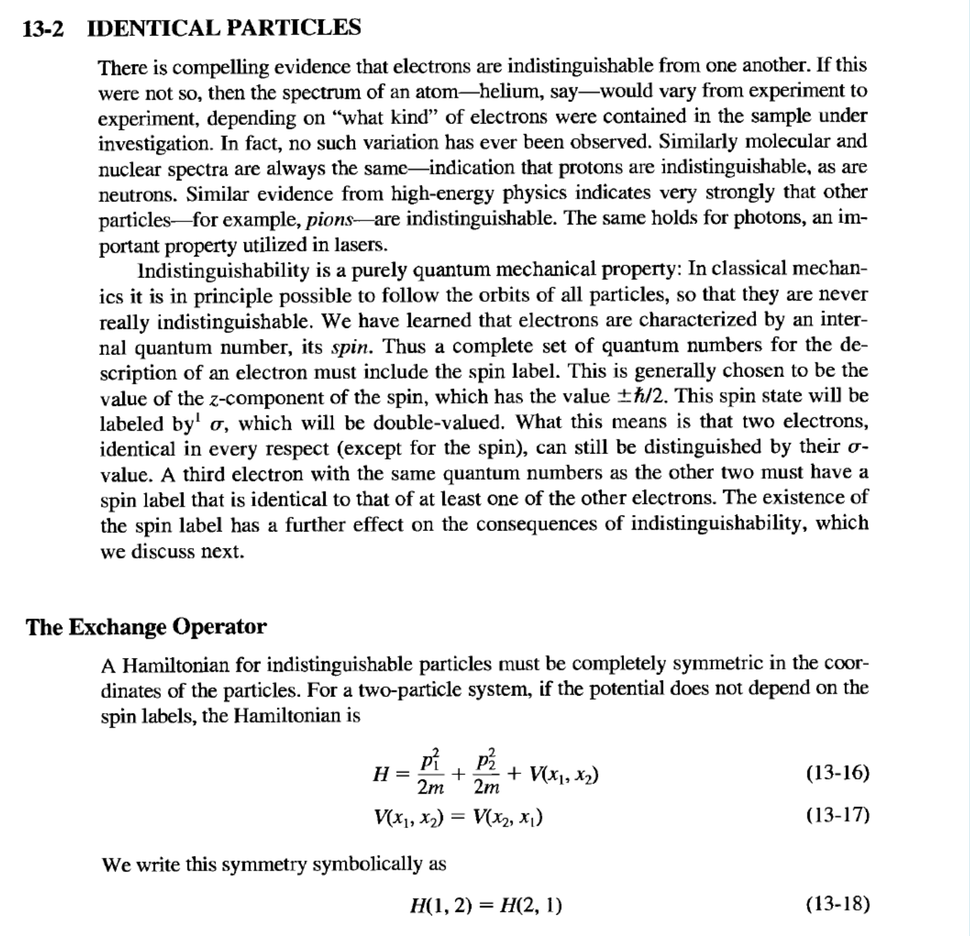
任兩電子不能存於同一量子態！

Pauli Exclusion Principle (1925)

可以證明，能量的本徵態也會滿足對稱性原則！

事實上任何合理的物理量的的本徵態都會滿足對稱性原則！

請參考Gasiorowicz 13-2



13-2 IDENTICAL PARTICLES

There is compelling evidence that electrons are indistinguishable from one another. If this were not so, then the spectrum of an atom—helium, say—would vary from experiment to experiment, depending on "what kind" of electrons were contained in the sample under investigation. In fact, no such variation has ever been observed. Similarly molecular and nuclear spectra are always the same—indication that protons are indistinguishable, as are neutrons. Similar evidence from high-energy physics indicates very strongly that other particles—for example, *pions*—are indistinguishable. The same holds for photons, an important property utilized in lasers.

Indistinguishability is a purely quantum mechanical property: In classical mechanics it is in principle possible to follow the orbits of all particles, so that they are never really indistinguishable. We have learned that electrons are characterized by an internal quantum number, its *spin*. Thus a complete set of quantum numbers for the description of an electron must include the spin label. This is generally chosen to be the value of the z-component of the spin, which has the value $\pm\hbar/2$. This spin state will be labeled by[1] σ, which will be double-valued. What this means is that two electrons, identical in every respect (except for the spin), can still be distinguished by their σ-value. A third electron with the same quantum numbers as the other two must have a spin label that is identical to that of at least one of the other electrons. The existence of the spin label has a further effect on the consequences of indistinguishability, which we discuss next.

The Exchange Operator

A Hamiltonian for indistinguishable particles must be completely symmetric in the coordinates of the particles. For a two-particle system, if the potential does not depend on the spin labels, the Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(x_1, x_2) \qquad (13\text{-}16)$$

$$V(x_1, x_2) = V(x_2, x_1) \qquad (13\text{-}17)$$

We write this symmetry symbolically as

$$H(1, 2) = H(2, 1) \qquad (13\text{-}18)$$

6. The $^{12}\mathrm{C}_2$ Molecule

Let us now consider the $^{12}\mathrm{C}_2$ molecule, a homonuclear diatomic molecule in which both nuclei have spin 0. This is a perfectly good diatomic molecule whose rotational spectrum can be analyzed experimentally, but it does not form a gas like H_2 or N_2 because it is chemically reactive (the carbon atoms like to form chains, rings, buckyballs, nanotubes, etc). Unfortunately there is no ordinary gas of homonuclear diatomic molecules with nuclear spin 0 that serves our purposes (^{4}He is a noble gas and does not form molecules in the ordinary sense, ^{16}O has been excluded because of its unusual electronic structure, other spin-0 isotopes are radioactive, etc). So we will work with $^{12}\mathrm{C}_2$.

The Hamiltonian describing the vibrations and rotations of this molecule is (1), where the potential V has a minimum at some radius r_0 (the bond length), creating a potential well that supports bound states. The excitations in this potential well are approximately harmonic for low quantum numbers, and correspond physically to the quantized vibrations of the molecule. The molecule can also rotate, and the total quantized energy is approximately the sum of a vibrational and a rotational contribution. See Eq. (16.82).

As usual with central force Hamiltonians, we may transform (1) from lab coordinates $(\mathbf{x}_1, \mathbf{x}_2)$ to center-of-mass and relative coordinates $(\mathbf{R}, \mathbf{r})$, defined in the case of equal masses by

$$\begin{aligned} \mathbf{R} &= \frac{\mathbf{x}_1 + \mathbf{x}_2}{2}, \\ \mathbf{r} &= \mathbf{x}_2 - \mathbf{x}_1. \end{aligned} \tag{23}$$

This is a special case of the transformation presented in Sec. 16.9, in which the two masses are equal. Under this transformation the Hamiltonian (1) becomes

$$H = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(r), \tag{24}$$

where $\mathbf{P}$ is the momentum conjugate to the center-of-mass position $\mathbf{R}$, and $\mathbf{p}$ is the momentum conjugate to the relative position $\mathbf{r}$, and where $r = |\mathbf{r}|$ is the distance between the two particles. The mass $M = 2m$ is the total mass of the system, while $\mu = m/2$ is the reduced mass. The momentum $\mathbf{P}$ is physically the total linear momentum of the system (it is $\mathbf{p}_1 + \mathbf{p}_2$). We can write this Hamiltonian as the sum of a center-of-mass and a relative term,

$$H = H_{\mathrm{CM}} + H_{\mathrm{rel}}, \tag{25}$$

where

$$H_{\mathrm{CM}} = \frac{\mathbf{P}^2}{2M} \tag{26}$$

is a free particle Hamiltonian, and where

$$H_{\mathrm{rel}} = \frac{\mathbf{p}^2}{2\mu} + V(r). \tag{27}$$

As for the wave function, we may transform it also to the new coordinates $(\mathbf{R}, \mathbf{r})$. We will write

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Psi(\mathbf{R}, \mathbf{r}). \tag{28}$$

The Schrödinger equation for (24) separates according to the decomposition (25), so that energy eigenfunctions have the form

$$\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\psi(\mathbf{r}), \tag{29}$$

where $\Phi(\mathbf{R})$ is an eigenfunction of $H_{\rm CM}$ and $\psi(\mathbf{r})$ is an eigenfunction of $H_{\rm rel}$. The 2-particle Hilbert space $\mathcal{E}_{\rm tot}$ is spanned by products of basis wave functions of this form, that is, it has the decomposition

$$\mathcal{E}_{\rm tot} = \mathcal{E}_{\rm CM} \otimes \mathcal{E}_{\rm rel}, \tag{30}$$

in addition to the decomposition Eq. (9). We will write Eq. (29) in ket language as

$$|\Psi\rangle = |\Phi\rangle|\psi\rangle, \tag{31}$$

omitting the $\otimes$ for simplicity. The eigenfunction $\Phi(\mathbf{R})$ is a free-particle energy eigenfunction, which we may take to be

$$\Phi(\mathbf{R}) = \exp(i\mathbf{P} \cdot \mathbf{R}/\hbar), \tag{32}$$

where $\mathbf{P}$ is the momentum eigenvalue. This plane wave is not the only choice for a free particle energy eigenfunction, but it is a simple one. As for the relative energy eigenfunction $\psi(\mathbf{r})$, it is a solution of a central force problem and must have the form

$$\psi_{n\ell m}(\mathbf{r}) = f_{n\ell}(r)Y_{\ell m}(\Omega), \tag{33}$$

where f is the radial wave function and (n, ℓ, m) are the usual central force quantum numbers. With center-of-mass and relative eigenfunctions (32) and (33), we will write the total energy eigenfunction (29) in ket language as

$$|\Psi\rangle = |\mathbf{P}\rangle|n\ell m\rangle. \tag{34}$$

The total energy of the product wave function (29) or (34) is

$$E_{\rm tot} = \frac{\mathbf{P}^2}{2M} + E_{n\ell}, \tag{35}$$

where $E_{n\ell}$ is the central force energy eigenvalue, which is independent of m because of the rotational invariance of $H_{\rm rel}$ (and the Wigner-Eckart theorem). In the case of a molecular potential V, this energy has the approximate form,

$$E_{n\ell} = \frac{\ell(\ell+1)\hbar^2}{2I} + (n + \tfrac{1}{2})\hbar\omega, \tag{36}$$

where $I = \mu r_0^2$ is the moment of inertia of the diatomic at its equilibrium bond length and n is the quantum number of the approximately harmonic vibrations whose frequency is ω. This approximation is rough and is valid only for small vibrational quantum numbers n (near the bottom of the well, where the harmonic approximation is best), but it conveys the right idea about the rotational-vibrational spectrum of the molecule. Notice that the first term in Eq. (36), the energy of a rigid rotor of moment of inertia I and angular momentum $\sqrt{\ell(\ell+1)}\hbar$, is also the centrifugal potential for a central force Hamiltonian in which the radius r is fixed at the equilibrium bond length r_0. The energy (36) is the sum of a rotational and a vibrational contribution.

Now let us consider the effect of the exchange operator E_{12} on these energy eigenfunctions. By swapping labels 1 and 2, it is easy to see from Eq. (23) that $\mathbf{R}$ and $\mathbf{r}$ transform under E_{12} according to

$$\begin{aligned} \mathbf{R} &\longrightarrow \mathbf{R}, \\ \mathbf{r} &\longrightarrow -\mathbf{r}, \end{aligned} \tag{37}$$

so the effect on the wave function is

$$\Psi(\mathbf{R}, \mathbf{r}) \xrightarrow{E_{12}} \Psi(\mathbf{R}, -\mathbf{r}). \tag{38}$$

The center-of-mass position is not affected, but the relative position vector is flipped through the origin. This behavior reminds us of the parity operator π, which flips all position vectors through the origin, and, in fact, E_{12} behaves the same as parity insofar as the relative coordinate is concerned. As a result it is easy to confuse exchange and parity, a bad idea since physically they are quite distinct. Nevertheless, since we know what parity does to central force eigenfunctions, it is easy to see the effect of exchange on two-particle eigenfunctions such as (29). In particular, parity does not affect the radial wave function $f_{n\ell}(r)$, but it multiplies the $Y_{\ell m}$ by $(-1)^\ell$ (a phase that is independent of m). See Eq. (21.52). As for the center-of-mass part of the wave function, by Eq. (38) exchange does nothing to it. Altogether, we have

$$E_{12}|\Psi\rangle = E_{12}|\mathbf{P}\rangle|n\ell m\rangle = (-1)^\ell|\Psi\rangle. \tag{39}$$

The energy eigenfunctions are automatically eigenfunctions of E_{12}; this is the simultaneous eigenbasis whose existence is promised by the commutation relation $[E_{12}, H] = 0$. We see that the exchange quantum number of the energy eigenfunction is $(-1)^\ell$.

7. The Symmetrization Postulate

So far we have just explored the mathematical consequences of the commutation relation $[E_{12}, H] = 0$. Now, however, we must take into account the important experimental fact that the states of odd ℓ in the rotational spectrum of $^{12}C_2$ do not exist. This can be determined by direct spectroscopic means, and there is similar evidence of missing rotational states, both spectroscopic and thermodynamic, for other homonuclear diatomic molecules. If one of the carbon atoms is replaced by a different isotope, say ^{14}C, then all angular momentum states ℓ are observed. In this case the masses are no longer equal and some of the transformations we have written down require modification, and the operator E_{12} is not very meaningful. Nevertheless, it is meaningful to talk about the angular momentum states ℓ of the rotor, and all of them are present if the nuclei are not identical. We can say that in the case of the $^{12}C_2$ molecule, only the subspace $\mathcal{E}_{\text{even}}$ in Eq. (6) is physical. It is perfectly possible to write down wave functions that are odd under exchange, including perfectly valid eigenfunctions of the Hamiltonian (1), but these do not correspond to anything physical. They are just mathematical objects without any correspondence with physical reality.

These facts about the $^{12}C_2$ molecule are a special case of a collection of experimental evidence that can be summarized in what we will call the *symmetrization postulate*:

Symmetrization Postulate. *In any system consisting of two or more identical particles, the wave function is symmetric under the exchange of any two identical bosons, and antisymmetric under the exchange of any two identical fermions.*

Recall that bosons are particles of integer spin, while fermions are particles of half-integer spin. Notice that a system may contain more than one different species of identical particles, for example, helium has two identical protons and two identical neutrons in the nucleus, and two identical electrons orbiting the nucleus. The symmetrization postulate applies to exchange of any pair of identical particles of any species. We have only defined the exchange operator in these notes for the case of two identical particles, but the definition is easily extended to multiparticle systems, something we shall do when we study such systems.

This postulate cannot be derived from the earlier (measurement) postulates of quantum mechanics discussed in Notes 2 or 3. Within the context of nonrelativistic quantum mechanics it must simply be taken as an experimental fact. Indeed it *is* an experimental fact, and historically this was how it was discovered. Nevertheless, within the framework of relativistic quantum field theory, it is possible to justify the symmetrization postulate on the basis of certain reasonable assumptions. These include the requirement that energy be bounded from below and that relativistic causality hold (signals cannot travel faster than the speed of light). This theoretical derivation of the symmetrization postulate was given by Pauli in 1940, in the form of the famous *spin and statistics theorem*. It is regarded as one of the triumphs of relativistic quantum field theory.

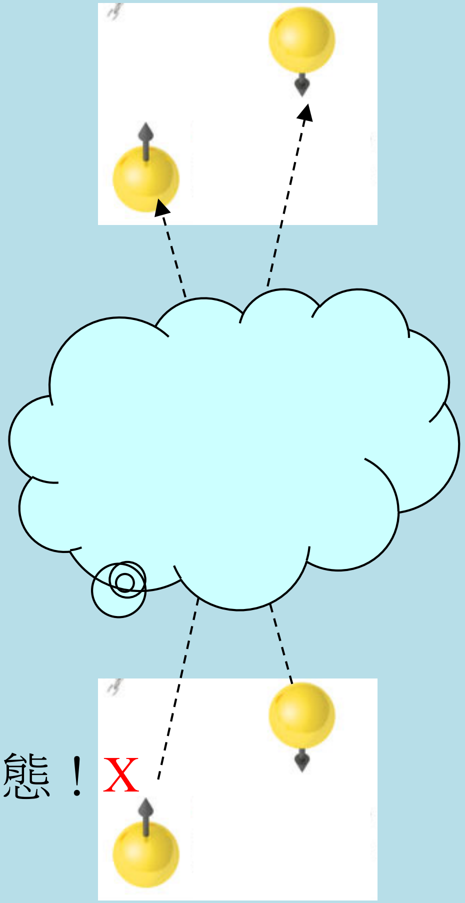
回到我們兩顆靜止電子的例子：

兩個電子互換時，波函數與自旋狀態的乘積必須變號：

如果兩個電子近乎靜止，那波函數可以忽略，

兩個電子互換時，自旋狀態必須變號：

$$|m_{s1}, m_{s2}\rangle = -|m_{s1}, S_{z1}\rangle$$



兩個電子互換時，很明顯$|\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle$會互換。

$$\left|m_{s1} = \frac{1}{2}, m_{s2} = -\frac{1}{2}\right\rangle \leftrightarrow \left|-\frac{1}{2}, \frac{1}{2}\right\rangle$$

$$|\downarrow\uparrow\rangle \leftrightarrow |\uparrow\downarrow\rangle$$

$|\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle$這兩個狀態單獨都不符合要求，電子無法採取此狀態！X

但若是兩者的線性組合就可以！

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \leftrightarrow \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) = -\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

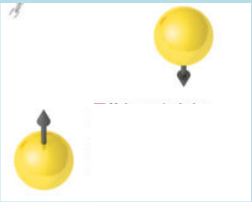
費米子V

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \leftrightarrow \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) = +\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

波色子 X

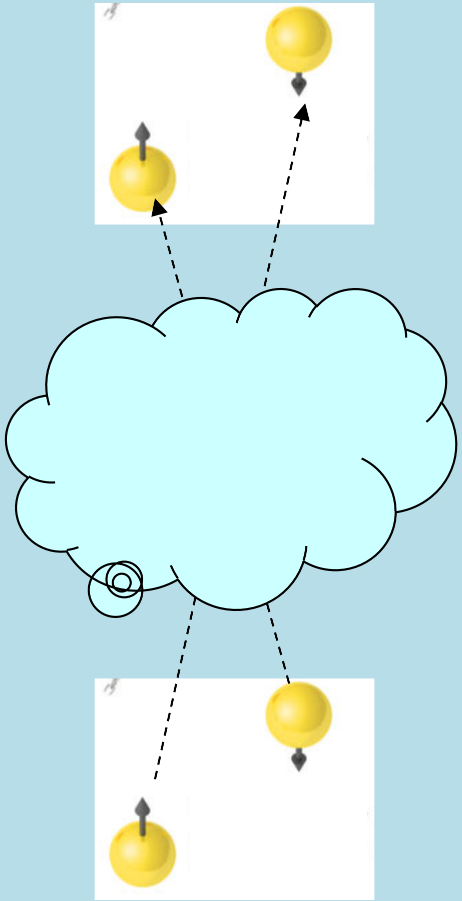
$$\frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$$

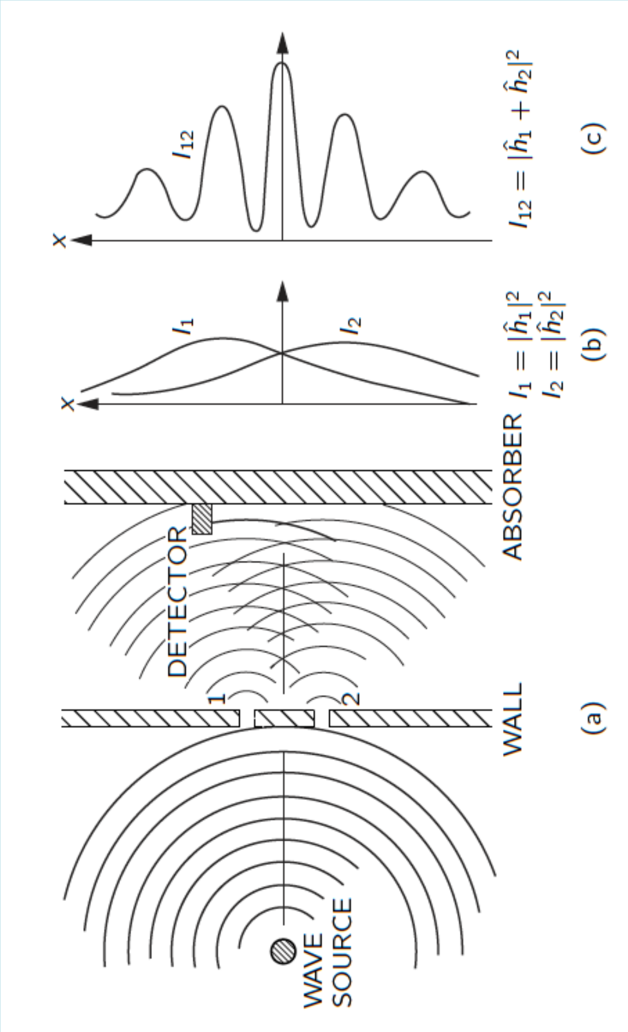
這組合，稱反對稱組合才是此狀態的正確描述！



$\frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$ 這反對稱線性疊加才是此末狀態的正確描述！

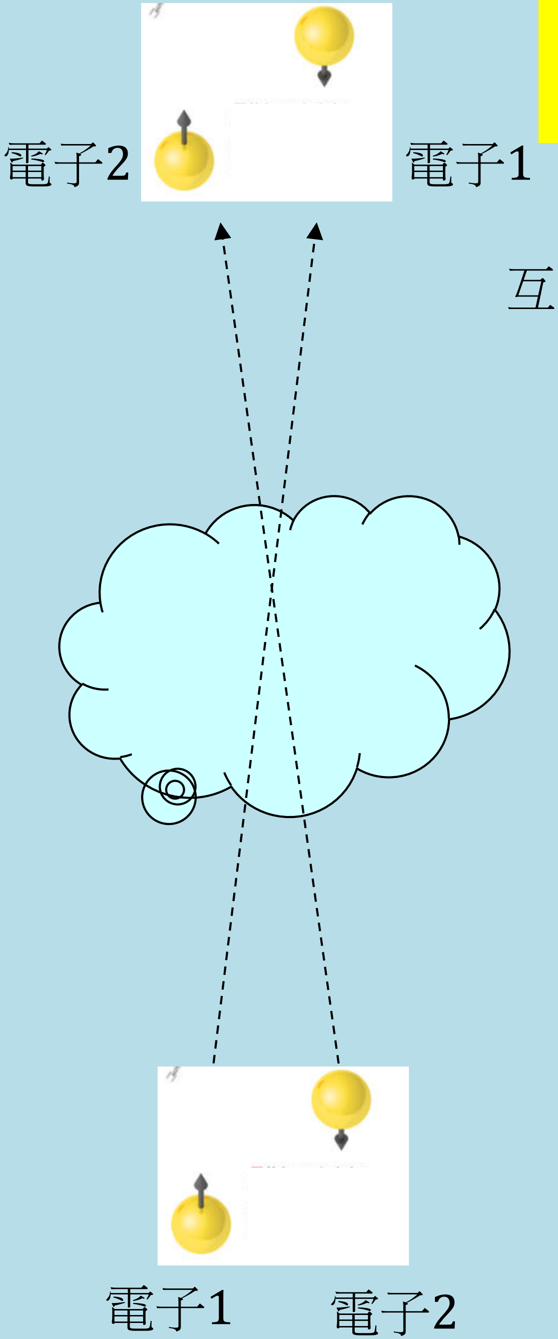
這就非常類似雙狹縫干涉，是兩個波函數疊加：



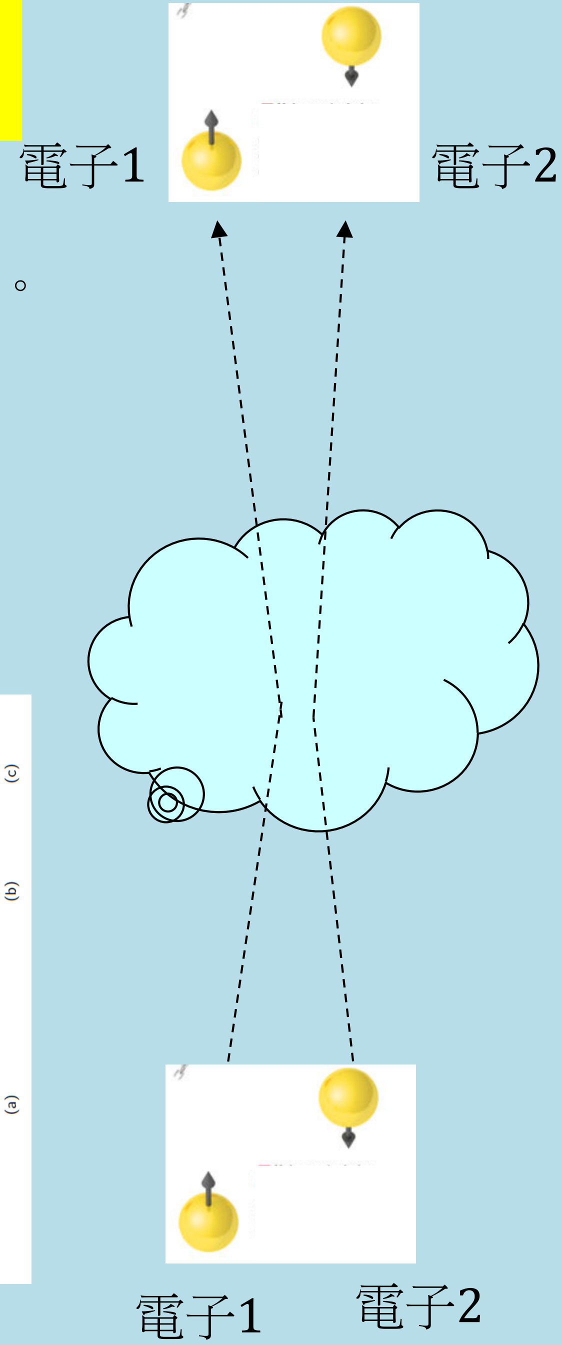


兩個可能性的振幅就必須疊加相減。平方後就是發生的機率。

$$\frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$$



互換前後機率不變。



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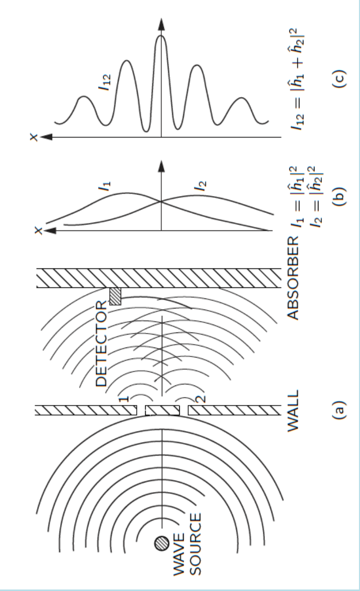
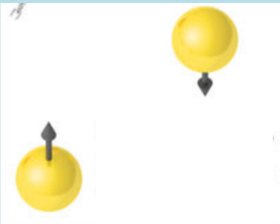


兩個電子的自旋狀態是一個四維空間。



很明顯可以以個別電子的S_{1z}, S_{2z}的本徵態為基底：$|\uparrow\uparrow\rangle$、$|\downarrow\uparrow\rangle$、$|\uparrow\downarrow\rangle$、$|\downarrow\downarrow\rangle$。

但他們都不是合法可以採取的狀態。

反對稱組合可以：

$$|0,0\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$$

有三個對稱的組合，但電子是費米子，就無法採取。
但若有空間波函數，就有機會。

$$|1,1\rangle = |\uparrow\uparrow\rangle$$

$$|10\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

$$|1,-1\rangle = |\downarrow\downarrow\rangle$$

這三個對稱化的自旋態，事實上是總自旋為1的狀態！ $\vec{S} = \vec{S}_1 + \vec{S}_2$

反對稱化的自旋態，事實上是總自旋為0的狀態！

以上手續可以推廣到位置波函數：從任一個雙粒子波函數出發：

$\psi_1(x_1)\psi_2(x_2)$ 一號粒子在狀態1，二號粒子在狀態2，但這不是合理狀態。

我們必須將它加上互換後的波函數$\psi_1(x_2)\cdot\psi_2(x_1)$：

這個程序稱為對稱化。

$$\psi_S(x_2,x_1)=\frac{1}{\sqrt{2}}[\psi_1(x_1)\cdot\psi_2(x_2)+\psi_1(x_2)\cdot\psi_2(x_1)]$$

對稱化後的波函數才是對稱的： $\psi_S(x_1,x_2)=\psi_S(x_2,x_1)$

或是將它減去互換後的波函數$\psi_1(x_2)\cdot\psi_2(x_1)$：

這個程序稱為反對稱化。

$$\psi_A(x_2,x_1)=\frac{1}{\sqrt{2}}[\psi_1(x_1)\cdot\psi_2(x_2)-\psi_1(x_2)\cdot\psi_2(x_1)]$$

反對稱化後的波函數才是反對稱的：$\psi_A(x_1,x_2)=-\psi_A(x_2,x_1)$

兩種情況下，機率密度在粒子互換後都是不變的！

這兩種狀態才是兩個全同電子可能存在的狀態！

前者適用於波色子，後者適用於費米子。

這樣的方法很容易擴展到粒子數大於2的情況：

將任一$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3)$加上任兩粒子互換後得到的波函數，

$$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3) \rightarrow \psi_S(x_1,x_2,x_3) \sim \psi_A(x_1)\psi_B(x_2)\psi_C(x_3) +$$

$$\psi_A(x_2)\psi_B(x_1)\psi_C(x_3) + \psi_A(x_1)\psi_B(x_3)\psi_C(x_2) + \psi_A(x_2)\psi_B(x_3)\psi_C(x_1) +$$

$$\psi_A(x_3)\psi_B(x_1)\psi_C(x_2) + \psi_A(x_3)\psi_B(x_2)\psi_C(x_1)$$

就是將所有可能互換形成的波函數都加起來，結果自然是對稱的！

驗證：任意兩個粒子互換，波函數是不變的！ $\psi_S(x_1,x_2,x_3) = \psi_S(x_2,x_1,x_3)$

這就稱為對稱化，波色子量子系統必定得選擇對稱化後的狀態。

反對稱程序可以推廣到到3個粒子的情況：

將任一$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3)$加上任兩粒子互換後得到的波函數，

奇數次互換乘上-1，偶數次互換乘上1：

$$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3) \rightarrow \psi_A(x_1,x_2,x_3) \sim \psi_A(x_1)\psi_B(x_2)\psi_C(x_3)$$

$$-\psi_A(x_2)\psi_B(x_1)\psi_C(x_3) - \psi_A(x_1)\psi_B(x_3)\psi_C(x_2) + \psi_A(x_2)\psi_B(x_3)\psi_C(x_1) +$$

$$+\psi_A(x_3)\psi_B(x_1)\psi_C(x_2) - \psi_A(x_3)\psi_B(x_2)\psi_C(x_1)$$

$$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3) \rightarrow \psi_A(x_1,x_2,x_3) \sim \psi_A(x_1)\psi_B(x_2)\psi_C(x_3)$$

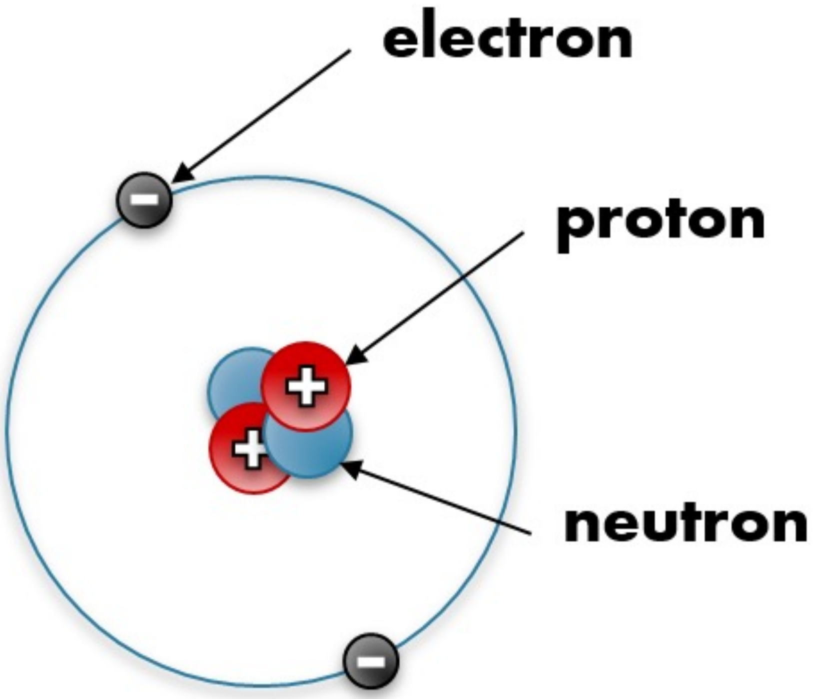
$$-\psi_A(x_2)\psi_B(x_1)\psi_C(x_3) - \psi_A(x_1)\psi_B(x_3)\psi_C(x_2) + \psi_A(x_2)\psi_B(x_3)\psi_C(x_1) +$$

$$+\psi_A(x_3)\psi_B(x_1)\psi_C(x_2) - \psi_A(x_3)\psi_B(x_2)\psi_C(x_1)$$

驗證：任意兩個粒子互換，波函數變號！ $\psi_A(x_1,x_2,x_3) = -\psi_A(x_2,x_1,x_3)$

稱為反對稱化，費米子量子系統必定得選擇反對稱化後的狀態。

但這樣的符號比較複雜，原則上可行，粒子多了就很難用。



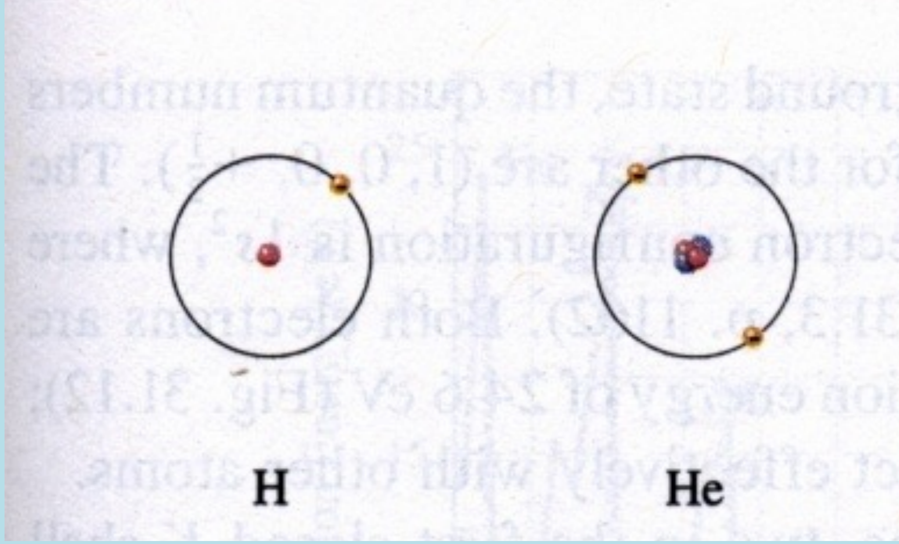
Helium Atom

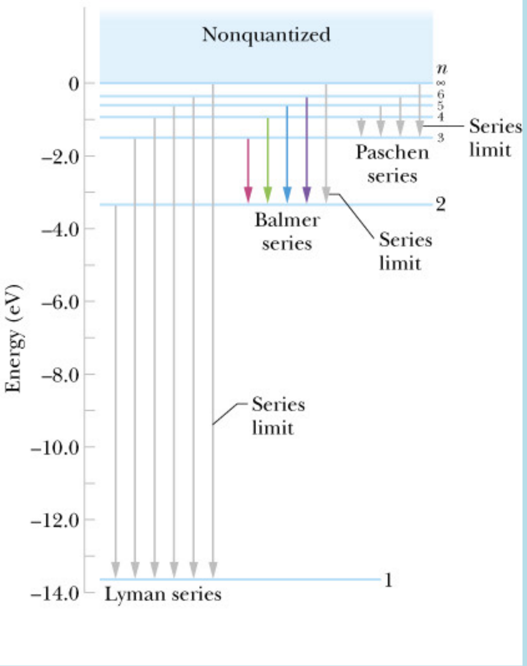
氦的原子核就完全如同氫的原子核，只是原子核電量加大為Ze ！

氦原子核，將給周圍的電子如同氫原子核一樣的庫倫位能。

因此，電子能態就完全如同氫原子，只要代入新的原子核電量。

可以用同樣的量子數nlm來標記！

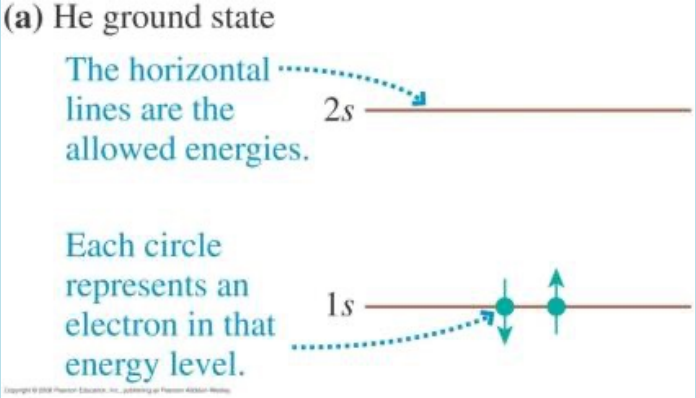




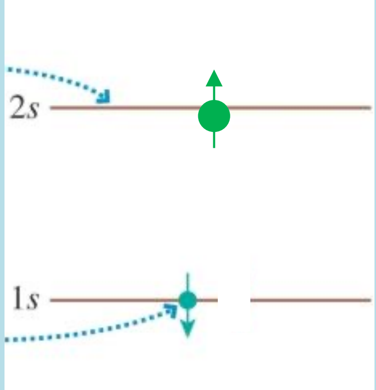
氦原子可以說是最簡單的多電子系統！

原子中的電子，會一個一個由最低的能階向上一一配置！

基態時，兩電子在同一個軌道基態上，自旋必須一個向上、一個向下。

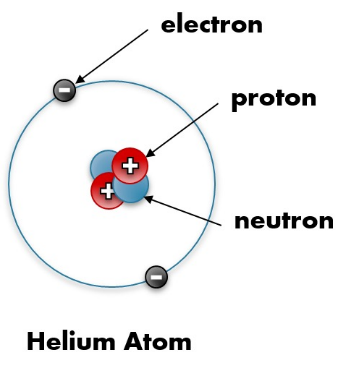


激發態就是電子跳到較高的能態。



以上圖像的前提是忽略電子與電子之間的庫倫力！電子的定態沒看到彼此。

而且波函數還必須考慮電子的費米全同性。



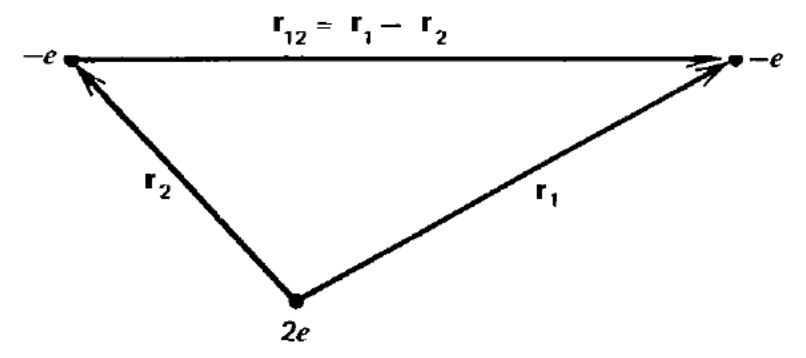
$$H = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

將電子彼此的靜電位能視為微擾處理。

在微擾的第零階，電子的確沒看到彼此。

$$H_1 = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

$$H_0 = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$



在微擾的第零階，可以忽略電子的排斥力，電子沒看到彼此。

兩電子的位置$\vec{r}_1, \vec{r}_2$彼此互相獨立。

位置波函數的兩電子位置$\vec{r}_1, \vec{r}_2$可作變數分離：

$$H_0 = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

個別電子的能量本徵值與波函數如同氫原子，只要代入氦原子核電量。

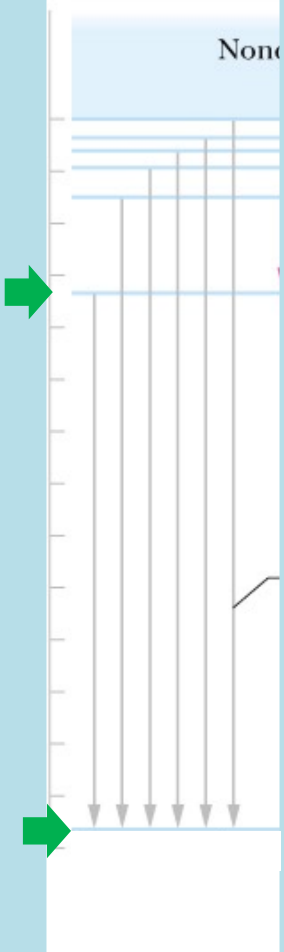
$$u(\vec{r}_1, \vec{r}_2) = \phi_{n_1 l_1 m_1}(\vec{r}_1) \cdot \phi_{n_2 l_2 m_2}(\vec{r}_2)$$

$$E_n = -\frac{m}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0 \hbar}\right)^2 \frac{1}{n^2}$$

氦原子核旁單一電子能量

能量本徵值為個別電子能量的和：

$$E = E_{n_1} + E_{n_2}$$



$n = 2, -13.6\ \text{eV}$

$n = 1, -54.4\ \text{eV}$

$$\left[H^{(1)} + H^{(2)}\right] u(\vec{r}_1, \vec{r}_2)$$

$$= H^{(1)} \phi_{n_1 l_1 m_1}(\vec{r}_1) \cdot \phi_{n_2 l_2 m_2}(\vec{r}_2) + \phi_{n_1 l_1 m_1}(\vec{r}_1) \cdot H^{(2)} \phi_{n_2 l_2 m_2}(\vec{r}_2)$$

$$= E_{n_1} \phi_{n_1 l_1 m_1}(\vec{r}_1) \cdot \phi_{n_2 l_2 m_2}(\vec{r}_2) + E_{n_2} \phi_{n_1 l_1 m_1}(\vec{r}_1) \cdot \phi_{n_2 l_2 m_2}(\vec{r}_2)$$

$$= E u(\vec{r}_1, \vec{r}_2)$$

這就是氦原子核旁電子的能階圖。

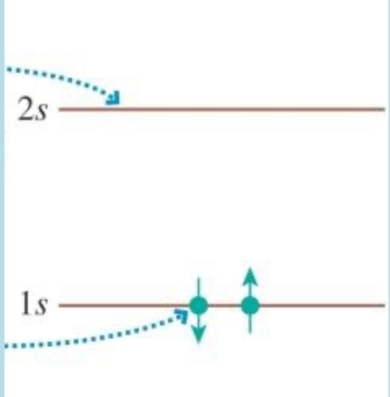
電子可以一個一個佔據不同的能態。

雙電子氦原子能量

氦原子有兩個電子：(n_1,n_2) $E = E_{n_1} + E_{n_2}$

整個氦原子的能量則可以兩個量子數(n_1,n_2)標記。

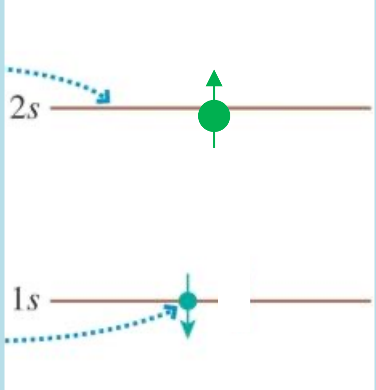
基態記為(1,1)，兩電子在同一個$n = 1$軌道上，自旋一向上一向下。



氦原子核旁單一電子能量

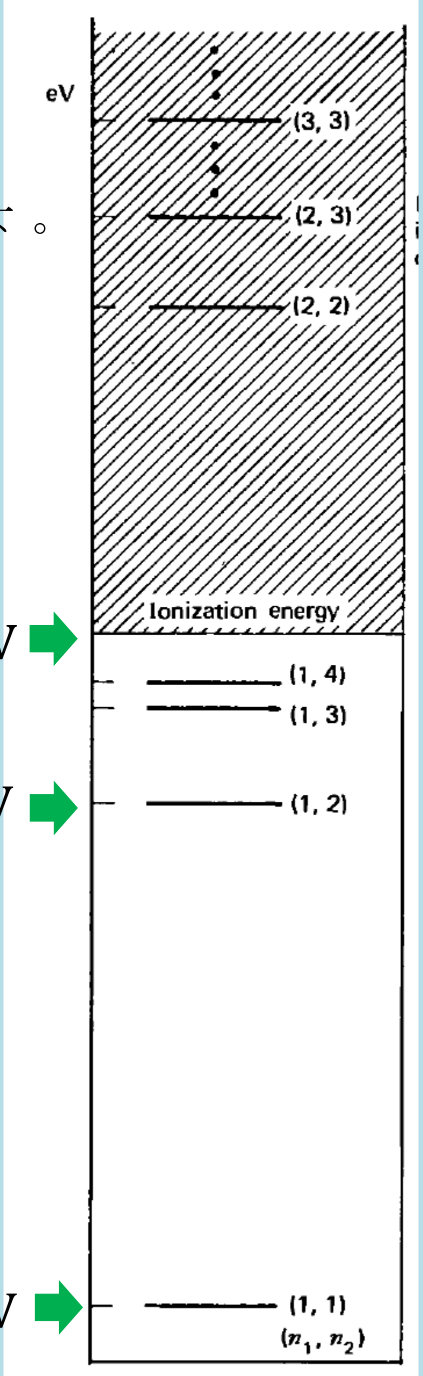
-108.8 eV

第一激發態就是(1,2)：一電子跳到次低的能態 。



$-54.4 - 13.6 = -68$ eV

注意能態(2,2)比$(1,\infty)$能量還高。



-54.4 eV

-68 eV

-108.8 eV

$(1,\infty)E=-54.4$ eV，一電子已游離，以上即形成連續能態。

氦原子的游離，只要一個電子到達無限遠即可！

束縛激發態是$(1,n)$，一電子留在基態。

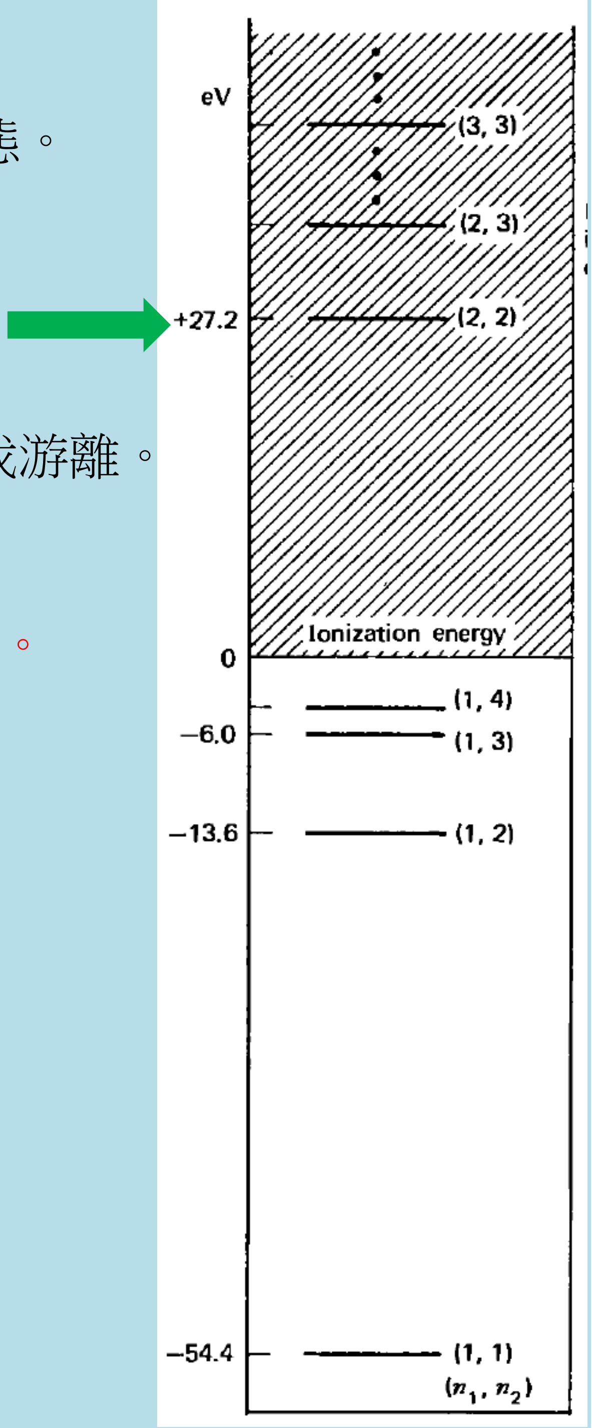
氦原子激發態的能階與氫原子樣式完全相同。

$(>1,n)$激發態與連續能態混在一起，這時氦原子可以自我游離。

例如 $(2,n)\leftrightarrow(1,>\infty)$

束縛激發態很容易就游離為$(1,>\infty)$，又很容易束縛回來。

表現在吸收光譜上，就是共振 resonance。



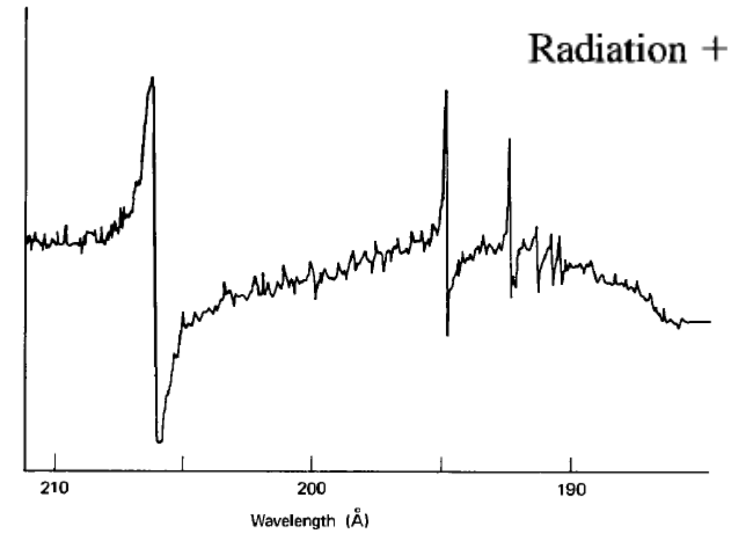
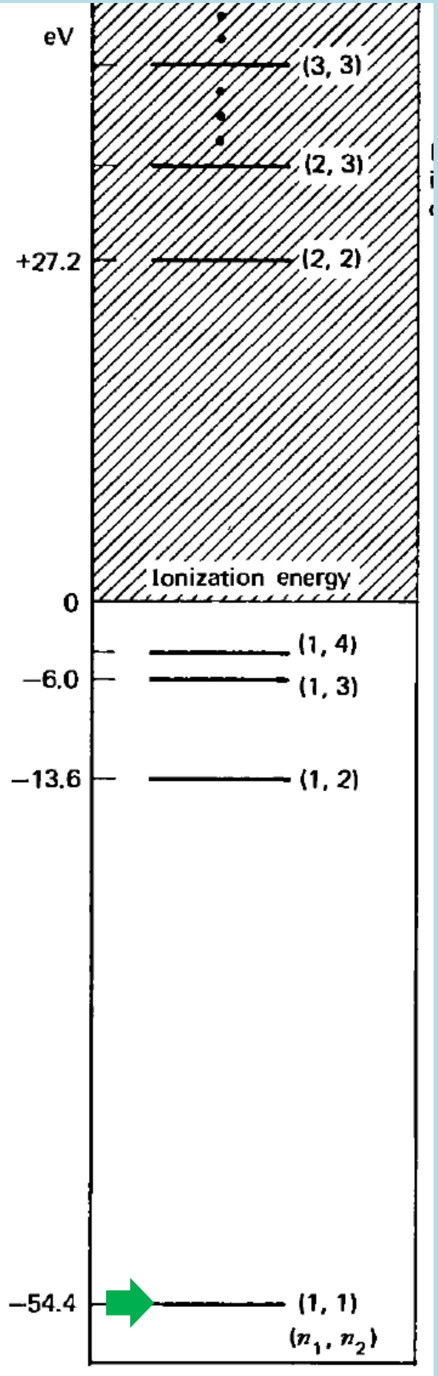
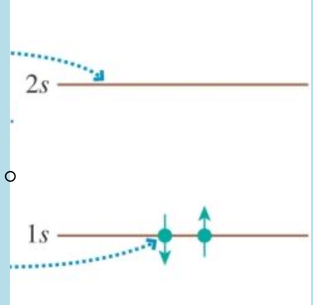


Figure 14-4 Resonance in the helium absorption spectrum above the continuum threshold; the first peak occurs at the energy corresponding to the location of the (2*s*)(2*p*) level. (From R. P. Madden and K. Codling, *Phys. Rev. Lett.* **10**, 516 (1963), by permission.)



Ground State (1,1)的波函數、包括自旋。



兩個電子都處於最低能量的$n = 1, l = 0, m = 0$態。

空間波函數就是兩個1,0,0波函數的乘積：

電子應該一個自旋向上、一個自旋向下，因此自然的猜想：

能量中不包含自旋，因此總波函數等於空間波函數乘上自旋狀態：

$$\phi(\vec{r}_1, \vec{r}_2, m_{s1}, m_{s2}) \sim \phi_{100}(\vec{r}_1) \cdot \phi_{100}(\vec{r}_2) \cdot |\uparrow\downarrow\rangle$$

但這個波函數顯然不是反對稱的！

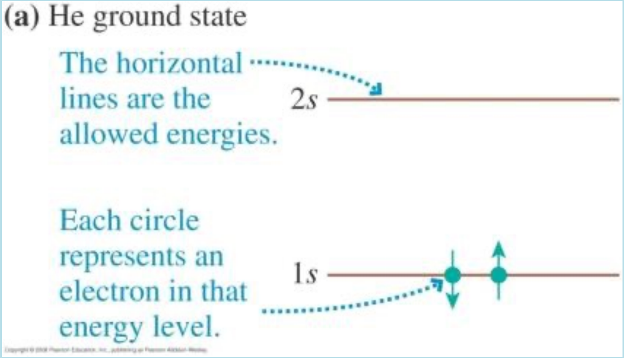
這裏空間波函數兩個粒子是互換對稱的，$\phi_{100}(\vec{r}_1) \cdot \phi_{100}(\vec{r}_2)$

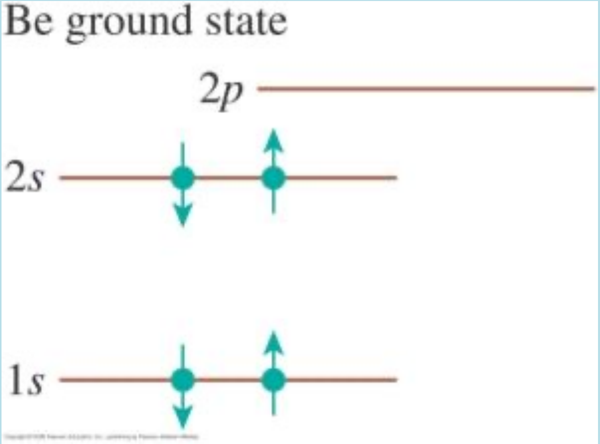
反對稱 = 空間對稱×自旋反對稱

我們必須反對稱化自旋的部分！

$$|\uparrow\downarrow\rangle \to \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \leftrightarrow -\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$



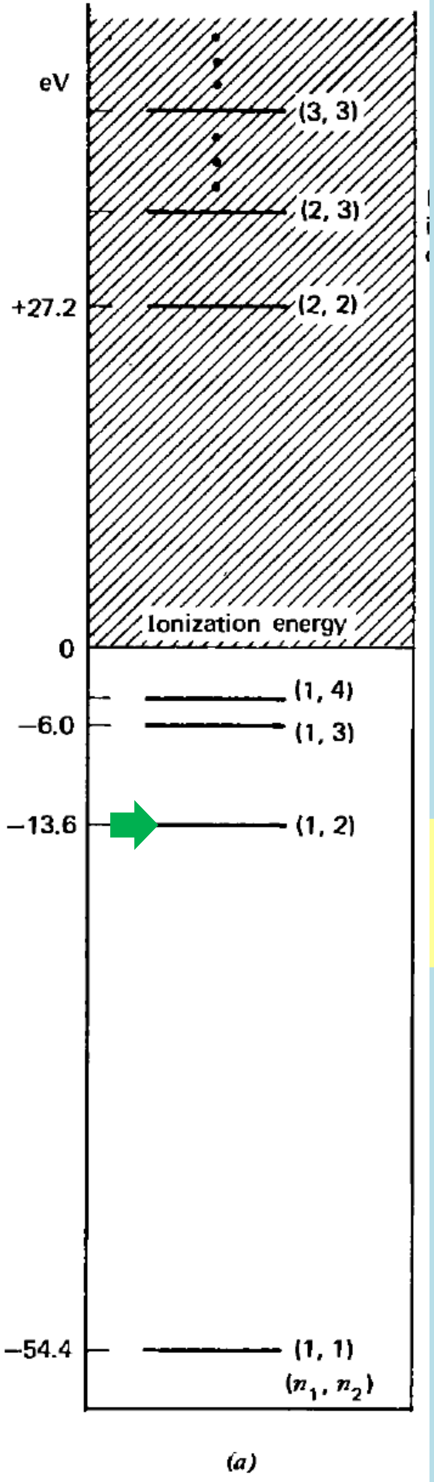


因此基態總波函數應該寫成：

$$\phi(\vec{r}_1,\vec{r}_2,m_{s1},m_{s2})\sim\phi_{100}(\vec{r}_1)\cdot\phi_{100}(\vec{r}_2)\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$$

注意這適用於其他任何一個態填入兩個電子的情況。

兩個電子不只要自旋一上一下，自旋狀態得是反對稱的！



Excited State (1,2)的波函數、包括自旋

現在空間波函數是兩個不同波函數的乘積，！

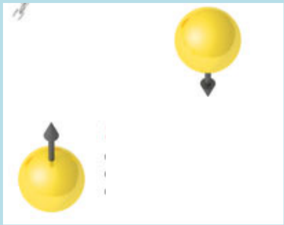
但總波函數還是需要滿足反對稱性。最容易的做法是：

空間波函數與自旋波函數，必須一個是對稱，一個是反對稱！

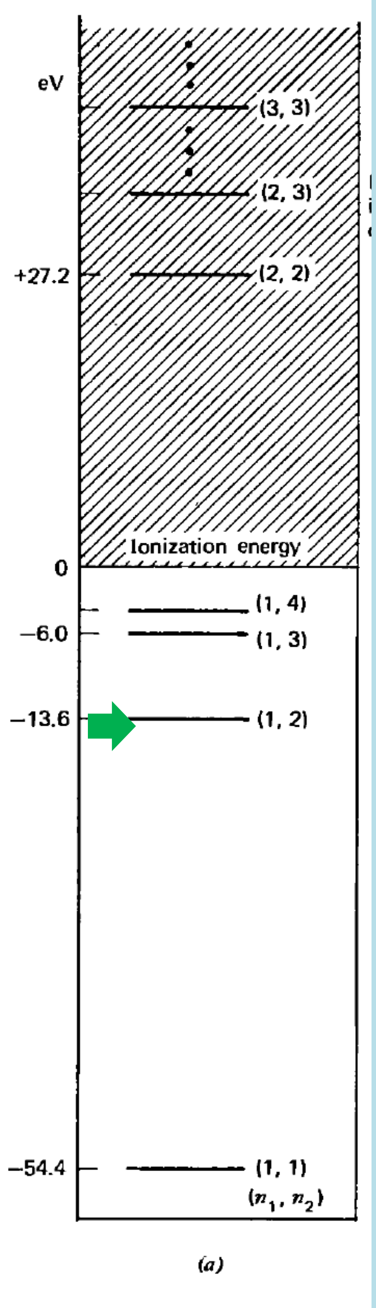
反對稱 ＝ 空間對稱×自旋反對稱

類似基態：

$$\phi^{S}_{1,2} = \frac{1}{\sqrt{2}}\left[\phi_{100}(\vec{r}_1)\cdot\phi_{2lm}(\vec{r}_2) + \phi_{100}(\vec{r}_2)\cdot\phi_{2lm}(\vec{r}_1)\right] \quad \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$



這一反對稱化的自旋態，事實上是總自旋為0的狀態！所以稱Singlet。



空間波函數也可以是反對稱的，那自旋波函數必須是對稱的：

反對稱 ＝ 空間反對稱×自旋對稱

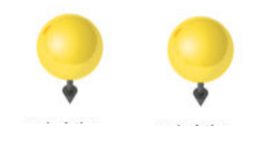
$$\phi^t_{1,2} = \frac{1}{\sqrt{2}}[\phi_{100}(\vec{r}_1)\cdot\phi_{2lm}(\vec{r}_2) - \phi_{100}(\vec{r}_2)\cdot\phi_{2lm}(\vec{r}_1)]\cdot$$

$$|\uparrow\uparrow\rangle$$

$$\frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

$$|\downarrow\downarrow\rangle$$

自旋狀態可以兩個都向上、或向下，也是對稱的。

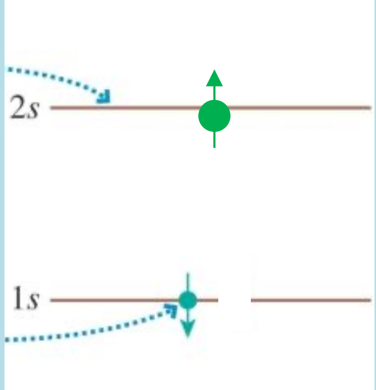


反對稱條件比不相容原理適用更廣。

所以能量較高的激發態$|\psi_-\rangle$共有三個！

令人驚訝的：自旋與軌道運動無作用，但卻連鎖在一起！

這三個對稱化的自旋態，事實上是總自旋為1的狀態！所以稱Triplet。



Excited State (1,2)的波函數、包括自旋

反對稱 ＝ 空間對稱×自旋反對稱

$$\phi^{s}_{1,2}=\frac{1}{\sqrt{2}}[\phi_{100}(\vec{r}_1)\cdot\phi_{2lm}(\vec{r}_2)+\phi_{100}(\vec{r}_2)\cdot\phi_{2lm}(\vec{r}_1)]\cdot\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$$

這一反對稱化的自旋態，事實上是總自旋為0的狀態！所以稱Singlet。

反對稱 ＝ 空間反對稱×自旋對稱

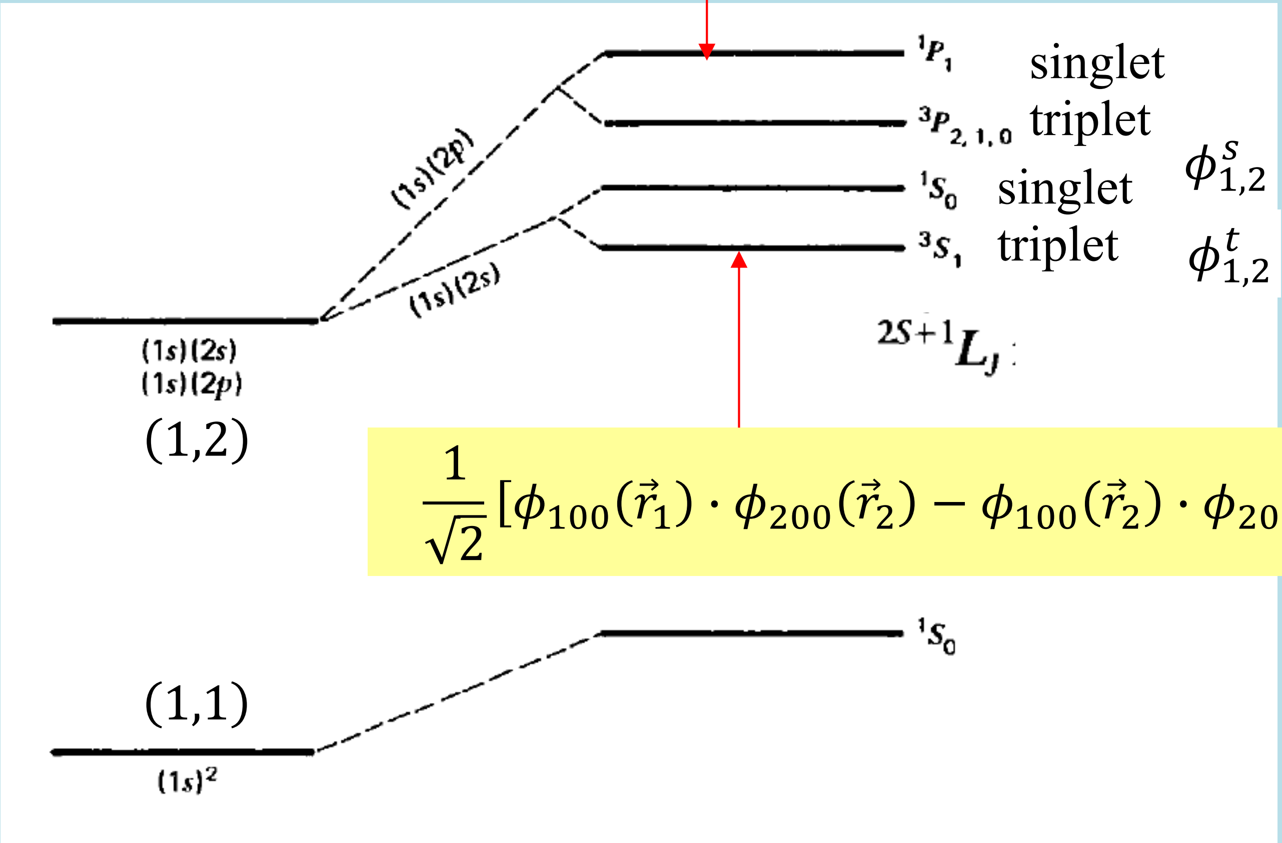
$|\uparrow\uparrow\rangle$

$$\phi^{t}_{1,2}=\frac{1}{\sqrt{2}}[\phi_{100}(\vec{r}_1)\cdot\phi_{2lm}(\vec{r}_2)-\phi_{100}(\vec{r}_2)\cdot\phi_{2lm}(\vec{r}_1)]\cdot\ \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle+|\uparrow\downarrow\rangle)$$

$|\downarrow\downarrow\rangle$

這三個對稱化的自旋態，事實上是總自旋為1的狀態！所以稱Triplet。

$$\frac{1}{\sqrt{2}}[\phi_{100}(\vec{r}_1)\cdot\phi_{21m}(\vec{r}_2)+\phi_{100}(\vec{r}_2)\cdot\phi_{21m}(\vec{r}_1)], \qquad m=1,0,-1$$

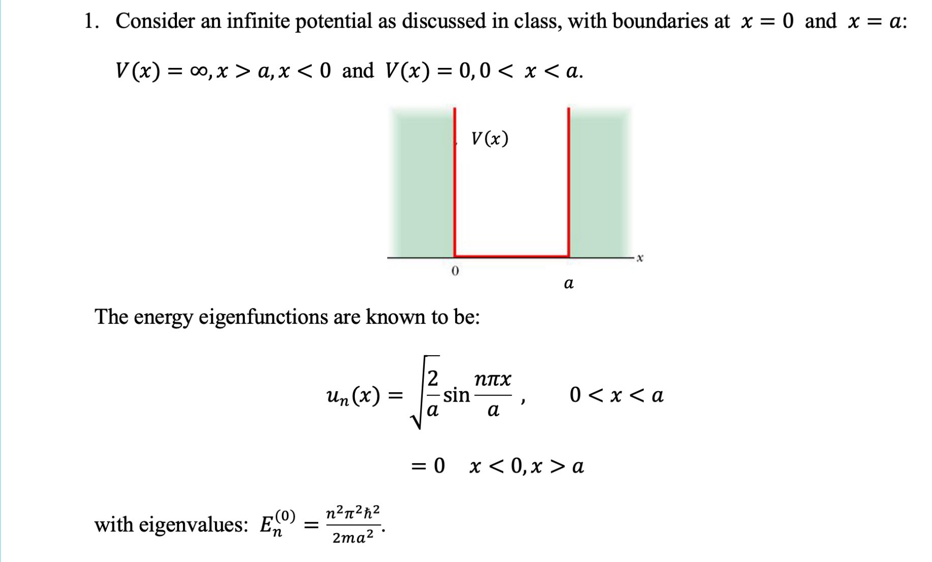


$$\frac{1}{\sqrt{2}}[\phi_{100}(\vec{r}_1)\cdot\phi_{200}(\vec{r}_2)-\phi_{100}(\vec{r}_2)\cdot\phi_{200}(\vec{r}_1)]$$

所以Excited State (1,2) $l=0,1$(三個態），各對應3個triplet， 1個singlet。

總共$4\times4=16$個態，但此時未微擾能量還是簡併的。 $E=E_1+E_2$

簡併將被電子彼此的排斥力作為微擾所破壞。



1. Consider an infinite potential as discussed in class, with boundaries at $x = 0$ and $x = a$:

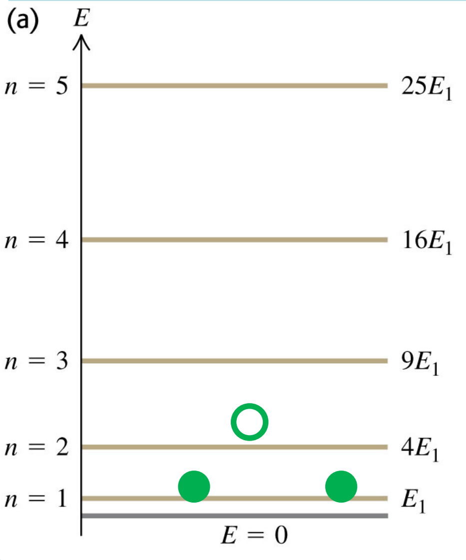
$V(x) = \infty, x > a, x < 0$ and $V(x) = 0, 0 < x < a$.

The energy eigenfunctions are known to be:

$$u_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \qquad 0 < x < a$$

$$= 0 \quad x < 0, x > a$$

with eigenvalues: $E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2ma^2}$.



單一電子能量

5. Consider an infinite box with boundaries at $x = 0$ and $x = a$. The energy eigenstates and eigenvalues are described in problem 2. Put two electrons in the box. The wavefunction of the ground state of the two-electron system, denoted by the two quantum number $(n_1 = 1, n_2 = 1)$, can be written as:

$$\frac{2}{a}\left[\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\right]\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

This overall antisymmetric wavefunction consists of a symmetric space part (of two identical wavefunction) and an antisymmetric spin part.

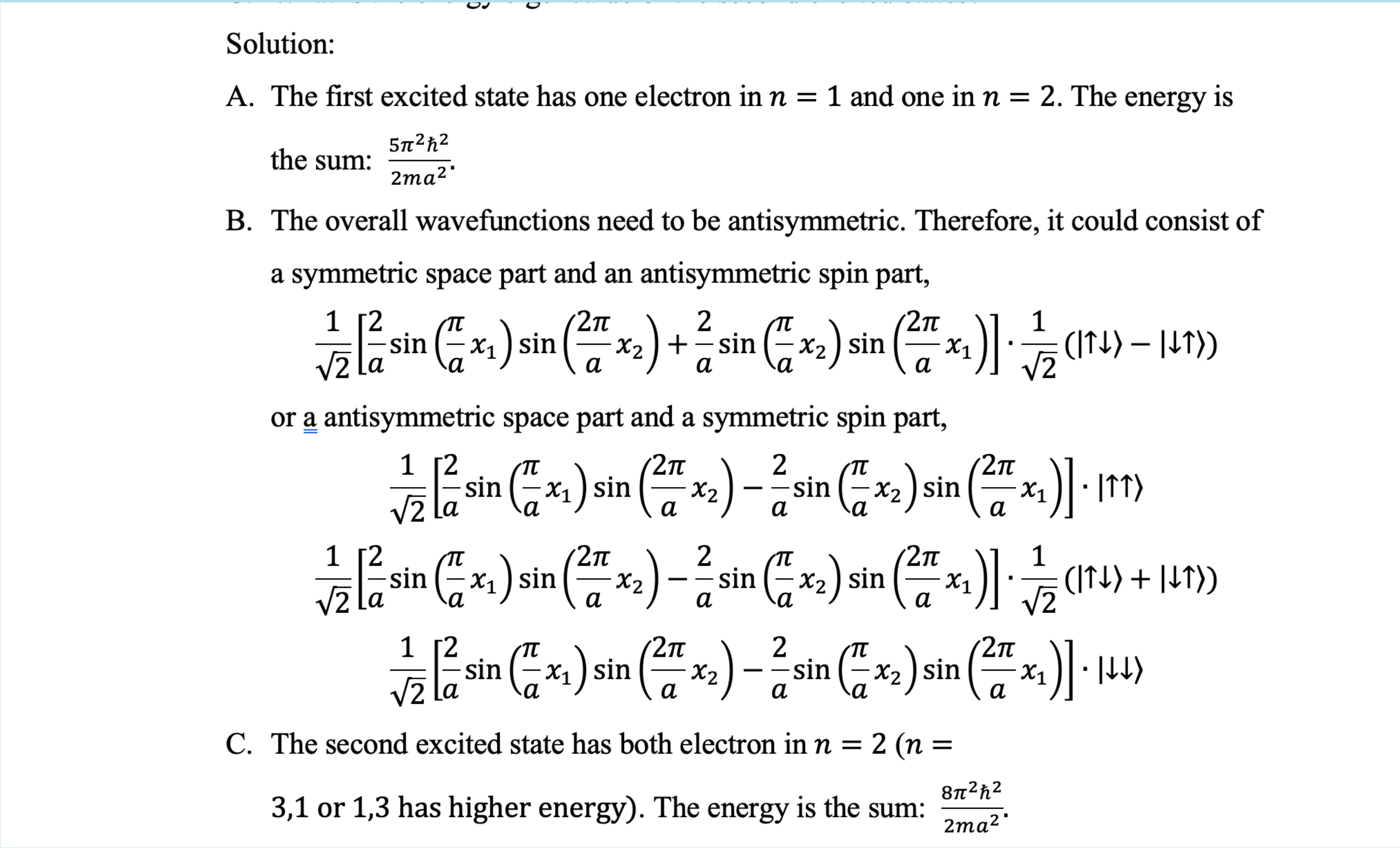
A. Consider the first excited state. What is the energy eigenvalue?

B. Write down the wavefunction of the **four** first excited state, using the above notation.

C. What is the energy eigenvalue of the second excited states?

Solution:

A. The first excited state has one electron in $n = 1$ and one in $n = 2$. The energy is the sum: $\frac{5\pi^2\hbar^2}{2ma^2}$.



Solution:

A. The first excited state has one electron in $n = 1$ and one in $n = 2$. The energy is the sum: $\frac{5\pi^2\hbar^2}{2ma^2}$.

B. The overall wavefunctions need to be antisymmetric. Therefore, it could consist of a symmetric space part and an antisymmetric spin part,

$$\frac{1}{\sqrt{2}}\left[\frac{2}{a}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{2\pi}{a}x_2\right)+\frac{2}{a}\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_1\right)\right]\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$$

or a antisymmetric space part and a symmetric spin part,

$$\frac{1}{\sqrt{2}}\left[\frac{2}{a}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{2\pi}{a}x_2\right)-\frac{2}{a}\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_1\right)\right]\cdot|\uparrow\uparrow\rangle$$

$$\frac{1}{\sqrt{2}}\left[\frac{2}{a}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{2\pi}{a}x_2\right)-\frac{2}{a}\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_1\right)\right]\cdot\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)$$

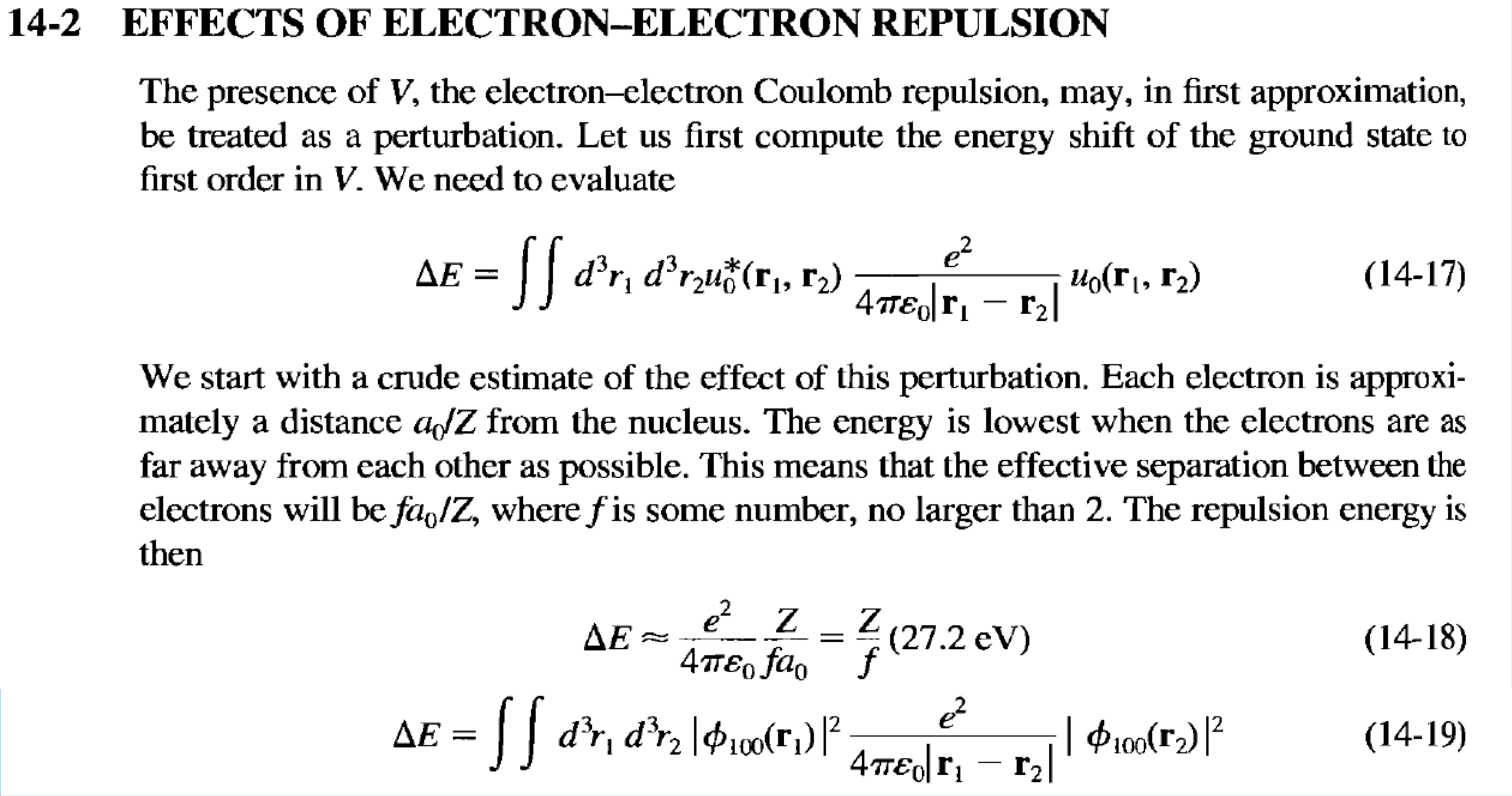
$$\frac{1}{\sqrt{2}}\left[\frac{2}{a}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{2\pi}{a}x_2\right)-\frac{2}{a}\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_1\right)\right]\cdot|\downarrow\downarrow\rangle$$

C. The second excited state has both electron in $n = 2$ ($n =$ 3,1 or 1,3 has higher energy). The energy is the sum: $\frac{8\pi^2\hbar^2}{2ma^2}$.

加入電子彼此的排斥力作為微擾的一階能量修正Ground State 1,1

$$E_{1,1}^{(1)} = \langle \phi_{1,1} | H_1 | \phi_{1,1} \rangle$$

H_1與自旋無關，$\langle \phi_{1,1} | H_1 | \phi_{1,1} \rangle$內的反對稱自旋狀態直接作內積，等於1。



14-2 EFFECTS OF ELECTRON–ELECTRON REPULSION

The presence of V, the electron–electron Coulomb repulsion, may, in first approximation, be treated as a perturbation. Let us first compute the energy shift of the ground state to first order in V. We need to evaluate

$$\Delta E = \int\int d^3r_1\, d^3r_2 u_0^*(\mathbf{r}_1, \mathbf{r}_2) \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} u_0(\mathbf{r}_1, \mathbf{r}_2) \tag{14-17}$$

We start with a crude estimate of the effect of this perturbation. Each electron is approximately a distance a_0/Z from the nucleus. The energy is lowest when the electrons are as far away from each other as possible. This means that the effective separation between the electrons will be fa_0/Z, where f is some number, no larger than 2. The repulsion energy is then

$$\Delta E \approx \frac{e^2}{4\pi\varepsilon_0} \frac{Z}{fa_0} = \frac{Z}{f}(27.2\text{ eV}) \tag{14-18}$$

$$\Delta E = \int\int d^3r_1\, d^3r_2\, |\phi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_{100}(\mathbf{r}_2)|^2 \tag{14-19}$$

$$\Delta E = \int\int d^3r_1\, d^3r_2\, |\phi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_{100}(\mathbf{r}_2)|^2 \tag{14-19}$$

The integral has a simple interpretation: Since $|\phi_{100}(\mathbf{r}_1)|^2$ is the probability density of finding electron 1 at $\mathbf{r}_1$ we may interpret $e|\phi_{100}(\mathbf{r}_1)|^2$ as the charge density for electron 1. Hence

$$U(\mathbf{r}_2) = -\int d^3r_1 \frac{e|\phi_{100}(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{14-20}$$

is the potential at $\mathbf{r}_2$ due to the charge distribution of electron 1, and

$$\Delta E = -\frac{1}{4\pi\varepsilon_0}\int d^3r_2 e|\phi_{100}(\mathbf{r}_2)|^2\, U(\mathbf{r}_2)$$

is therefore the electrostatic energy of interaction of electron 2 with that potential. The integral can be worked out. With

$$\phi_{100}(\mathbf{r}) = \frac{2}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \tag{14-21}$$

we have

$$\Delta E = \left(\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right)^2 \frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r_1^2\, dr_1 e^{-2Zr_1/a_0}\int_0^\infty r_2^2\, dr_2 e^{-2Zr_2/a_0}\int d\Omega_1\int d\Omega_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{14-22}$$

We shall use the fact that

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \frac{1}{(r_1^2+r_2^2-2r_1r_2\cos\theta)^{1/2}} \tag{14-23}$$

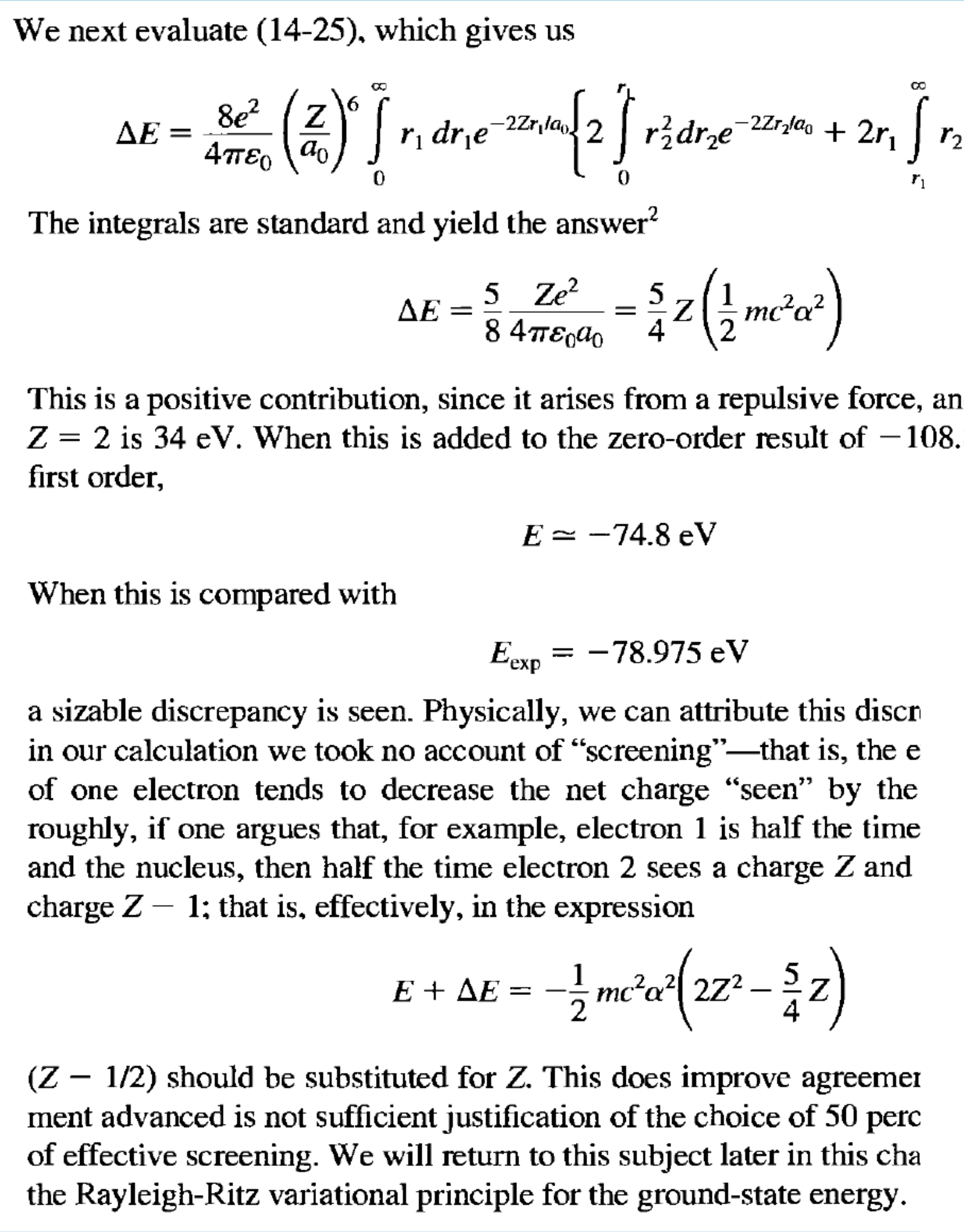
where θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. We may proceed in one of two ways.

(a) Most directly, we choose the direction of $\mathbf{r}_1$ as the z-axis for the $d\Omega_2$ integration, and get

$$\begin{aligned}\int d\Omega_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} &= \int_0^{2\pi} d\phi\int_{-1}^{1} d(\cos\theta)\,\frac{1}{(r_1^2+r_2^2-2r_1r_2\cos\theta)^{1/2}}\\ &= -2\pi\frac{1}{r_1r_2}\left[(r_1^2+r_2^2-2r_1r_2\cos\theta)^{1/2}\right]_{\cos\theta=-1}^{\cos\theta=+1} \qquad (14\text{-}24)\\ &= \frac{2\pi}{r_1r_2}(r_1+r_2-|r_1-r_2|)\end{aligned}$$

The integration over $d\Omega_1$ is trivial since nothing depends on that direction, and it gives 4π. This leaves us with

$$8\frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{a_0}\right)^6\int_0^\infty r_1\, dr_1 e^{-2Zr_1/a_0}\int_0^\infty r_2\, dr_2 e^{-2Zr_2/a_0}(r_1+r_2-|r_1-r_2|) \tag{14-25}$$



We next evaluate (14-25), which gives us

$$\Delta E = \frac{8e^2}{4\pi\varepsilon_0}\left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1\,dr_1 e^{-2Zr_1/a_0}\left\{2\int_0^{r_1} r_2^2 dr_2 e^{-2Zr_2/a_0} + 2r_1\int_{r_1}^\infty r_2\,dr_2 e^{-2Zr_2/a_0}\right\}$$

The integrals are standard and yield the answer[2]

$$\Delta E = \frac{5}{8}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = \frac{5}{4}Z\left(\frac{1}{2}mc^2\alpha^2\right) \tag{14-27}$$

This is a positive contribution, since it arises from a repulsive force, and its magnitude for $Z = 2$ is 34 eV. When this is added to the zero-order result of -108.8 eV we obtain, to first order,

$$E \simeq -74.8 \text{ eV}$$

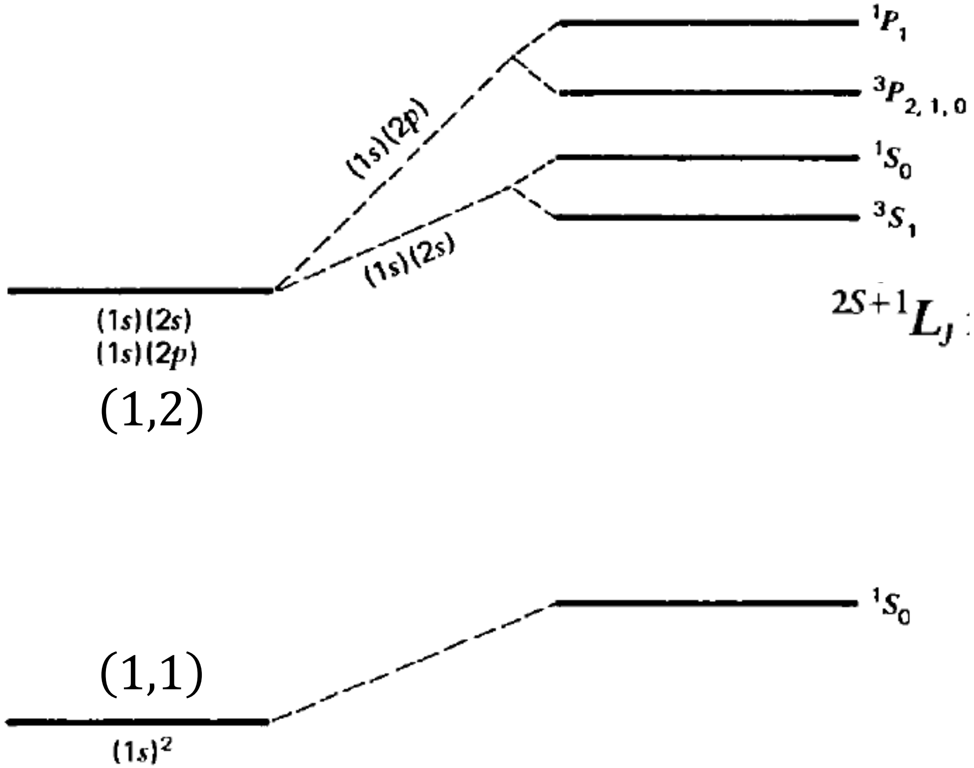
When this is compared with

$$E_{\text{exp}} = -78.975 \text{ eV}$$

a sizable discrepancy is seen. Physically, we can attribute this discr
in our calculation we took no account of "screening"—that is, the e
of one electron tends to decrease the net charge "seen" by the
roughly, if one argues that, for example, electron 1 is half the time
and the nucleus, then half the time electron 2 sees a charge Z and
charge $Z - 1$; that is, effectively, in the expression

$$E + \Delta E = -\frac{1}{2}mc^2\alpha^2\left(2Z^2 - \frac{5}{4}Z\right)$$

$(Z - 1/2)$ should be substituted for Z. This does improve agreeme
ment advanced is not sufficient justification of the choice of 50 perc
of effective screening. We will return to this subject later in this cha
the Rayleigh-Ritz variational principle for the ground-state energy.



一階能量修正Excited State 2,1 $E_{1,2}^{(1)} = \langle \phi_{1,2}^{s,t} | H_1 | \phi_{1,2}^{s,t} \rangle$

$-$ for triplet
$+$ for singlet

H_1與自旋無關，$\langle \phi_{1,2}^{s,t} | H_1 | \phi_{1,2}^{s,t} \rangle$內自旋狀態直接作內積，皆等於1，例如：$\langle \uparrow\uparrow | \uparrow\uparrow \rangle = 1$

因此只要積分空間波函數：

$$= \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 d^3\vec{r}_2 |\phi_{100}(\vec{r}_1)\phi_{210}(\vec{r}_2) \pm \phi_{100}(\vec{r}_2)\phi_{210}(\vec{r}_1)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 d^3\vec{r}_2 \cdot |\phi_{100}(\vec{r}_1)|^2 |\phi_{210}(\vec{r}_2)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

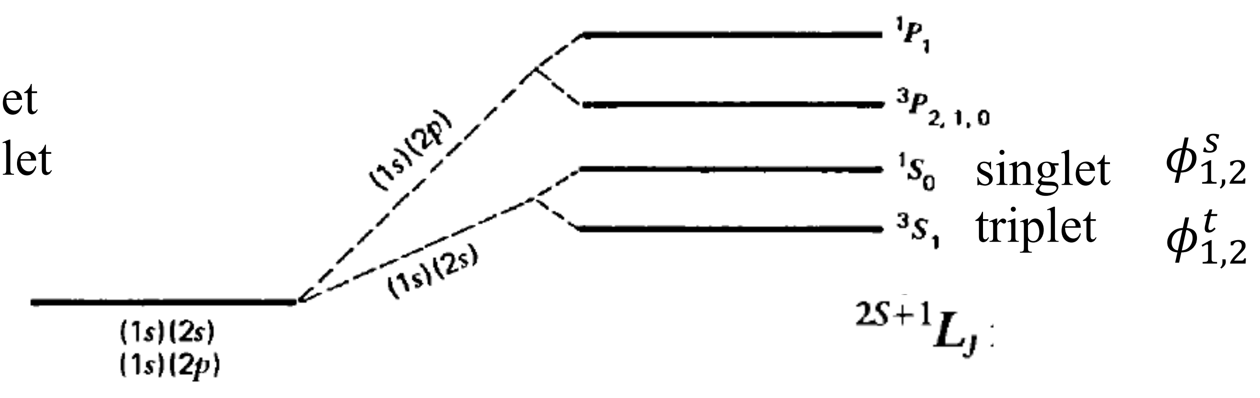
$$\pm \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 d^3\vec{r}_2 \cdot \phi_{100}^*(\vec{r}_1)\phi_{210}^*(\vec{r}_2) \cdot \phi_{100}(\vec{r}_2)\phi_{210}(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

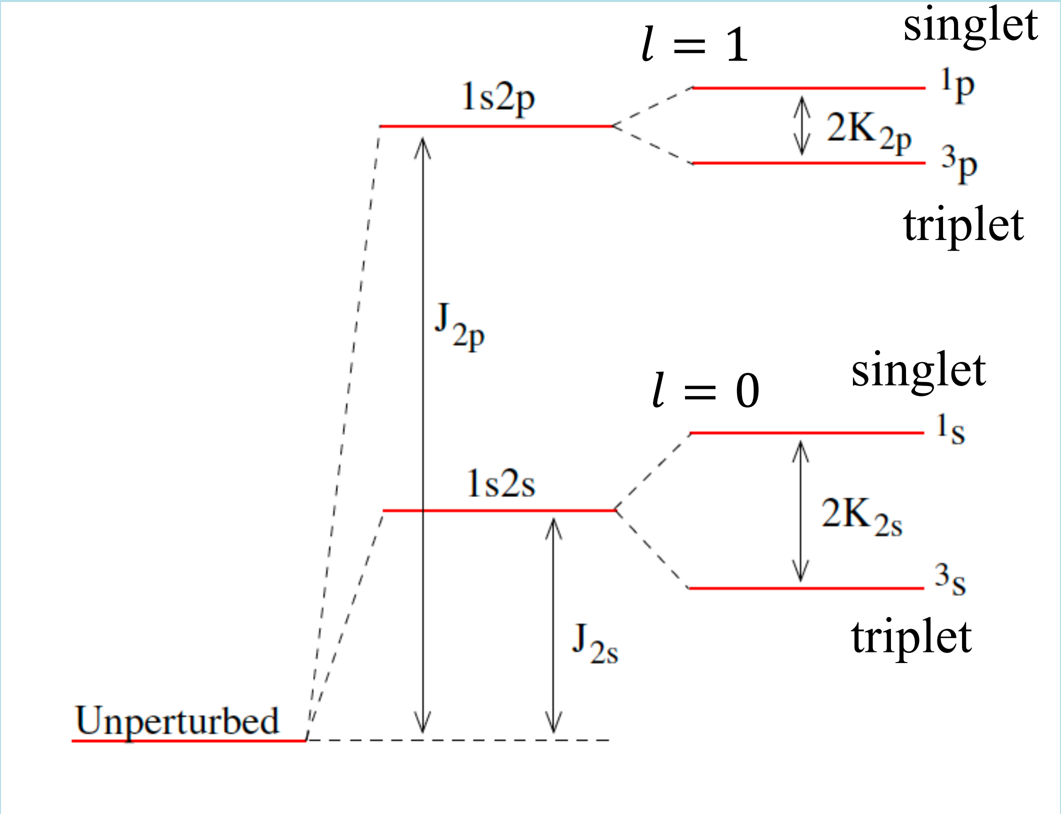
$E_{1,2}^{(1)} \equiv J_{12} \pm K_{12}$

$-$ for triplet
$+$ for singlet

$K_{12} > 0$

$\Delta E_{s=1\,T} < \Delta E_{s=0\,S}$



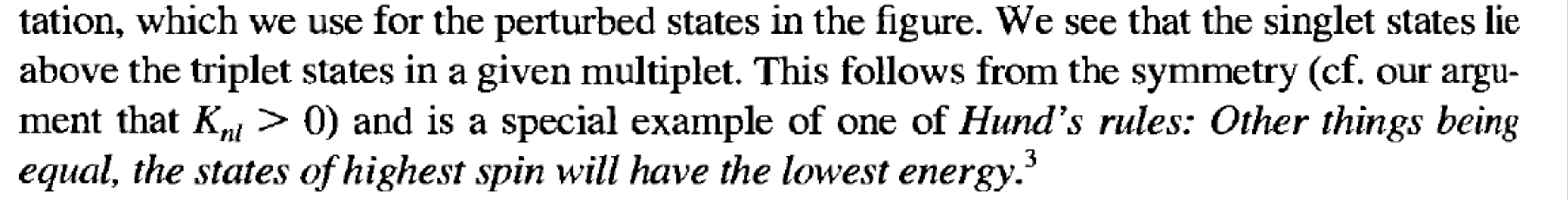


$$E^{(1)}_{1,2} \equiv J_{12} \pm K_{12}$$

$$\Delta E_{s=1\ T} < \Delta E_{s=0\ S}$$

這有一個簡單的原因：triplet的空間波函數是反對稱。

兩電子靠近機率較低，彼此排斥庫倫位能較小，因此triplet的能量較低。



tation, which we use for the perturbed states in the figure. We see that the singlet states lie above the triplet states in a given multiplet. This follows from the symmetry (cf. our argument that $K_{nl} > 0$) and is a special example of one of *Hund's rules: Other things being equal, the states of highest spin will have the lowest energy.*[3]

兩個電子似乎希望自旋同向，此時能量較低，

交換對稱性使得與自旋無關的能量，顯得是由自旋決定：稱為exchange force.

for the spatially symmetric singlet state. An interesting aspect of this result is that, although the perturbing potential (14-4) does not depend on the spins of the electrons, the symmetry of the wave function does make the potential act as if it were spin-dependent. We may write (14-30) in a form that exhibits this. Let the spins of the two electrons be $\mathbf{s}_1$ and $\mathbf{s}_2$. Then the total spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, and

$$\mathbf{S}^2 = \mathbf{s}_1^2 + \mathbf{s}_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \tag{14-32}$$

If we act with this on triplet and singlet states (14-16) and (14-13) that are also eigenstates of $\mathbf{s}_1^2$ and $\mathbf{s}_2^2$, we get

$$S(S+1)\hbar^2 = \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \tag{14-33}$$

that is,

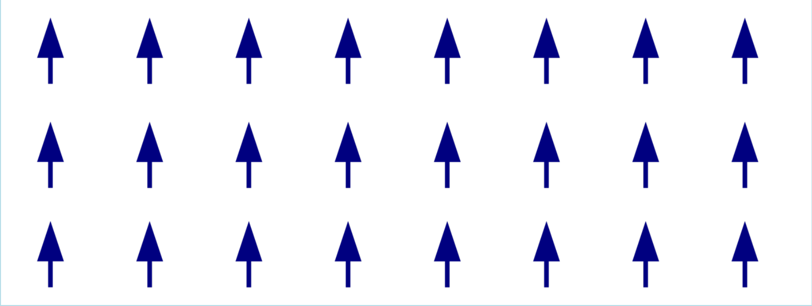
$$2\mathbf{s}_1 \cdot \mathbf{s}_2/\hbar^2 = S(S+1) - \frac{3}{2} = \begin{cases} \frac{1}{2} & \text{triplet} \\ -\frac{3}{2} & \text{singlet} \end{cases} \tag{14-34}$$

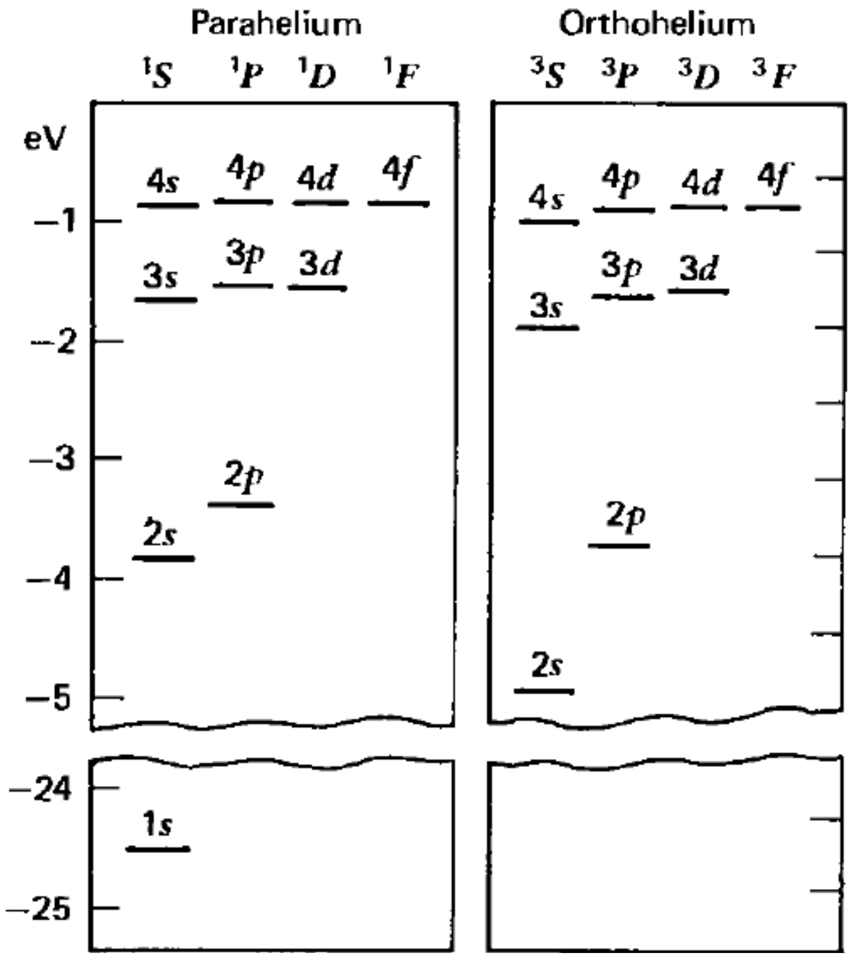
We may thus write, in terms of the $\boldsymbol{\sigma}$'s related to the spins by $\mathbf{s}_i = (1/2)\hbar\boldsymbol{\sigma}_i$,

$$\Delta E_{n,l} = J_{n,l} - \frac{1}{2}(1 + \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)K_{nl} \tag{14-35}$$

This result has implications beyond the explanation of some of the details of the spectrum of helium. As was first pointed out by Heisenberg, the *exchange forces* provide a mechanism by means of which spin-dependent effects are of magnitude comparable to those that are independent of spin. Usually, as illustrated in spin-orbit coupling or hyperfine coupling (see Ch. 12) spin-dependent forces have a magnetic origin, and are thus reduced by factors of $O(v^2/c^2) = O(\alpha^2)$ compared to the electrical forces. Such weak forces could not be strong enough to keep the electron spins aligned in a ferromagnet, except at extremely low temperatures. In fact, exchange forces are responsible for the phenomenon of ferromagnetism.

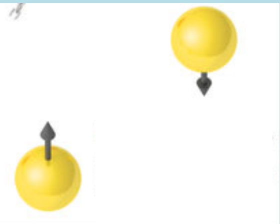
Ferromagnetism 鐵磁性





If we excite helium from the ground state by shining ultraviolet light on it, we find that the *selection rule* $\Delta L = 1$, which we will derive later, implies an excitation to the P states. Furthermore, there is a selection rule $\Delta S = 0$; that is, only transitions singlet → singlet and triplet → triplet dominate.[4] Hence the state most strongly excited from the ground state is the $^1P_1$ state. The other levels may also become occupied through other mechanisms—for example, collisional excitation. Once occupied, the radiative transitions to the ground state are very improbable. The ^3P state, which may be populated when atoms in the $^1P_1$ state undergo collisions with other atoms in the gas, can only decay to the $^3S_1$ state, and that state is *metastable*, since it cannot decay to the ground state easily. The fact that there are no transitions, to good approximation, between triplet states and singlet states led, at one time, to the belief that there existed two kinds of helium, orthohelium (triplet) and parahelium (singlet).

兩個電子的自旋狀態是一個四維空間。



很明顯可以以個別電子的S_{1z}, S_{2z}的本徵態為基底：$|\uparrow\uparrow\rangle$、$|\downarrow\uparrow\rangle$、$|\uparrow\downarrow\rangle$、$|\downarrow\downarrow\rangle$。

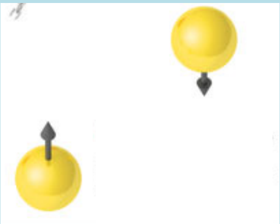
$$\left|S_{z1}=\frac{\hbar}{2}, S_{z2}=\frac{\hbar}{2}\right\rangle \equiv \left|\frac{\hbar}{2}, \frac{\hbar}{2}\right\rangle \equiv |\uparrow\uparrow\rangle$$

$$\left|-\frac{\hbar}{2}, \frac{\hbar}{2}\right\rangle \equiv |\downarrow\uparrow\rangle$$

$$\left|\frac{\hbar}{2}, -\frac{\hbar}{2}\right\rangle \equiv |\uparrow\downarrow\rangle$$

$$\left|-\frac{\hbar}{2}, -\frac{\hbar}{2}\right\rangle \equiv |\downarrow\downarrow\rangle$$

我們也可以總自旋S^2, S_z的本徵態做基底



自旋是一個向量，因此可以加總： $\vec{S} = \vec{S}_1 + \vec{S}_2$

總自旋角動量，依舊滿足角動量應該滿足的對易關係，

$$[S_x, S_y] = [S_{1x} + S_{2x}, S_{1y} + S_{2y}] = [S_{1x}, S_{1y}] + [S_{2x}, S_{2y}] = i\hbar S_{1z} + i\hbar S_{2z} = i\hbar S_z$$

$$[S_x, S_y] = i\hbar S_z$$

因此角動量的性質$\vec{S}$都滿足，例如： $[S^2, S_z] = 0$

S^2及S_z可以有共同的本徵態$|S, m_s\rangle$

之前以對易關係推導出來的本徵態、本徵值結果都成立：

$$|s = 0, m_s = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$|10\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

$$|1,1\rangle = |\uparrow\uparrow\rangle$$

$$|1,-1\rangle = |\downarrow\downarrow\rangle$$

以上這些對稱與反對稱的自旋狀態是總自旋S^2, S_z的本徵態。

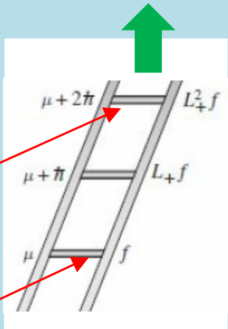
推導：

$|\uparrow\uparrow\rangle$ $\vec{S}=\vec{S}_1+\vec{S}_2$ $S_z=S_{1z}+S_{2z}$ $m_s=m_{s1}+m_{s2}=1$

注意在空間中沒有m_s更大的狀態了，

這表示總Raising Operator S_+作用在$|\uparrow\uparrow\rangle$，無法再升，只能等於零！

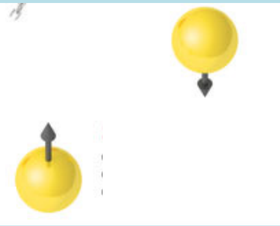
$$S_+|\uparrow\uparrow\rangle=0$$



這洽是$|s=1,m_s=1\rangle$特有的性質。

因此 $|s=1,m_s=1\rangle=|1,1\rangle=|\uparrow\uparrow\rangle$

同理：$|1,-1\rangle=|\downarrow\downarrow\rangle$



$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ 此反對稱的疊加態是z方向總自旋為零的態：$m_s = 0$。

$\vec{S} = \vec{S}_1 + \vec{S}_2$ $S_z = S_{1z} + S_{2z}$ $m_s = m_{s1} + m_{s2} = 0$

而且它是總自旋為零的狀態！計算此態的總自旋角動量：

$$S^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) =$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 = (S_x - iS_y)(S_x + iS_y) - i[S_x, S_y] + S_z^2 = S_-S_+ + S_z^2 - \hbar S_z$$

$$= (S_+S_- + S_z^2 - \hbar S_z)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$= (S_{1+} + S_{2+})(S_{1-} + S_{2-})(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

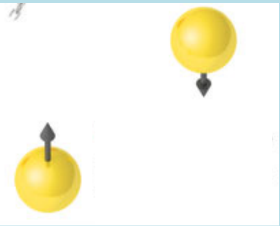
$$= -(S_{1+} + S_{2+})S_{2-}|\downarrow\uparrow\rangle + (S_{1+} + S_{2+})S_{1-}|\uparrow\downarrow\rangle$$

兩個項數學上相等，只要把第二項的1標為2，2標為1。因此抵消。 $= 0$

此反對稱疊加態$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$是$s = 0$。

此特定疊加是$s = 0$。這個空間只有一個態。稱為Singlet。

$$|s=0,m_s=0\rangle=\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$$



與它正交的是對稱化的態：

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)$$

這也是唯一剩下的態，它只能是$s=1$，$m_s=0$ 。

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)=|10\rangle$$

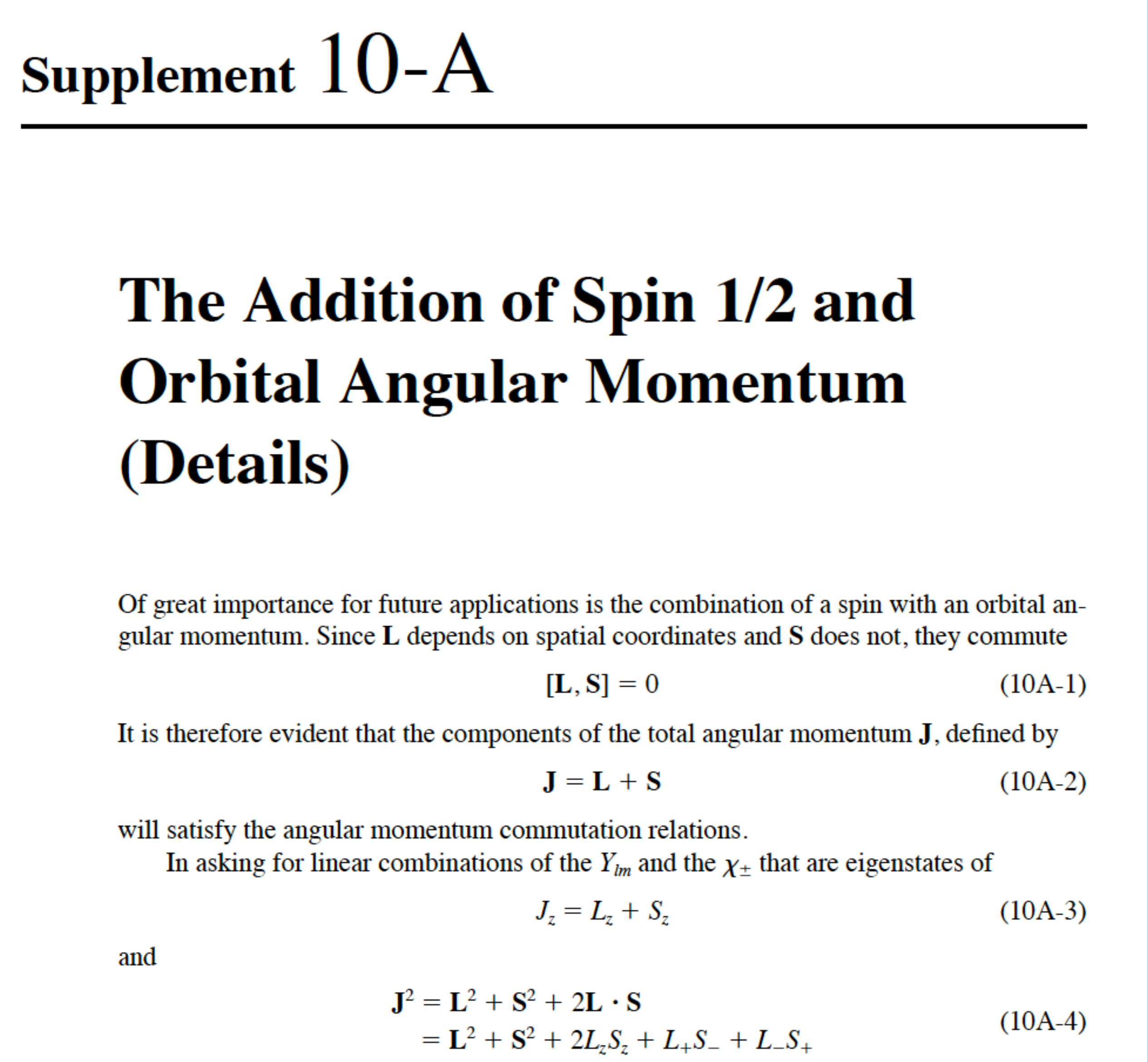
剛剛另外還有兩個很明顯的對稱自旋態：

$$|s=1,m_s=1\rangle=|1,1\rangle=|\uparrow\uparrow\rangle$$

$$|1,-1\rangle=|\downarrow\downarrow\rangle$$

對稱態共有三個，剛好是$s=1$的本徵態數目！ 稱為Triplet。

兩個雙自旋態組合的對稱性與總角動量有關。



Supplement 10-A

The Addition of Spin 1/2 and Orbital Angular Momentum (Details)

Of great importance for future applications is the combination of a spin with an orbital angular momentum. Since $\mathbf{L}$ depends on spatial coordinates and $\mathbf{S}$ does not, they commute

$$[\mathbf{L}, \mathbf{S}] = 0 \tag{10A-1}$$

It is therefore evident that the components of the total angular momentum $\mathbf{J}$, defined by

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{10A-2}$$

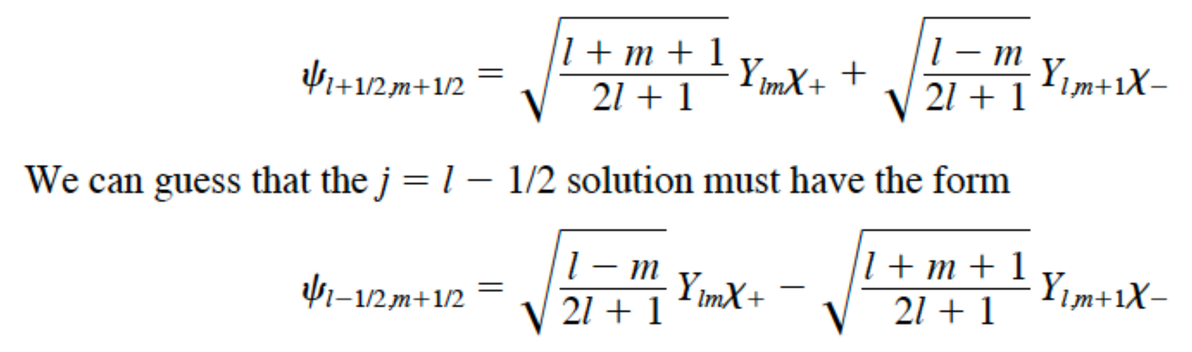
will satisfy the angular momentum commutation relations.

In asking for linear combinations of the Y_{lm} and the $\chi_{\pm}$ that are eigenstates of

$$J_z = L_z + S_z \tag{10A-3}$$

and

$$\begin{aligned} \mathbf{J}^2 &= \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \\ &= \mathbf{L}^2 + \mathbf{S}^2 + 2L_zS_z + L_+S_- + L_-S_+ \end{aligned} \tag{10A-4}$$



$$\psi_{l+1/2,m+1/2} = \sqrt{\frac{l+m+1}{2l+1}}\, Y_{lm}\chi_+ + \sqrt{\frac{l-m}{2l+1}}\, Y_{l,m+1}\chi_-$$

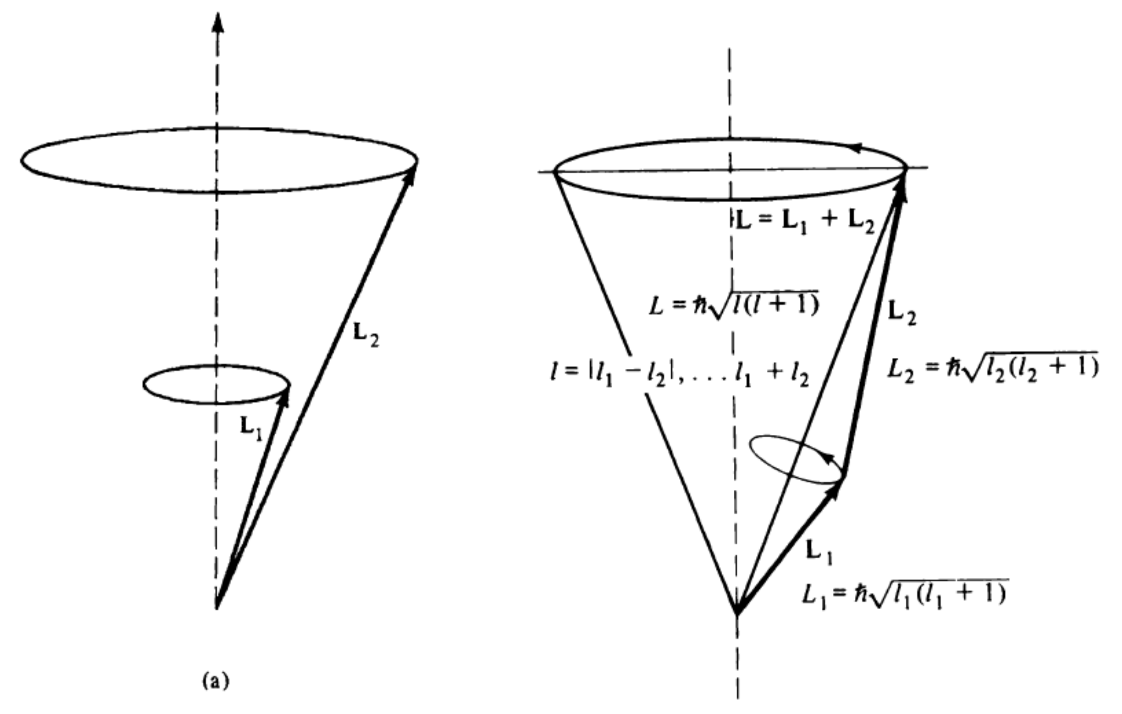
We can guess that the $j = l - 1/2$ solution must have the form

$$\psi_{l-1/2,m+1/2} = \sqrt{\frac{l-m}{2l+1}}\, Y_{lm}\chi_+ - \sqrt{\frac{l+m+1}{2l+1}}\, Y_{l,m+1}\chi_-$$

任意兩個角動量相加的通則：

$$j = l_1 + l_2,\ l_1 + l_2 - 1,\ l_1 + l_2 - 2, \ldots, |l_1 - l_2|$$

$$m_j = j, j-1, j-2, \ldots, -j$$

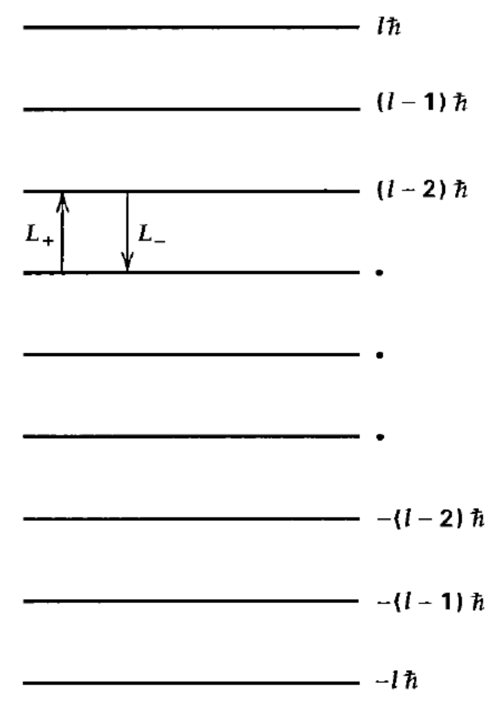


$$\begin{aligned}
\sum_{j=j_1-j_2}^{j_1+j_2}(2j+1) &= 2\left(\sum_{j=0}^{j_1+j_2} j - \sum_{j=0}^{j_1-j_2-1} j\right) + (j_1+j_2-(j_1-j_2)+1) \\
&= (j_1+j_2)(j_1+j_2+1) - (j_1-j_2-1)(j_1-j_2) + 2j_2 + 1 \qquad (20.7.24) \\
&= (j_1+j_2)^2 - (j_1-j_2)^2 + 2j_1 + 2j_2 + 1 \\
&= 2j_1(2j_2+1) + 2j_2 + 1 = (2j_1+1)(2j_2+1).
\end{aligned}$$

補充推導：

S^2, S_z的本徵態$|s, m_s\rangle$是$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$的線性組合：

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \qquad S_z = S_{1z} + S_{2z}$$



總自旋S_z最大的態是$|\uparrow\uparrow\rangle$ $m_s = \frac{1}{2} + \frac{1}{2} = 1$

Raising operators S_+作用於$|\uparrow\uparrow\rangle$應該無法再增加S_z。

$$S_+|\uparrow\uparrow\rangle = 0$$

這樣無法再以S_+昇S_z的態，若它的$m_s = 1$，則$s = 1$。

s也可以直接算：

$$S_-S_+ = (S_x - iS_y)(S_x + iS_y) = S_x^2 + S_y^2 + i[S_x, S_y] = S^2 - S_z^2 - \hbar S_z$$

左手邊作用於$|\uparrow\uparrow\rangle$為零，因此：

$$S^2|\uparrow\uparrow\rangle = (S_z^2 + \hbar S_z)|\uparrow\uparrow\rangle = 1(1+1)\hbar|\uparrow\uparrow\rangle \qquad s = 1$$

$$|s = 1, m_s = 1\rangle = |1,1\rangle = |\uparrow\uparrow\rangle$$

$$|s = 1, m_s = -1\rangle = |1,-1\rangle = |\downarrow\downarrow\rangle$$

接著可以用Lowering, Raising operators $S_\pm$，來從$|1,1\rangle$得到$|1,0\rangle$。

$$|1,0\rangle = S_-|1,1\rangle = (S_{1-} + S_{2-})|\uparrow\uparrow\rangle$$

$$= S_{1-}|\uparrow\uparrow\rangle + S_{2-}|\uparrow\uparrow\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

而與$|1,0\rangle$正交的狀態即是$|0,0\rangle$：

$$|0,0\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)$$

可以驗證：

$$S_-|0,0\rangle = \frac{1}{\sqrt{2}}S_-(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) = 0$$

$$S_+|0,0\rangle = \frac{1}{\sqrt{2}}S_+(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) = 0$$

唯一無法昇也無法降S_z的態即是$|0,0\rangle$。

3.1　全同粒子系的量子态的描述

对于全同粒子组成的体系，由于粒子的全同性（不可分辨性），任何两个粒子的置换并不导致一个新的量子态. 通过深入分析可以得出（见卷Ⅰ，5.5 节），这种对称性对全同粒子系的量子态给予了很强的限制，即对于全同粒子系，在自然界中能实现的量子态，只可能是具有一定置换对称性的量子态. 它们或者是对于任何两个粒子交换不变的对称态，或者是对任何两个粒子交换改变正负号的反对称态. 对于前者，粒子系的统计性质遵守 Bose 统计，故称为 Bose 子；对于后者，则遵守 Fermi 统计，故称为 Fermi 子. 所有实验都表明，统计性与粒子的自旋值密切相关，即 Bose 子的自旋（单位 $\hbar$）为整数（包括 0），而 Fermi 子的自旋为半奇数.

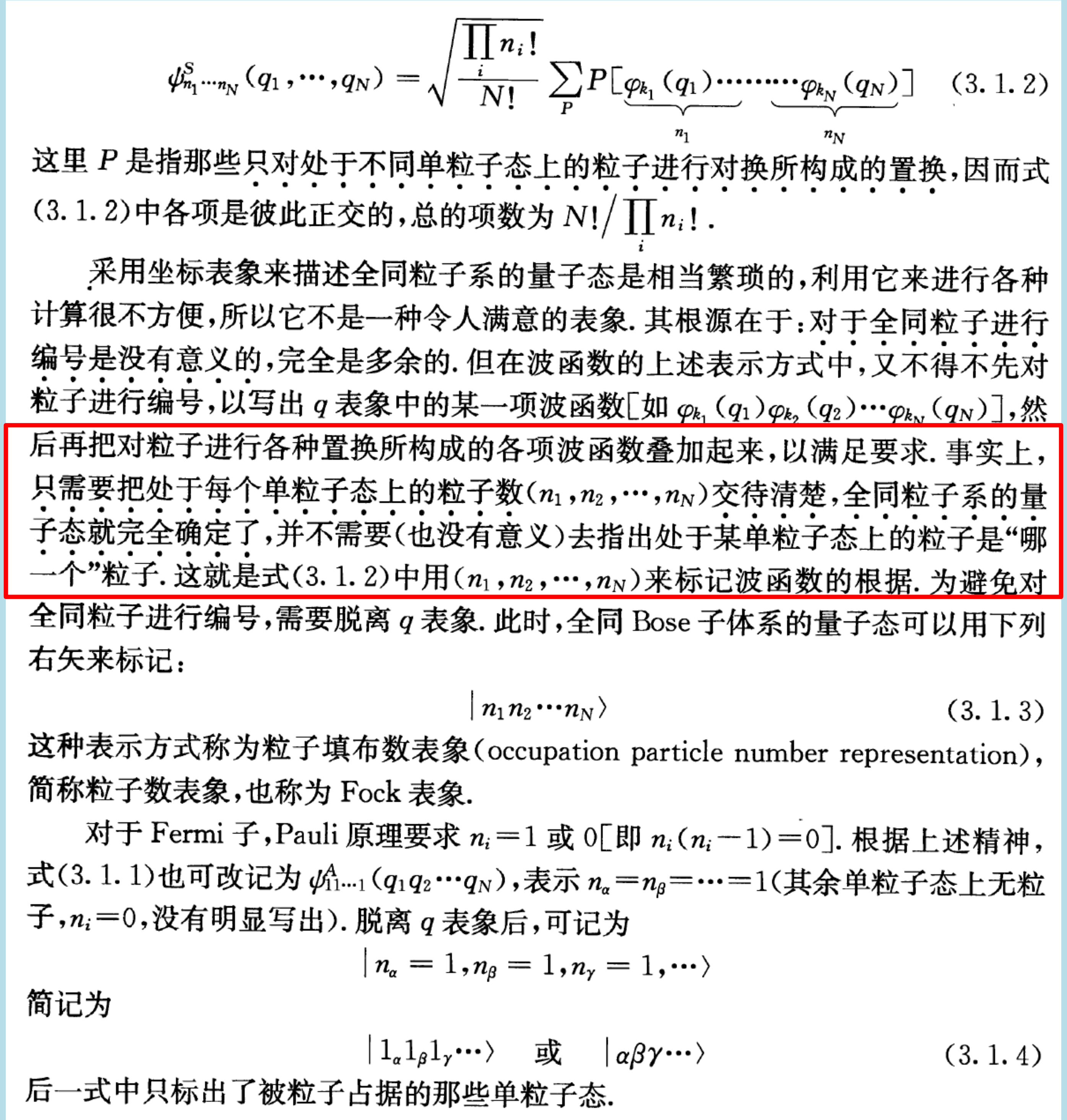
3.1.1　粒子数表象

在卷Ⅰ，5.5 节中，全同粒子系的量子态的描述采用了坐标表象，以下简称 q 表象（q 表示单粒子的全部坐标，如粒子有自旋，除空间坐标外，还应包含自旋变量）. 在 q 表象中，N 个全同 Fermi 子的归一化的量子态表示成

$$
\begin{aligned}
\psi^{A}_{\alpha\beta\gamma\cdots}(q_1,\cdots,q_N) &= \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_\alpha(q_1)\cdots\varphi_\alpha(q_N) \\ \varphi_\beta(q_1)\cdots\varphi_\beta(q_N) \\ \varphi_\gamma(q_1)\cdots\varphi_\gamma(q_N) \\ \vdots \qquad\qquad \vdots \end{vmatrix} \\
&= \frac{1}{\sqrt{N!}}\sum_P \delta_P P[\varphi_\alpha(q_1)\varphi_\beta(q_2)\varphi_\gamma(q_3)\cdots]
\end{aligned}
\tag{3.1.1}
$$

上式表示在每个单粒子态（假设已归一化）$\varphi_\alpha, \varphi_\beta, \varphi_\gamma, \cdots$ 上分别有一个粒子，P 表示粒子之间的某种置换，δ_P（$=\pm1$）是置换 P 的奇偶性（参阅附录 B.2.2）. 由式（3.1.1）可以看出，处于每个单粒子态上的全同 Fermi 子的数目不能超过 1（Pauli 原理）.

对于全同 Bose 子体系，情况与此不同. 它们的波函数对于任何两个粒子的交换要求是对称的. 因此，处于每一个单粒子态上的 Bose 子的数目没有什么限制. 设在单粒子态 $\varphi_{k_1}, \varphi_{k_2}, \cdots, \varphi_{k_N}$ 上分别有 $n_1, n_2, \cdots, {}_N$ 个粒子（$\sum\limits_i n_i = N$，n_i 中有的可以为 0，有的可以大于 1），则归一化的交换对称波函数可表示为



$$\psi^S_{n_1\cdots n_N}(q_1,\cdots,q_N)=\sqrt{\frac{\prod\limits_i n_i!}{N!}}\sum_P P[\underbrace{\varphi_{k_1}(q_1)\cdots}_{n_1}\cdots\underbrace{\varphi_{k_N}(q_N)}_{n_N}] \tag{3.1.2}$$

这里 P 是指那些只对处于不同单粒子态上的粒子进行对换所构成的置换，因而式(3.1.2)中各项是彼此正交的，总的项数为 $N!\Big/\prod\limits_i n_i!$.

采用坐标表象来描述全同粒子系的量子态是相当繁琐的，利用它来进行各种计算很不方便，所以它不是一种令人满意的表象. 其根源在于：对于全同粒子进行编号是没有意义的，完全是多余的. 但在波函数的上述表示方式中，又不得不先对粒子进行编号，以写出 q 表象中的某一项波函数[如 $\varphi_{k_1}(q_1)\varphi_{k_2}(q_2)\cdots\varphi_{k_N}(q_N)$]，然后再把对粒子进行各种置换所构成的各项波函数叠加起来，以满足要求. 事实上，只需要把处于每个单粒子态上的粒子数$(n_1,n_2,\cdots,n_N)$交待清楚，全同粒子系的量子态就完全确定了，并不需要(也没有意义)去指出处于某单粒子态上的粒子是“哪一个”粒子. 这就是式(3.1.2)中用$(n_1,n_2,\cdots,n_N)$来标记波函数的根据. 为避免对全同粒子进行编号，需要脱离 q 表象. 此时，全同 Bose 子体系的量子态可以用下列右矢来标记：

$$|n_1n_2\cdots n_N\rangle \tag{3.1.3}$$

这种表示方式称为粒子填布数表象(occupation particle number representation)，简称粒子数表象，也称为 Fock 表象.

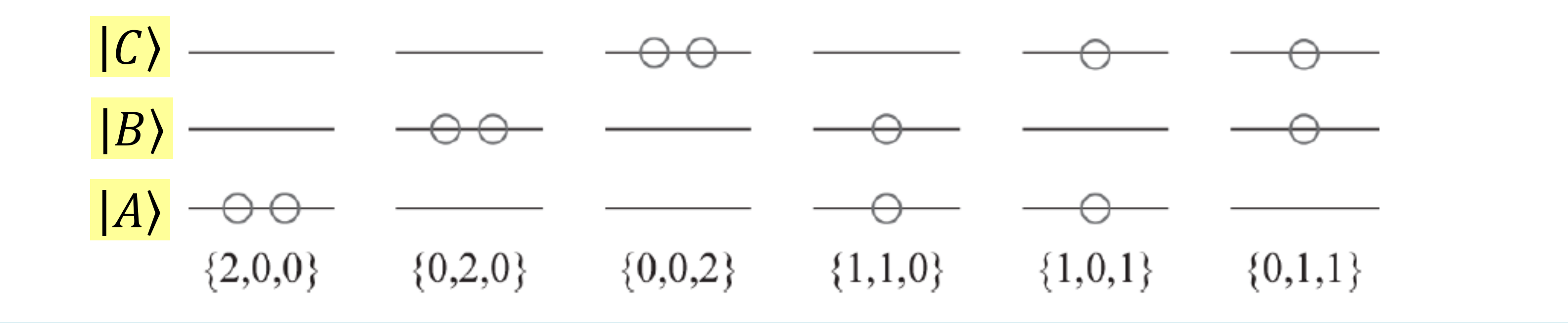
对于 Fermi 子，Pauli 原理要求 $n_i=1$ 或 0[即 $n_i(n_i-1)=0$]. 根据上述精神，式(3.1.1)也可改记为 $\psi^A_{11\cdots1}(q_1q_2\cdots q_N)$，表示 $n_\alpha=n_\beta=\cdots=1$(其余单粒子态上无粒子，$n_i=0$，没有明显写出). 脱离 q 表象后，可记为

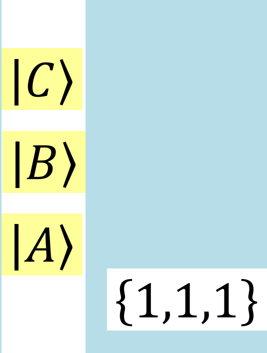
$$|n_\alpha=1,n_\beta=1,n_\gamma=1,\cdots\rangle$$

简记为

$$|1_\alpha1_\beta1_\gamma\cdots\rangle \quad 或 \quad |\alpha\beta\gamma\cdots\rangle \tag{3.1.4}$$

后一式中只标出了被粒子占据的那些单粒子态.





狀態不要編號，符號就會很簡單。

只要標明每一個可能狀態的粒子數即可

Occupation Number Representation 狀態佔據數表象

記住：若是費米子，佔據數不能超過1。

例如{1,1,1}這個態，用波函數寫，就會變成：

$$\psi_A(x_1)\psi_B(x_2)\psi_C(x_3) + \psi_A(x_2)\psi_B(x_1)\psi_C(x_3) + \psi_A(x_1)\psi_B(x_3)\psi_C(x_2) +$$

$$\psi_A(x_2)\psi_B(x_3)\psi_C(x_1) + \psi_A(x_3)\psi_B(x_1)\psi_C(x_2) + \psi_A(x_3)\psi_B(x_2)\psi_C(x_1)$$

這樣的表象，粒子數目還可以自然的有變化！