

一、量子力学绪论

德布罗意关系

E: 粒子能量 p; 粒子动量 ν ; 粒子波频率 λ : 粒子波波长 ω : 粒子波角频率 k : 粒子波矢
波动性内部转换: $k = 2\pi/\lambda, w = 2\pi\nu, \hbar = h/2\pi, \lambda = h/p$

波矢与动量关系 $k = p/\hbar$,

角频率与能量关系 $\omega = E/\hbar$

色散关系 非相对论粒子的色散关系: $E = p^2/2m, \omega = \hbar k^2/2m$

极端相对论粒子的色散关系: $E = cp, p = E/c = h\nu/c = h/\lambda$

康普顿效应证明光的粒子性: 散射光频率与散射角度有关

普朗克常数 $h = 6.626 \times 10^{-34} J \cdot s$

$\hbar = h/2\pi = 1.055 \times 10^{-34} J \cdot s$

电子电荷 $e = -1.602 \times 10^{-19} C$

电子静止质量 $m_e = 9.109 \times 10^{-31} kg$

质子静止质量 $m_p = 1.672 \times 10^{-27} kg$

二、波函数与薛定谔方程

波函数

平面波不能有限归一化, 此时 $|\psi(r, t)|^2$ 表示相对几率密度; $|\psi(r, t)|^2 = 1$ 时, 表示波函数在全空间均匀分布

一维平面波波函数为 $\psi(x, t) = A e^{\frac{i}{\hbar}(px-Et)}$

态叠加原理

态叠加: $\psi_1 \psi_2$ 为体系的可能状态, 则 $\psi = c_1 \psi_1 + c_2 \psi_2$ 也是体系的可能状态, c 为复常数对一个量子体系, 可用完备的状态集合 $\{\psi_n\}$ 来表示任意的状态 ψ , 即 $\psi = \sum_n c_n \psi_n$

对于动量平面波, 动量几率幅 $c(p, t)$ 与波函数 $\psi(r, t)$ 为傅里叶变换关系 $c(p, t) = \int \psi(r, t) e^{-\frac{i}{\hbar} pr} dr$

动量本征函数为 $\psi_p(r) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar} pr}$

动量几率幅 $c(p, t)$ 也可以完全描写单个粒子的波动性, $|c(p, t)|^2$ 表示动量几率密度

$\delta(x-x') = \frac{1}{2\pi} \int e^{ik(x-x')/\hbar} dk$ 称为坐标本征态

$\psi(x) = \int_{-\infty}^{\infty} \delta(x-x') \psi(x') dx' =$

$\int \psi(x') \frac{1}{2\pi} \int e^{ik(x-x')/\hbar} dk dx'$

$= \int (\int \psi(x') \frac{1}{2\pi} e^{ikx'} dx') e^{ikx} dk = \int C(k) e^{ikx} dk$

$c(p) = C(k) \frac{1}{\sqrt{2\pi\hbar}}$

薛定谔方程

单粒子系统薛定谔方程:

$i\hbar \frac{\partial}{\partial t} \psi = \hat{E}\psi = H\psi = -\frac{\hbar^2}{2\mu} \nabla^2 \psi + U(\vec{r})\psi$

几率流密度 几率密度: $w(\vec{r}, t) = |\psi(\vec{r}, t)|^2 = \psi^*(\vec{r}, t)\psi(\vec{r}, t)$

考虑几率密度的时变特性 $\frac{\partial}{\partial t} w(\vec{r}, t)$

$\frac{\partial}{\partial t} w(\vec{r}, t) = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi$ 其中 $\frac{\partial \psi}{\partial t}$ 和 $\frac{\partial \psi^*}{\partial t}$ 两项均可从薛定谔方程(或其共轭式)中得到

代入后结果:

$\frac{\partial}{\partial t} w(\vec{r}, t) = \frac{i\hbar}{2\mu} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) = \frac{i\hbar}{2\mu} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*)$

定义几率流密度 $\vec{J} = \frac{i\hbar}{2\mu} (\psi \nabla \psi^* - \psi^* \nabla \psi)$ 有几率流

守恒式 $\frac{\partial w}{\partial t} + \nabla \cdot \vec{J} = 0$

定态薛定谔方程的分离变量解

定态薛定谔方程: $H\psi = E\psi$ 也即能量本征方程, 其中 H 为哈密顿算符, E 为本征值

对应的 $\psi(r)$ 为能量本征函数(态), 有时也将 $\psi_n(r, t) = \psi_n(r) \exp(-\frac{i}{\hbar} Et)$ 称为能量本征函数含时的薛定谔方程: 对应定态的本征函数为完备的状态集 $\{\psi_n\}$

故有一般解为 $\psi(r, t) = \sum_n c_n \psi_n(r) \exp(-\frac{i}{\hbar} Et)$

对于自由粒子波函数, 动量本征态一定是能量本征态, 而能量本征态不一定是动量本征态(有不同的方向)

三、一维运动问题

一维无限深势阱

一维运动方程: $\frac{d^2}{dx^2} \psi + \frac{2\mu(E-U(x))}{\hbar^2} \psi = 0$

一维无限深势阱的势能方程表达为:

$U(x) = \begin{cases} 0, |x| < a \\ +\infty, |x| > a \end{cases}$ 帽子外波函数为 0

阱内: 令 $k = \frac{\sqrt{2\mu E}}{\hbar}$ 得 $k = \frac{n\pi}{2a}, n = 1, 2, 3, \dots$

因此有体系分立能级: $E_n = \frac{\hbar^2 \pi^2}{8\mu a^2} n^2$ 由归一化给出

$B = \frac{1}{\sqrt{a}}$ 因此完整定态解为

$\psi_n(x) = \begin{cases} \frac{1}{\sqrt{a}} \sin[\frac{n\pi}{2a}(x+a)], |x| < a \\ 0, |x| \geq a \end{cases}$

根据特解(定态解), 可以给出通解 $\psi(x, t) = \sum_n c_n \psi_n(x) \exp(-\frac{i}{\hbar} Et)$

一维无限深势阱的定态解为两个传播方向相反的平面波叠加形成的驻波

一维运动问题分析

基态: 体系中能量最低的状态, 基态能量称为零点能定态: 即能量本征态, 定态下一切力学量的本征值和相对分布不随时间改变

束缚态: 无穷远处波函数为 0 的状态(即对应粒子被束缚在势阱中) vs 散射态

能级简并: 对于相同的能量本征值 E_k , 其对应的本征函数 ψ_k 不唯一

共轭定理: 定态薛定谔方程的解满足共轭对称性, 因此若能级非简并必为实解

推论: 对于确定的能量本征值, 必有一组实解可做其全部定态解的基本

反射定理: 势能函数关于原点对称时, 其对应定态解也满足空间对称性

推论: 对于确定的能量本征值, 若该能级非简并则必有确定宇称

宇称: 空间反射变换算符的本征值

非简并定理: 一维束缚态必为非简并态, 能量分立, 且势能空间对称时必有确定宇称

证明: 假设简并, 对于同一个 E , 方程有两个线性

独立的解, 而由 $\psi\psi' - \psi'\psi = c()$

对于束缚态无穷远处为 0, $c=0, \ln(\psi) = \ln(\psi') + C$, 两个解线性相关, 矛盾

一维有限深势阱

$$\psi(x) = \begin{cases} Ce^{\beta x}, & (x < -a/2) \\ A \cos kx + B \sin kx, & (-a/2 < x < a/2) \\ De^{-\beta x}, & (a/2 < x) \end{cases}$$

其中 $\beta = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}, k = \sqrt{\frac{2mE}{\hbar^2}}$

解得 $E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2$

$E_n = \frac{2\hbar^2}{ma^2} \xi_n^2, 0 < \xi_1 < \frac{\pi}{2} < \xi_2 < \pi < \dots$

偶宇称态 ($B=0, C=D$) 奇宇称态 ($A=0, C=-D$)

基态为偶宇称态, 激发态奇偶相间, 对应能级低于无限深势阱

束缚态的能级总数为 $N = 1 + [\frac{a}{\hbar\pi} \sqrt{2mV_0}]$

三维无限深势阱 按照直角坐标系分离变量 $\psi(r) = X(x)Y(y)Z(z)$

求解得到: $E_{n,m,l} = \frac{\hbar^2 \pi^2}{2m} (n^2/a^2 + m^2/b^2 + l^2/c^2)$

对应的波函数为:

$$\psi_{n,m,l}(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi y}{b}\right) \sin\left(\frac{l\pi z}{c}\right)$$

二维极限: c 趋近于 0, $l=1$ 和 $l=2$ 能级差距极大, 粒子冻结在 $l=1$ 能态, 一维极限类似

平行平面极板

粒子在 x, y 方向上自由, 在 z 方向上受限, 波函数为 $\psi(x, y, z) = C \exp(i(k_x x + k_y y)) \sin(k_z z), k_z = \frac{n\pi}{a} k_x$ 和 k_y 任意实数(连续)

能量分立的原理是束缚态条件(无穷远处波函数为 0)只在分立值成立

一维线性谐振子

势能方程为 $U(x) = \frac{1}{2} m \omega^2 x^2$

能级为 $E_n = (n + \frac{1}{2})\hbar\omega$

归一化波函数为

$$\psi_n(x) = N_n H_N(n\alpha) \exp(-\alpha^2 x^2/2)$$

其中 $\alpha = \sqrt{\frac{m\omega}{\hbar}}, N_n = \sqrt{\frac{\alpha}{\sqrt{\pi^2 n!}}}$

常用谐振子状态:

$n=0$ (基态): $E_0 = \frac{1}{2} \hbar\omega, \psi_0(x) = (\frac{m}{\hbar\omega})^{\frac{1}{2}} e^{-\frac{m\omega x^2}{\hbar^2}}$ 偶宇称, 基态能 $E_0 = \frac{1}{2} \hbar\omega$

$n=1$ (第1激发态): $E_1 = \frac{3}{2} \hbar\omega, \psi_1(x) = (\frac{m}{\hbar\omega})^{\frac{1}{2}} \alpha x e^{-\frac{m\omega x^2}{\hbar^2}}$ 奇宇称

$n=2$ (第2激发态): $E_2 = \frac{5}{2} \hbar\omega, \psi_2(x) = (\frac{m}{\hbar\omega})^{\frac{1}{2}} (\alpha x^2 - \frac{1}{2}) e^{-\frac{m\omega x^2}{\hbar^2}}$ 偶宇称

谐振子定态必为束缚态

相干态定义: 将基态波包平移(中心从 $x=0$ 移到 $x=x_0$)得到的态

特点: 1. 不是能量本征态 2. 不是定态, 几率密度随时间变化 3. 波包形状保持不变, 波包中心周期性变化

$|\psi(x, t)|^2 = |\psi(x - x_0 \cos \omega t)|^2$

量子隧穿效应

背景: 粒子可以进入 $E < U$ 的区域, 由定态薛定谔方程, 这一区域的波函数可以不为 0

一维散射问题的一般性描述: 无穷远处波函数不一定为 0, 只考虑定态问题

如图所示, 画出了势阱和势垒的示意图

势阱: $U(x) = 0, E > U$ (即 $E > U$)

势垒: $U(x) > 0, E < U$ (即 $E < U$)

势阱内: $U(x) = \frac{1}{2} m \omega^2 x^2, E < U$ (即 $E < U$)

势阱外: $U(x) = 0, E > U$ (即 $E > U$)

势垒外: $U(x) = 0, E < U$ (即 $E < U$)

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重要结论：球谐函数 $Y_{l,m}(\theta, \phi)$ 是角动量算符 L^2, L_z 的共同本征函数

不考虑自旋时， L^2 的简并度为 $2l+1$

球谐函数正交归一：

共轭性质： $Y_{l,m}^*(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi)$

$\int d\Omega = 0$, $Y_{l,m}(x, y, z) = \frac{1}{\sqrt{4\pi}} e^{-\frac{1}{2}r^2}$, 方向相反, 也即 $Y_{l,m}$ 为零, $\int d\Omega = \int d\Omega = 0$, 无方向性
 $\int d\Omega = 1$, $Y_{l,m}(x, y, z) = \frac{1}{\sqrt{4\pi}} \sqrt{m!} \exp(\pm i\phi)$, 有方向性
 $\int d\Omega = 0$, $Y_{l,m}$ 为零!

氢原子模型

中心力场模型：运动分解为质心运动 + 相对质心运动，通过分离变量，只关心相对运动

再取 F, 分离变量, $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

分离变量集：相对运动： $\left[\frac{\partial^2}{\partial r^2} + U(r) \right] \psi(r) = E \psi(r) \Rightarrow$ 后续关心相对运动
 质心运动： $\frac{1}{2m} \nabla_{\text{质心}}^2 \psi(r) = (E - \bar{E}) \psi(r)$

之后分离变量 $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

根据哈密顿量表达式将动量分为径向动量和转动动量
 $\left\{ \begin{array}{l} \frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} = \lambda \hbar^2 \quad [\text{以前级数求解得 } \lambda = l(l+1)] \\ -\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[U(r) + \frac{\lambda \hbar^2}{2m r^2} \right] R = ER(r) \end{array} \right.$

得到能量本征值，有束缚态解，离散谱 ($E > 0$ 时非束缚态，连续谱)
 $E = -\frac{me^2}{2\hbar^2 n^2} \left(\frac{ze^2}{4\pi\epsilon_0} \right)^2, n = 1, 2, 3, \dots$

其中 $n = n_r + l + 1, l = 0, 1, 2, \dots, n_r$ 为径量子数
 氢原子能谱： $E_n = -\frac{13.6}{n^2} eV$

宇称性质只与角量子数 l 有关， l 为奇数时为奇宇称， l 为偶数时为偶宇称

$\psi_{n,l,m}(-\vec{r}) = (-1)^l \psi_{n,l,m}(\vec{r})$

$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \times$

$\left(\frac{2r}{na}\right)^l e^{-\frac{r}{na}} L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) Y_{lm}(\theta, \phi)$

$\psi_{100} = \sqrt{\frac{1}{\pi a^3}} \exp\left(-\frac{r}{a}\right) = \sqrt{\frac{4}{a^3}} \exp\left(-\frac{r}{a}\right) Y_{00}(\theta, \phi)$

$\psi_{200} = \sqrt{\frac{1}{2a^3}} \left(1 - \frac{r}{2a}\right) \exp\left(-\frac{r}{2a}\right) Y_{00}(\theta, \phi)$

$\psi_{21m} = \sqrt{\frac{1}{6a^3}} \left(\frac{r}{2a}\right) \exp\left(-\frac{r}{2a}\right) Y_{1m}(\theta, \phi), (m = 1, 0, -1)$

五、本征函数系与测量问题

本征函数系

正交性定理：同一个厄米算符属于不同本征值的本征函数彼此正交

共同本征函数定理：若两个算符 F, G 满足 $[F, G] = 0$ ，则 F, G 有组成完全系的共同本征函数

证明：利用 F, G 分别的完全系组合展开 TODO

力学量完全集（完备算符集）：相互之间两两对易，能够对一个量子体系全部状态进行非简并分类标记的最少数目的力学量算符

TODO：对易相关例题

三维空间单粒子选取方法：

坐标 $\{x, y, z\}$ 动量 $\{px, py, pz\}$ 转动 $\{L_z, L^2\}$

原子状态： H, L^2, L_z, S_z

算符与力学量的关系

力学量平均值计算：

$F = \sum_n \lambda_n W(\lambda_n) = \sum_n \lambda_n |C_n|^2, C_n = \int \phi_n^*(x) \psi(x, t) dx$

平均值公式： $\bar{F} = \int \psi^*(x, t) \hat{F} \psi(x, t) dx$

若未归一化，可用 $\int \psi^*(x, t) \psi(x, t) dx$

证明：将波函数用对应力学量 F 的本征函数系展开

$\int \psi^* F \psi dx = \int \sum_n (\lambda_n C_n)^* \hat{F} \sum_m (\lambda_m C_m) dx = \sum_n \lambda_n^* \hat{F} \lambda_m C_m dx = C_m^* C_m$
 $= \sum_n \lambda_n^* \lambda_m \lambda_n dx, C_m^* C_m = \sum_n \lambda_n^* \lambda_n C_n \lambda_n^* C_n = \sum_n \lambda_n |\lambda_n|^2$
 因此： $\bar{F} = \sum_n \lambda_n |\lambda_n|^2 = \int \psi^* F \psi dx$ 。证毕。

测量问题总结：测量值为本征值，测量几率由几率幅（波函数）决定

不确定关系

不确定度：厄密算符 $\Delta F = \hat{F} - \bar{F}$

有 $(\Delta F)^2 = \hat{F}^2 - \bar{F}^2$

不确定关系：若不对易算符 $[\hat{F}, \hat{G}] = \hat{F}\hat{G} - \hat{G}\hat{F} = i\hat{C}$ 则有 $(\Delta F)^2 (\Delta G)^2 \geq \frac{1}{4} |\hat{C}|^2$

证明：利用积分非负性：

证明：取积分 $I(\lambda) = \int [(\hat{F} - \lambda\hat{I})\psi]^* (\hat{F} - \lambda\hat{I})\psi dx = 0$ 。
 $I(\lambda) = \int [\zeta(\lambda\hat{F}^2 + \lambda^2\hat{I})^* [\zeta(\lambda\hat{F}^2 + \lambda^2\hat{I})]]\psi dx$

$= \zeta^2 \int (\lambda\hat{F}^2 + \lambda^2\hat{I})^* dx - \zeta^2 [\zeta(\lambda\hat{F}^2 + \lambda^2\hat{I})^* (\lambda\hat{F}^2 + \lambda^2\hat{I})] dx + \int [\lambda\hat{F}^2 + \lambda^2\hat{I}]^* (\lambda\hat{F}^2 + \lambda^2\hat{I}) dx$

$= \zeta^2 \int \lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2 dx - \zeta^2 \int \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2 dx + \int \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2 dx + \int \lambda^2 \hat{I}^2 \lambda^2 \hat{F}^2 dx$

$= (\lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2)^2 - \zeta^2 \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2$
 $= (\lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2)^2 - \zeta^2 \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2$
 $\Delta F = \sqrt{(\lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2)^2 - \zeta^2 \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2}$

取等价条件： $I(\lambda) = 0 \Rightarrow (\lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2)^2 = \zeta^2 \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2$ 此时 $\lambda^2 \hat{F}^2 + \lambda^2 \hat{I}^2 = \zeta^2 \lambda^2 \hat{F}^2 \lambda^2 \hat{I}^2$

线性谐振子零点能 证明：

同一样况下： $\int |\psi(x)|^2 dx = \frac{1}{\sqrt{\pi}} e^{-\frac{1}{2}r^2}$ 其中 $x \cdot \hat{p} = \hat{x}$ 为波动包宽度 \hat{x} , \hat{p} 相互制约的线性谐振子的定义： $\hat{E} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$, 其中 $\hat{x} = 0, \hat{p} = 0$

$(\hat{x}\hat{p})^2 = \hat{x}^2 \hat{p}^2 = \hat{x}^2, (\hat{p}\hat{x})^2 = \hat{p}^2 \hat{x}^2$ 且等价于 $(\hat{x}\hat{p})^2 = \frac{1}{2} m\omega^2 \hat{x}^2$

$\Rightarrow \hat{E} = \frac{(\hat{p}^2 + \frac{1}{2} m\omega^2 \hat{x}^2)^2}{2m} \geq \frac{m\omega^2}{2m} \hat{x}^2 \geq \frac{1}{2} m\omega^2 \hat{x}^2$ 得到“非常”等价于 $\hat{E}_0 = \frac{1}{2} m\omega^2 \hat{x}^2$

守恒量

力学量期望随时间的变化：考虑力学量期望值对时间的导数：

$\frac{dF}{dt} = J^* \frac{\partial^2}{\partial t^2} \psi dx + \int \frac{\partial \psi}{\partial t} \hat{F} \psi dx + \int \psi \frac{\partial^2}{\partial t^2} \hat{F} dx$ ↑ 通常带省略！

考虑 \hat{S} 表象： $\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \hat{A} \psi, \frac{\partial^2 \psi}{\partial t^2} = \frac{-1}{\hbar^2} \hat{A}^2 \psi$ 且有 $\frac{\partial \hat{F}}{\partial t} = \frac{-1}{i\hbar} \hat{F} \hat{A} + \frac{1}{\hbar^2} \int \psi \hat{F} \hat{A}^2 dx$

$\therefore \frac{dF}{dt} = \frac{-1}{i\hbar} \int \psi \hat{F} \hat{A}^2 dx - \frac{1}{\hbar^2} \int \psi \hat{F} \hat{A}^2 dx - \int \psi \frac{\partial^2}{\partial t^2} \hat{F} dx$ 证明见后

$\hat{F} = \frac{1}{i\hbar} \int \psi \hat{F} \hat{A}^2 dx - \frac{1}{\hbar^2} \int \psi \hat{F} \hat{A}^2 dx - \int \psi \frac{\partial^2}{\partial t^2} \hat{F} dx$

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