第四章 近似方法

Techniques of Approximation

§4.1 变分法 The Variation Method

4.1.1 变分原理 The Variation Theorem

设给定体系的Hamilton算符 $\hat{H}$,其本征函数为 ψ_i，则 $\hat{H}\psi_i = E_i\psi_i$

$\{\psi_i\} \equiv \psi_0, \psi_1, \psi_2, \cdots, \psi_i, \psi_{i+1}, \cdots$ 组成一个正交归一的完备集

$E_0 \le E_1 \le E_2 \le \cdots \le E_i \le E_{i+1} \le \cdots$ $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

ϕ为满足这一体系边界条件的任何品优函数，则

$$W = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \ge E_0$$

用任何近似状态函数计算的能量平均值，一定大于或等于基态本征态 ψ_0 的本征值 E_0

证明：ϕ可以用完备集$\{\psi_i\}$展开(Hermit算符本征函数的完备性)

$$\phi = \sum_i c_i \psi_i$$

$$\varDelta = \int \phi^* (\hat{H} - E_0)\phi d\tau = \int \phi^* \hat{H} \phi d\tau - E_0 \int \phi^* \phi d\tau$$

$$= \int \left(\sum_i c_i^* \psi_i^* \right) \hat{H} \left(\sum_i c_i \psi_i \right) d\tau - E_0 \int \left(\sum_i c_i^* \psi_i^* \right) \left(\sum_i c_i \psi_i \right) d\tau$$

$$= \sum_i \sum_j c_i^* c_j E_i \delta_{ij} - E_0 \sum_i \sum_j c_i^* c_j \delta_{ij}$$

$$= \sum_i c_i^* c_i (E_i - E_0) \geq 0$$

$$\therefore \quad W = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

例1：一维势箱，抛物线函数$\phi = x(l-x)$满足边界条件

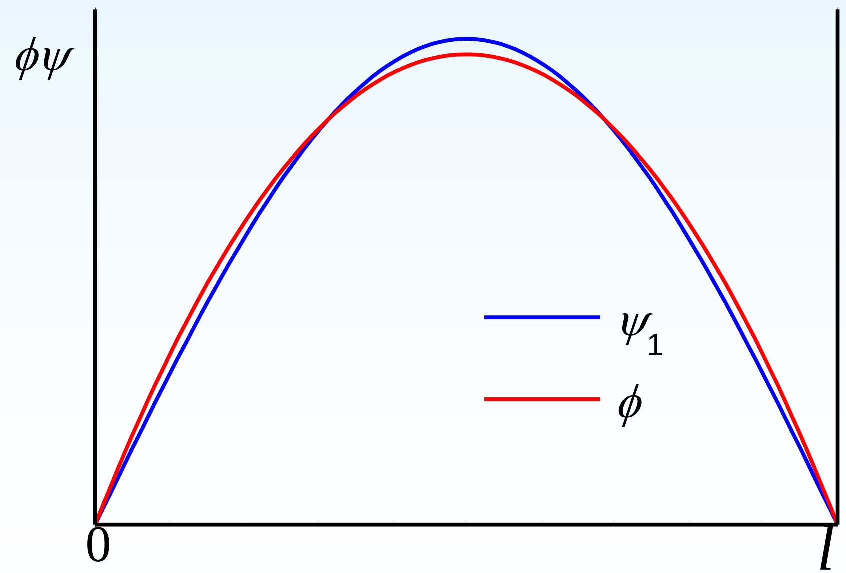
$$\int \phi^* \hat{H} \phi d\tau = -\frac{\hbar^2}{2m}\int_0^l (xl - x^2)\frac{d^2}{dx^2}(xl - x^2)dx$$

$$= \frac{\hbar^2}{m}\int_0^l (xl - x^2)dx = \frac{\hbar^2 l^3}{6m}$$

$$\int \phi^* \phi d\tau = \int_0^l (xl - x^2)^2 dx = \int_0^l (x^4 - 2lx^3 + x^2 l^2)dx = \frac{l^5}{30}$$

$$W = \frac{5\hbar^2}{ml^2} = \frac{5h^2}{4\pi^2 ml^2} > \frac{h^2}{8ml^2}$$

误差为1.3%



例2：氦原子，令变分函数为He⁺波函数的乘积

$$\phi=\psi_1\psi_2=\sqrt{\frac{8}{\pi}}e^{-Zr_1}\sqrt{\frac{8}{\pi}}e^{-Zr_2}$$

$$\hat{H}=\left(-\frac{1}{2}\nabla_1^2-\frac{Z}{r_1}\right)+\left(-\frac{1}{2}\nabla_2^2-\frac{Z}{r_2}\right)+\frac{1}{r_{12}}=\hat{H}_1+\hat{H}_2+\frac{1}{r_{12}}$$

$$\hat{H}_1\psi_1=E_1\psi_1 \qquad \hat{H}_2\psi_2=E_2\psi_2 \qquad \langle\phi|1/r_{12}|\phi\rangle=5Z/8$$

$$E_1=-Z^2/2 \qquad E_2=-Z^2/2$$

$$\begin{aligned}W&=\langle\phi|\hat{H}|\phi\rangle=\langle\phi|\hat{H}_1+\hat{H}_2+1/r_{12}|\phi\rangle\\&=\langle\phi|\hat{H}_1|\phi\rangle+\langle\phi|\hat{H}_2|\phi\rangle+\langle\phi|1/r_{12}|\phi\rangle\\&=E_1+E_2+\langle\phi|1/r_{12}|\phi\rangle\\&=-Z^2+5Z/8=-2.75(hartree)=-74.8(eV)\end{aligned}$$

实验测得

$E_0=-(I_1+I_2)=-78.986\text{eV}$

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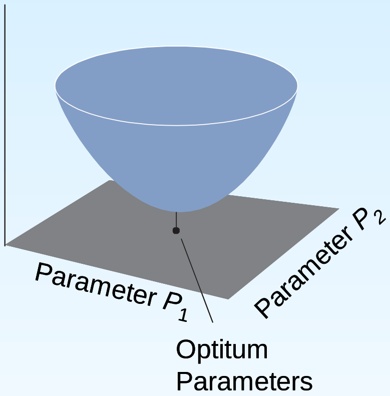
4.1.2 变分法 The Variation Method

利用变分原理可以求体系的近似基态波函数ϕ和基态能量W，在选择ϕ时使其包含若干可调节的参数λ_i，W是这些参数的函数$W=W(\lambda_1,\lambda_2,\ldots)$，$W$的上限是$E_0$，因此W的最小值最接近$E_0$，求$W$对$\lambda_1,\lambda_2,\ldots$的偏导，令其等于零

$$\frac{\partial W}{\partial \lambda_1}=\frac{\partial W}{\partial \lambda_2}=\cdots=0$$



可求出W等于最低值W_0时，$\lambda_1,\lambda_2,\ldots$应采取哪些值

ϕ称为尝试变分函数(trial variation function)

一般而言，ϕ选择的函数越适宜(越接近真实函数形式)，包含的可调参数越多，则W_0与E_0越接近。

例3：氢原子，以$\psi = e^{-kr}$为变分函数,求基态能量

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \qquad \nabla^2 = \frac{1}{r}\frac{d^2}{dr^2}r$$

$$\langle \psi | \psi \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} e^{-2kr} r^2 dr = \frac{\pi}{k^3}$$

$$\langle \psi | 1/r | \psi \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} e^{-2kr} r dr = \frac{\pi}{k^2}$$

$$\langle \psi | \nabla^2 | \psi \rangle = \int \psi^* \left(\frac{1}{r}\frac{d^2}{dr^2} \right) r e^{-kr} d\tau = \int \psi^* \left(k^2 - \frac{2k}{r} \right) \psi d\tau = -\frac{\pi}{k}$$

$$W = \left(\frac{\pi}{2k} - \frac{\pi}{k^2} \right) \frac{k^3}{\pi} = \frac{k^2}{2} - k$$

$$\frac{dW}{dk} = k - 1 = 0 \qquad k = 1 \qquad \varepsilon = -\frac{1}{2}$$

例4：氦原子，将Z改为可调参数λ，则

$$\phi=\psi_1\psi_2=\sqrt{\frac{8}{\pi}}e^{-\lambda r_1}\sqrt{\frac{8}{\pi}}e^{-\lambda r_2}$$

$$W=\left\langle\phi\middle|\hat{H}\middle|\phi\right\rangle=\left\langle\phi\middle|\hat{H}_1\middle|\phi\right\rangle+\left\langle\phi\middle|\hat{H}_2\middle|\phi\right\rangle+\left\langle\phi\middle|1/r_{12}\middle|\phi\right\rangle$$

$$\left\langle\phi\middle|\hat{H}_1\middle|\phi\right\rangle=\left\langle\phi\middle|\hat{H}_2\middle|\phi\right\rangle=\lambda^2/2-Z\lambda \qquad \left\langle\phi\middle|1/r_{12}\middle|\phi\right\rangle=5\lambda/8$$

$$W=\lambda^2-2Z\lambda+5\lambda/8$$

$$dW/d\lambda=2\lambda-2Z+5/8=0$$

$$\lambda=Z-5/16$$ 5/16 反映屏蔽效应

W=–2.84(hartree)=–77.5(eV)　误差1.9%

4.1.3 线性变分法 Linear Variation Method

若变分函数ϕ采用若干独立函数ψ_i的线性组合$\phi=\sum_i c_i\psi_i$ 这样的变分方法称为线性变分法，ψ_i(基函数basis function)必须满足边界条件

$$W=\frac{\left\langle\phi\middle|\hat{H}\middle|\phi\right\rangle}{\langle\phi|\phi\rangle}=\frac{\int\sum_i c_i\psi_i^*\hat{H}\sum_j c_j\psi_j d\tau}{\int\sum_i\sum_j c_ic_j\psi_i^*\psi_j d\tau}=\frac{\sum_i\sum_j c_ic_jH_{ij}}{\sum_i\sum_j c_ic_jS_{ij}}$$

$$H_{ij}=\int\psi_i^*\hat{H}\psi_j d\tau=\left\langle i\middle|\hat{H}\middle|j\right\rangle=H_{ji}\qquad S_{ij}=\int\psi_i^*\psi_j d\tau=\langle i|j\rangle=S_{ji}$$

$$W\sum_i\sum_j c_ic_jS_{ij}=\sum_i\sum_j c_ic_jH_{ij}$$

$$\frac{\partial W}{\partial c_k}\sum_i\sum_j c_ic_jS_{ij}+W\frac{\partial}{\partial c_k}\sum_i\sum_j c_ic_jS_{ij}=\frac{\partial}{\partial c_k}\sum_i\sum_j c_ic_jH_{ij}$$

$$\Downarrow$$

$$\frac{\partial W}{\partial c_k}=0\quad(k=1,2,3,\cdots,n)$$

$$W\frac{\partial}{\partial c_k}\sum_i\sum_j c_i c_j S_{ij} = \frac{\partial}{\partial c_k}\sum_i\sum_j c_i c_j H_{ij}$$

$$\frac{\partial}{\partial c_k}\sum_i\sum_j c_i c_j S_{ij} = \sum_i c_i S_{ik} + \sum_j c_j S_{kj} = 2\sum_i c_i S_{ik}$$

$$\frac{\partial}{\partial c_k}\sum_i\sum_j c_i c_j H_{ij} = \sum_i c_i H_{ik} + \sum_j c_j H_{kj} = 2\sum_j c_i H_{ik}$$

$$W\sum_i c_i S_{ik} = \sum_i c_i H_{ik}$$

$$\sum_i c_i (H_{ik} - WS_{ik}) = 0$$ 久期方程Secular Equation

久期方程是含有n个独立变量$c_1, c_2, \ldots, c_n$,的齐次线性方程组，如该方程组有非零解，其本征行列式(久期行列式)必须为零

$$\left|H_{ik} - WS_{ik}\right| = \begin{vmatrix} H_{11}-S_{11}W & H_{12}-S_{12}W & \cdots & H_{1n}-S_{1n}W \\ H_{21}-S_{21}W & H_{22}-S_{22}W & \cdots & H_{2n}-S_{2n}W \\ \vdots & \vdots & \vdots & \vdots \\ H_{n1}-S_{n1}W & H_{n2}-S_{n2}W & \cdots & H_{nn}-S_{nn}W \end{vmatrix} = 0$$

解久期行列式可以得到n个实根(可以证明，由于矩阵元H_{ik}和S_{ik}是Hermite对称的)，其最小的W_0是E_0的上限，将W_0代回久期方程，可以求出c_1, c_2, …, c_n(加归一化条件)，可得到基态近似波函数ϕ_0

同样可以证明，按从低到高排列的$W_1\le W_2\le\ldots\le W_{n\text{-}1}$ 分别为激发态本征值$E_1, E_2,\ldots,E_{n\text{-}1}$ 的上限(McDonald定理)，相应得到的变分函数$\phi_1, \phi_2, \ldots, \phi_{n-1}$可作为各激发态的近似波函数，这些函数相互正交并与$\phi_0$正交。

具体应用：分子轨道理论

变分法除能够得到能量本征值的上限，也可以得到本征值的下限

$$W=\bar{E}\equiv\int\phi^*\hat{H}\phi d\tau \qquad \overline{E^2}=\int\phi^*\hat{H}^2\phi d\tau$$

$$\Delta\equiv\overline{E^2}-W^2$$

$$W+\sqrt{\Delta}\ge E_k\ge W-\sqrt{\Delta}$$

由于计算Δ积分比较困难，该方法在实际应用中比简单的变分法困难，但借助使Δ为极小的方法，可以使得到的函数尽可能地接近正确的本征函数

§4.2 定态微扰理论

Time-independent Perturbation Theory

假定一个不含时的Hamilton算符的体系不能精确求解

$$\hat{H}\psi_k = E_k\psi_k$$

而 $\hat{H}_0\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}$ 可求解

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$\boldsymbol{H}$与$\boldsymbol{H}_0$相差很小，我们将具有$\boldsymbol{H_0}$的体系称为未微扰体系，$\boldsymbol{H}$称为微扰体系，$\boldsymbol{H'}$称为微扰。

如 非谐振子: $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + \dfrac{1}{2}kx^2 + cx^3 + dx^4$

如c和d都很小，则$\boldsymbol{H}$与谐振子$\boldsymbol{H_0}$相关 $\hat{H}_0 = -\dfrac{\hbar^2}{2m}\nabla^2 + \dfrac{1}{2}kx^2$ $\hat{H}' = cx^3 + dx^4$

微扰要一点一点加，使未微扰体系连续变到微扰体系

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

4.2.1 非简并微扰理论 Nondegenerate Perturbation Theory

$$\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$\psi_n^{(0)}$为能量为$E_n^{(0)}$的未微扰非简并能级的波函数，ψ_n为微扰函数.

$$(\hat{H}^0 + \lambda\hat{H}')\psi_n = E_n\psi_n$$

ψ_n和E_n的依赖于参数λ，按λ的幂次Taylor展开

$$\psi_n = \psi_n\big|_{\lambda=0} + \frac{\partial\psi_n}{\partial\lambda}\bigg|_{\lambda=0}\lambda + \frac{\partial^2\psi_n}{\partial\lambda^2}\bigg|_{\lambda=0}\frac{\lambda^2}{2!} + \cdots$$

$$E_n = E_n\big|_{\lambda=0} + \frac{\partial E_n}{\partial\lambda}\bigg|_{\lambda=0}\lambda + \frac{\partial^2 E_n}{\partial\lambda^2}\bigg|_{\lambda=0}\frac{\lambda^2}{2!} + \cdots$$

$$\psi_n^{(k)} = \frac{1}{k!}\frac{\partial^2\psi_n}{\partial\lambda^2}\bigg|_{\lambda=0}$$

$$E_n^{(k)} = \frac{1}{k!}\frac{\partial^2 E_n}{\partial\lambda^2}\bigg|_{\lambda=0}$$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots + \lambda^k\psi_n^{(k)} + \cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots$$

k=1,2,3…， $\psi_n^{(k)}$和$\psi_n^{(k)}$称为波函数和能级的k级校正

$$(\hat{H}^0+\lambda\hat{H}')(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots+\lambda^k\psi_n^{(k)}+\cdots)$$
$$=(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\cdots+\lambda^kE_n^{(k)}+\cdots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots+\lambda^k\psi_n^{(k)}+\cdots)$$

合并λ相同的幂的系数

$$(\hat{H}^0\psi_n^{(0)}-E_n^{(0)}\psi_n^{(0)})+\lambda(\hat{H}^0\psi_n^{(1)}+\hat{H}'\psi_n^{(0)}-E_n^{(0)}\psi_n^{(1)}-E_n^{(1)}\psi_n^{(0)})$$
$$+\lambda^2(\hat{H}^0\psi_n^{(2)}+\hat{H}'\psi_n^{(1)}-E_n^{(0)}\psi_n^{(2)}-E_n^{(1)}\psi_n^{(1)}-E_n^{(2)}\psi_n^{(0)})+\cdots=0$$

如果该级数是一致收敛的，则λ系数必为零

λ^0 $\quad \hat{H}^0\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)}$ **无微扰体系**

λ^1 $\quad \hat{H}^0\psi_n^{(1)}+\hat{H}'\psi_n^{(0)}=E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)}$

$(\hat{H}^0-E_n^{(0)})\psi_n^{(1)}=(E_n^{(1)}-\hat{H}')\psi_n^{(0)}$ **一级微扰**

将$\psi_n^{(1)}$用未微扰的波函数展开 $\psi_n^{(1)}=\sum_j a_j^{(1)}\psi_j^{(0)}$

$$\sum_j a_j^{(1)}(\hat{H}^0-E_n^{(0)})\psi_j^{(0)}=(E_n^{(1)}-\hat{H}')\psi_n^{(0)}$$

两端同乘$\psi_m^{(0)*}$并对整个空间积分

$$\int \psi_m^{(0)*} \sum_j a_j^{(1)} (\hat{H}^0 - E_n^{(0)}) \psi_j^{(0)} d\tau = \int \psi_m^{(0)*} (E_n^{(1)} - \hat{H}') \psi_n^{(0)} d\tau$$

$$\sum_j a_j^{(1)} (E_j^{(0)} - E_n^{(0)}) \int \psi_m^{(0)*} \psi_j^{(0)} d\tau = \int \psi_m^{(0)*} (E_n^{(1)} - \hat{H}') \psi_n^{(0)} d\tau$$

$$\langle \psi_m^{(0)} | \psi_j^{(0)} \rangle = \delta_{mj}$$

$$a_m^{(1)} (E_m^{(0)} - E_n^{(0)}) = E_n^{(1)} \delta_{mn} - \int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

$m=n$

$$\boxed{E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = H'_{nn}}$$

能量的一级修正值等于微扰算符***H'***对体系相应未微扰态的平均值

$m \neq n$

$$\boxed{a_m^{(1)} = \frac{\int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_m^{(0)}}}$$

可确定除$a_n^{(1)}$外所有系数，习惯上选$a_n^{(1)}=0$

波函数一级校正
$$\boxed{\psi_n^{(1)} = \sum_{m \neq n} \frac{\int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}}$$

$$\lambda^2 \quad (\hat{H}^0 - E_n^{(0)})\psi_n^{(2)} = E_n^{(2)}\psi_n^{(0)} + (E_n^{(1)} - \hat{H}')\psi_n^{(1)}$$

二级微扰

$$\psi_n^{(2)} = \sum_j a_j^{(2)}\psi_j^{(0)}$$

$$\sum_j a_j^{(2)}(E_j^{(0)} - E_n^{(0)})\psi_j^{(0)} = E_n^{(2)}\psi_n^{(0)} + (E_n^{(1)} - \hat{H}')\psi_n^{(1)}$$

两端同乘 $\psi_m^{(0)*}$ 并对整个空间积分

$$\sum_j a_j^{(2)}(E_j^{(0)} - E_n^{(0)})\delta_{mj} = E_n^{(2)}\delta_{mn} + E_n^{(1)}\int\psi_m^{(0)*}\psi_n^{(1)}d\tau - \int\psi_m^{(0)*}\hat{H}'\psi_n^{(1)}d\tau$$

$$a_m^{(2)}(E_m^{(0)} - E_n^{(0)}) = E_n^{(2)}\delta_{mn} + E_n^{(1)}\int\psi_m^{(0)*}\psi_n^{(1)}d\tau - \int\psi_m^{(0)*}\hat{H}'\psi_n^{(1)}d\tau$$

$m=n$

$$E_n^{(2)} + E_n^{(1)}\int\psi_n^{(0)*}\psi_n^{(1)}d\tau - \int\psi_n^{(0)*}\hat{H}'\psi_n^{(1)}d\tau = 0$$

欲求二级微扰，必须先得到一级修正波函数

$$\int\psi_n^{(0)*}\psi_n^{(1)}d\tau = \sum_{k\neq n}\frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}}\int\psi_n^{(0)*}\psi_k^{(0)}d\tau = 0$$

$$H'_{kn} = \left\langle \psi_k^{(0)} \middle| \hat{H}' \middle| \psi_n^{(0)} \right\rangle$$

$$E_n^{(2)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(1)} d\tau = \sum_{k\neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \int \psi_n^{(0)*} \hat{H}' \psi_k^{(0)} d\tau$$

$$= \sum_{k\neq n} \frac{H'_{kn} H'_{nk}}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} \frac{\left|H'_{kn}\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

一级微扰:

$$\boxed{E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(0)} \right\rangle = H'_{nn}}$$

$$\boxed{\psi_n \approx \psi_n^{(0)} + \sum_{m\neq n} \frac{\int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}}$$

二级微扰:

$$\boxed{E_n^{(2)} = \sum_{k\neq n} \frac{\left|H'_{kn}\right|^2}{E_n^{(0)} - E_k^{(0)}}}$$

$$\boxed{E_n \approx E_n^{(0)} + H'_{nn} + \sum_{k\neq n} \frac{\left|H'_{kn}\right|^2}{E_n^{(0)} - E_k^{(0)}}}$$

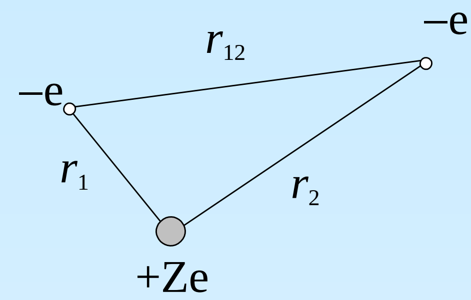
(i) 一级修正计算方便

(ii) 二级修正必须求第*n*态与其它全部态*k*之间的*H'*矩阵元，许多情况下不能精确求出

(iii) 波函数一级修正项中，最重要的贡献来自最靠近*n*态的项

(iv) 计算时必须使用归一化的未微扰波函数。

例5: 氦原子基态



$$\hat{H} = \boxed{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}} + \frac{1}{r_{12}}$$

$$\hat{H}^{(0)} = \hat{H}_1^{(0)} + \hat{H}_2^{(0)} \qquad \hat{H}' = \frac{1}{r_{12}}$$

$$\psi^{(0)}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = F_1(r_1,\theta_1,\phi_1)F_2(r_2,\theta_2,\phi_2)$$

$$E^{(0)} = E_1^{(0)} + E_2^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

$n_1=1,\ n_2=1$

$$\psi^{(0)} = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$$

$$E^{(0)} = -Z^2$$

$1/r_{12}$按球谐函数展开

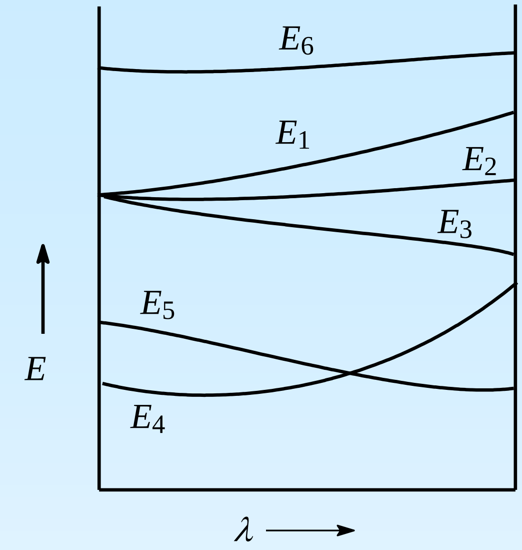
$$\frac{1}{r_{12}} = \begin{cases} \dfrac{1}{r_1}\sum_l\sum_m \dfrac{4\pi}{2l+1}\left(\dfrac{r_2}{r_1}\right)^l [Y_l^m(\theta_1,\phi_1)]^* Y_l^m(\theta_2,\phi_2) & r_1 \geq r_2 \\ \dfrac{1}{r_2}\sum_l\sum_m \dfrac{4\pi}{2l+1}\left(\dfrac{r_1}{r_2}\right)^l [Y_l^m(\theta_1,\phi_1)]^* Y_l^m(\theta_2,\phi_2) & r_2 \geq r_1 \end{cases}$$

$E^{(1)}=5Z/8$

$E \approx E^{(0)}+E^{(1)}= -2.75$(hartree)$=-74.8$eV 误差5.3%

4.2.2 简并能级的微扰理论

Perturbation Theory for a Degenerate Energy Level



未微扰Schrodinger方程 $\hat{H}^0\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$

$$E_1^{(0)} = E_2^{(0)} = \cdots = E_d^{(0)}$$

微扰: $(\hat{H}^0 + \lambda\hat{H}')\psi_j = E_j\psi_j$

$$\lim_{\lambda\to 0} E_j = E_j^{(0)} \quad □$$

$$\lim_{\lambda\to 0} \psi_j = \psi_j^{(0)} \quad ? \qquad \lim_{\lambda\to 0} \psi_n = \sum_{i=1}^{d} c_i\psi_i^{(0)} \quad 1 \le n \le d$$

设零级波函数为 $\psi_n^{(0)}$ $\quad \psi_n^{(0)} = \sum_{i=1}^{d} c_i\psi_i^{(0)} \quad 1 \le n \le d$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots$$

$$E_n = E_d^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \qquad n = 1, 2, \cdots, d$$

$$(\hat{H}^0+\lambda\hat{H}')(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots)$$
$$=(E_d^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\cdots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots)$$

λ^0 $\quad \hat{H}^0\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)}$ $\quad \varphi_n^{(0)}(n=1,2,\ldots,d)$的每个线性组合都是$\boldsymbol{H^0}$的本征值为$E_d^{(0)}$的本征函数

λ^1 $\quad \hat{H}^0\psi_n^{(1)}+\hat{H}'\psi_n^{(0)}=E_d^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)}$

$$\hat{H}^0\psi_n^{(1)}-E_d^{(0)}\psi_n^{(1)}=E_n^{(1)}\psi_n^{(0)}-\hat{H}'\psi_n^{(0)} \qquad n=1,2,\ldots,d$$

两端同乘$\psi_m^{(0)*}$并对整个空间积分

m是d级简并的未微扰状态之一, $1\le m\le d$

$$\left\langle\psi_m^{(0)}\middle|\hat{H}^0\middle|\psi_n^{(1)}\right\rangle-E_d^{(0)}\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle=E_n^{(1)}\left\langle\psi_m^{(0)}\middle|\psi_n^{(0)}\right\rangle-\left\langle\psi_m^{(0)}\middle|\hat{H}'\middle|\psi_n^{(0)}\right\rangle \qquad 1\le m\le d$$

$=0$

$$\left\langle\psi_m^{(0)}\middle|\hat{H}'\middle|\psi_n^{(0)}\right\rangle-E_n^{(1)}\left\langle\psi_m^{(0)}\middle|\psi_n^{(0)}\right\rangle=0$$

$$\sum_{i=1}^{d}\left[\left\langle\psi_m^{(0)}\,|\,\hat{H}'\,|\,\psi_i^{(0)}\right\rangle-E_n^{(1)}\delta_{mi}\right]c_i=0$$

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$$
\begin{cases}
(H'_{11}-E_n^{(1)})c_1+H'_{12}c_2+\cdots+H'_{1d}c_d=0 \\
H'_{21}c_1+(H'_{22}c_2-E_n^{(1)})+\cdots+H'_{2d}c_d=0 \\
\cdots\cdots\cdots \\
H'_{d1}c_1+H'_{d2}c_2+\cdots+(H'_{dd}-E_n^{(1)})c_d=0
\end{cases}
$$

$$H'_{mi}=\left\langle \psi_m^{(0)}\,|\,\hat{H}'\,|\,\psi_i^{(0)}\right\rangle$$

$$
\begin{vmatrix}
H'_{11}-E_n^{(1)} & H'_{12} & \cdots & H'_{1d} \\
H'_{21} & H'_{22}c_2-E_n^{(1)} & \cdots & H'_{2d} \\
\cdots & \cdots & \cdots & \cdots \\
H'_{d1} & H'_{d2} & \cdots & H'_{dd}-E_n^{(1)}
\end{vmatrix}=0
$$

该方程的d个根, $E_1^{(1)}, E_2^{(1)},\ldots, E_d^{(1)}$，既为$d$级简并的非微扰能级的一级校正，如果所有的根不同，校正后能级分裂成d个非简并能级。

将$E_1^{(1)}, E_2^{(1)},\ldots, E_d^{(1)}$分别带回久期行列式，加归一化条件，可求出$c_1$, $c_2,\ldots,c_d$