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简单体系的精确解

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Schrödinger Eqn.

- 3D Occasion:

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V\left(\boldsymbol{r}\right)\right)\psi=E\psi$$

- 1D Occasion:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\psi=E\psi$$

- PDEs, often unable to solve analytically.
- Discussion on simple occasions would be beneficial.

Syllabus

- Free Particles
- Infinite Deep Well
  - Finite Deep Well (Briefly)
  - Tunnel Penetration (Briefly)
- Hydrogen Atom (Not Today)
  - Some Mathematical Tricks (Interesting)

Free Particles (1D): To solve the equation

- $V(x) = 0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = E\psi$$

$$\psi = C_1 e^{\mathrm{i}\frac{\sqrt{2mE}}{\hbar}x} + C_2 e^{-\mathrm{i}\frac{\sqrt{2mE}}{\hbar}x}$$

Free Particles (1D): To explain the solution

- No boundary conditions
- Momentum Operator: $\hat{p}_x = -\mathrm{i}\hbar\partial_x$
- We'd better adapt a general convention with clear physical explanation:

$$\psi(x;p) = \mathrm{e}^{\mathrm{i}\frac{px}{\hbar}}$$

- From such a solution, one can recognize that $p^2 = 2mE$
- Just the classical Non-relativistic Dispersion (Energy-Momentum) Relationship

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Free Particles (1D): Normalization Difficulty

- The WF here is not square-integrable: $\int_{-\infty}^{+\infty} \mathrm{d}x \ \psi^* \psi = \int_{-\infty}^{+\infty} \mathrm{d}x \ 1 \rightarrow \infty$
- Whatever you assign a factor to ψ, the WF is always not a "well-behaved WF".
- Uncertainty Relationship: $\Delta x \Delta p \geq \hbar/2$. As momentum is accurately determined, position is completely delocalized thus probability of observing the particle is equal everywhere in the space and even infinitely far away.
- Linear combination of solutions are also solutions of the S-Eqn. (Postulate I): A spectrum of the free particle's momenta, then able to be normalized.

Free Particles (1D): Normalization

- Normalized Free Particle WFs are not eigenfunctions of momentum operator, but such WF can be Fourier transformed to give superposition form of momentum eigenstates:

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \mathrm{d}x \ \psi(x) \mathrm{e}^{-\mathrm{i}\frac{px}{\hbar}}$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \mathrm{d}p \ \phi(p) \mathrm{e}^{\mathrm{i}\frac{px}{\hbar}}$$

- This is another convention of coefficients for Fourier transform commonly using in QM.

Free Particles (1D): e. g. Gaussian

- Consider a normalized WF with Gauss form:

$$\psi(x)=\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}\mathrm{e}^{-ax^2}$$

- Do a Fourier transform to acquire its momentum spectrum.

$$\int_{-\infty}^{\infty} e^{-(ax^2+bx)}dx = \int_{-\infty}^{\infty} e^{-y^2+(b^2/4a)}\frac{1}{\sqrt{a}}dy = \frac{1}{\sqrt{a}}e^{b^2/4a}\int_{-\infty}^{\infty} e^{-y^2}dy = \sqrt{\frac{\pi}{a}}e^{b^2/4a}.$$

$$\phi(k) = \frac{1}{\sqrt{2\pi}}A\int_{-\infty}^{\infty} e^{-ax^2}e^{-ikx}dx = \frac{1}{\sqrt{2\pi}}\left(\frac{2a}{\pi}\right)^{1/4}\sqrt{\frac{\pi}{a}}e^{-k^2/4a} = \frac{1}{(2\pi a)^{1/4}}e^{-k^2/4a}.$$

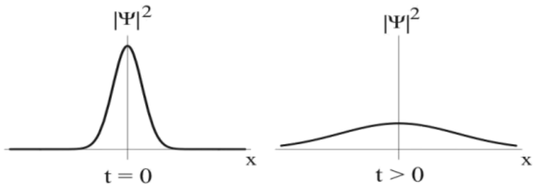
Free Particles (1D): e. g. Gaussian

- Time-dependent Schrödinger Eqn. can be represented as follow:

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}\mathrm{d}p\;\phi(p)\,\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px-Et)}$$

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\frac{1}{(2\pi a)^{1/4}}\int_{-\infty}^{\infty}\underbrace{e^{-k^2/4a}e^{i(kx-\hbar k^2t/2m)}}_{e^{-[(\frac{1}{4a}+i\hbar t/2m)k^2-ixk]}}dk$$

$$=\frac{1}{\sqrt{2\pi}(2\pi a)^{1/4}}\frac{\sqrt{\pi}}{\sqrt{\frac{1}{4a}+i\hbar t/2m}}e^{-x^2/4(\frac{1}{4a}+i\hbar t/2m)}=\boxed{\left(\frac{2a}{\pi}\right)^{1/4}\frac{e^{-ax^2/(1+2i\hbar at/m)}}{\sqrt{1+2i\hbar at/m}}.}$$



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Free Particles (1D): Velocity Paradox

- Velocity of a simple momentum mode:

$$\psi(x;p)=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px-Et)}=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(px-\frac{p^2}{2m}t\right)}$$

$$p=\hbar k, E=\hbar\omega, v=\frac{\omega}{k}=\frac{E}{p}=\frac{p}{2m},\cdots ?$$

- Actually, the velocity of a simple momentum mode doesn't represent the velocity of the particle. Because SMM-WFs are not well-behaved thus non-physical.

Free Particles (1D): Wave Packet Explanation

- Physical states, i.e. superposition of SMM-WFs, can be regarded as a Wave Packet.
  - Sum up Single Momentum Mode **Wave** Function to get **Wave** Packet.
- The physical velocity shall be regarded as the velocity of WP, i.e. group velocity.
- Consider a WP having a major momentum p_0 but a small momentum deviation around p_0, then φ(p) is concentrating at p_0 :

$$\Psi(x,0)=\frac{1}{\sqrt{2\pi\hbar}}\int_{p\sim p_0} \mathrm{d}p\ \phi(p)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}px}$$

Free Particles (1D): Wave Packet Explanation

- Substitute *p* by p_0+s, to make it clear.
- After time *t*, it evolves. Because momenta distributes rather concentrated, it's appropriate to Taylor expand the *E*~*p* relation:

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{s\sim 0}\mathrm{d}s\ \phi(p_0+s)\,\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left((p_0+s)x-(E_0+E's)t\right)}$$

$$=\frac{1}{\sqrt{2\pi\hbar}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_0E'-E_0)t}\int_{s\sim 0}\mathrm{d}s\ \phi(p_0+s)\,\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_0+s)(x-E't)}$$

$$=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_0E'-E_0)t}\Psi(x-E't,0)$$

Free Particles (1D): Wave Packet Explanation

- For free particles, the *E~p* relation is

$$E = \frac{p^2}{2m}, \frac{\mathrm{d}E}{\mathrm{d}p} = \frac{p}{m}$$

- Now the velocity paradox is settled: regarding group velocity instead of phase velocity, i.e. the one of SMM-WFs as the particle one.

Free Particles (3D): To solve the equation

- Variable separation enables independent considerations analogous to 1D on different directions.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

Free Particles (3D): Momentum Eigenstates

- In 3D, momenta are vectors with 3 independent components.

$$\psi\left(\boldsymbol{x};\boldsymbol{p}\right)=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}}$$

Wells

- A case slightly more difficult.
- $V(x) = -V_0$, for $-a<x<a$; for other x, $V(x) = 0$.
- Boundary conditions need to be considered.
  - Continuity of ψ: Required all the time: Discontinuity of WF means infinite momentum at this position.
  - Continuity of $d\psi/dx$: Required when the well is finitely deep, but can’t be established when the well is infinitely deep.

Finite Wells: Symmetry Constraints

- For a 1D potential with space reversal symmetry, the solution can be only even or odd, which added a constraint to the coefficients.
  - For 1D case, no degeneracy will occur.
  - Even and odd solutions belong to 2 different irreducible representation of the symmetry group for the potential.

Finite Wells

- Width: $2a$, Height: V_0
- Solve the ODE at different regions:

$$\psi(x)=\begin{cases}\psi(-x), x\le 0;\\ A\cos\frac{\sqrt{2m(E+V_0)}x}{\hbar}, 0\le x\le a;\\ B\exp\left(-\frac{\sqrt{2mE}x}{\hbar}\right)+C\exp\left(\frac{\sqrt{2mE}x}{\hbar}\right), x\ge a;\end{cases}$$

$$\psi(x)=\begin{cases}-\psi(-x), x\le 0;\\ A\sin\frac{\sqrt{2m(E+V_0)}x}{\hbar}, 0\le x\le a;\\ B\exp\left(-\frac{\sqrt{2mE}x}{\hbar}\right)+C\exp\left(\frac{\sqrt{2mE}x}{\hbar}\right), x\ge a;\end{cases}$$

Finite Wells: Boundary Conditions

- We will consider bounded states majorly, so assume $V>E$ first.
  - When $x \leq -a$ or $x \geq a$, if the WF gets exponentially larger when moving away from the well, then E is becoming infinite, which is non-physical. So coefficient C is zero.
  - ψ should be continuous, without further explanation.
  - Momenta at edges of the well are well-defined, so $d\psi/dx$ is continuous. A, and B shall satisfy such condition, i.e. left derivative = right derivative.

Finite Wells: Boundary Conditions, Even

$$A\cos\frac{\sqrt{2m(E+V_0)}a}{\hbar}=B\exp\left(-\frac{\sqrt{2mE}a}{\hbar}\right),$$

$$-A\frac{\sqrt{2m(E+V_0)}}{\hbar}\sin\frac{\sqrt{2m(E+V_0)}a}{\hbar}=-B\frac{\sqrt{2mE}}{\hbar}\exp\left(-\frac{\sqrt{2mE}a}{\hbar}\right)$$

$$z:=\frac{\sqrt{2m(E+V_0)}}{\hbar},z_0=\frac{\sqrt{2mV_0}}{\hbar}$$

$$\tan z=\sqrt{\left(\frac{z_0}{z}\right)^2-1}$$

Finite Wells: Boundary Conditions, Odd

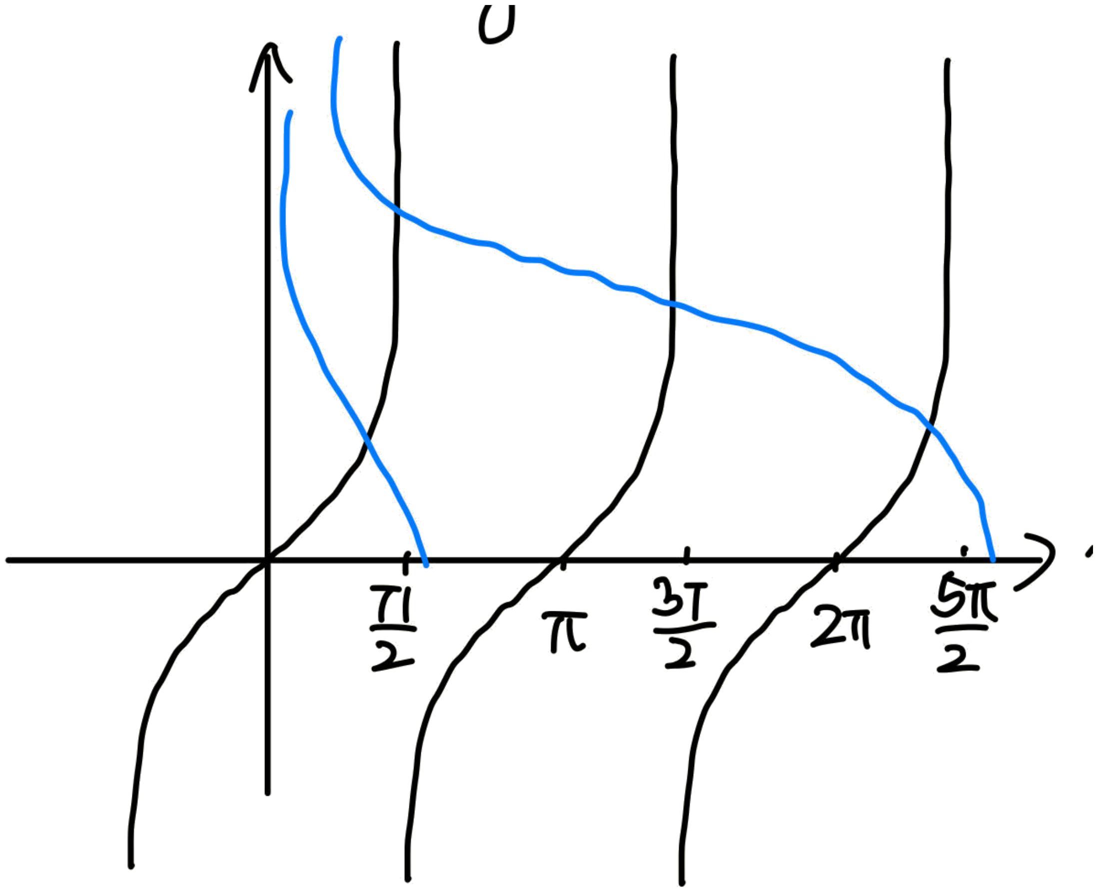
$$A\sin\frac{\sqrt{2m(E+V_0)}a}{\hbar} = -B\exp\left(-\frac{\sqrt{2mE}a}{\hbar}\right),$$

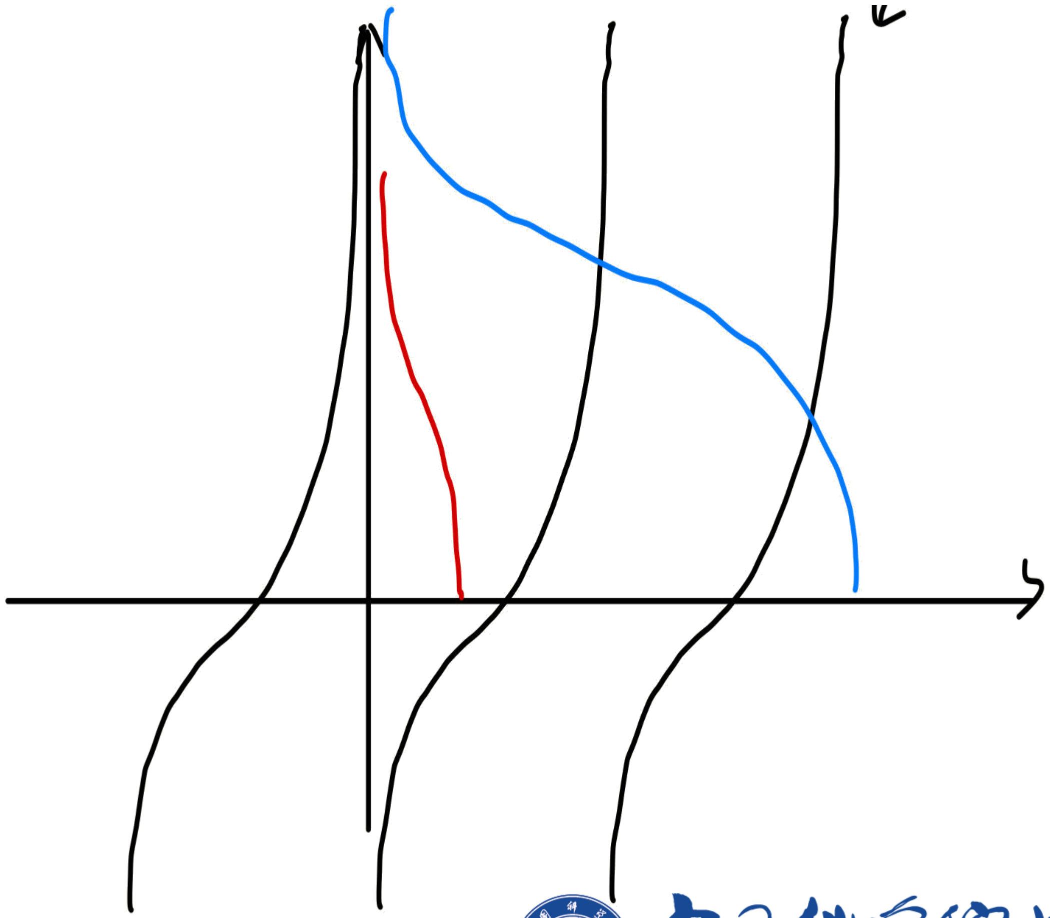
$$A\frac{\sqrt{2m(E+V_0)}}{\hbar}\cos\frac{\sqrt{2m(E+V_0)}a}{\hbar} = B\frac{\sqrt{2mE}}{\hbar}\exp\left(-\frac{\sqrt{2mE}a}{\hbar}\right)$$

$$z := \frac{\sqrt{2m(E+V_0)}}{\hbar}, z_0 = \frac{\sqrt{2mV_0}}{\hbar}$$

$$-\cot z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

Finite Wells: To determine E





Infinite Well: As V_0 becomes infinite…

- We are changing some notations:
  - Well width: 0~*a*, bottom potential = 0, potential out of well: infinite.
- Boundary Condition:
  - 0 outside the well, any finite presence out of the well cause infinite eigenvalue.
  - ψ should be continuous, without further explanation.
  - Momenta at edges of the well are not well-defined(imagine the particle bounced backwards), so $d\psi/dx$ is discontinuous.

Infinite Well: Solutions

- Can be solved analytically.

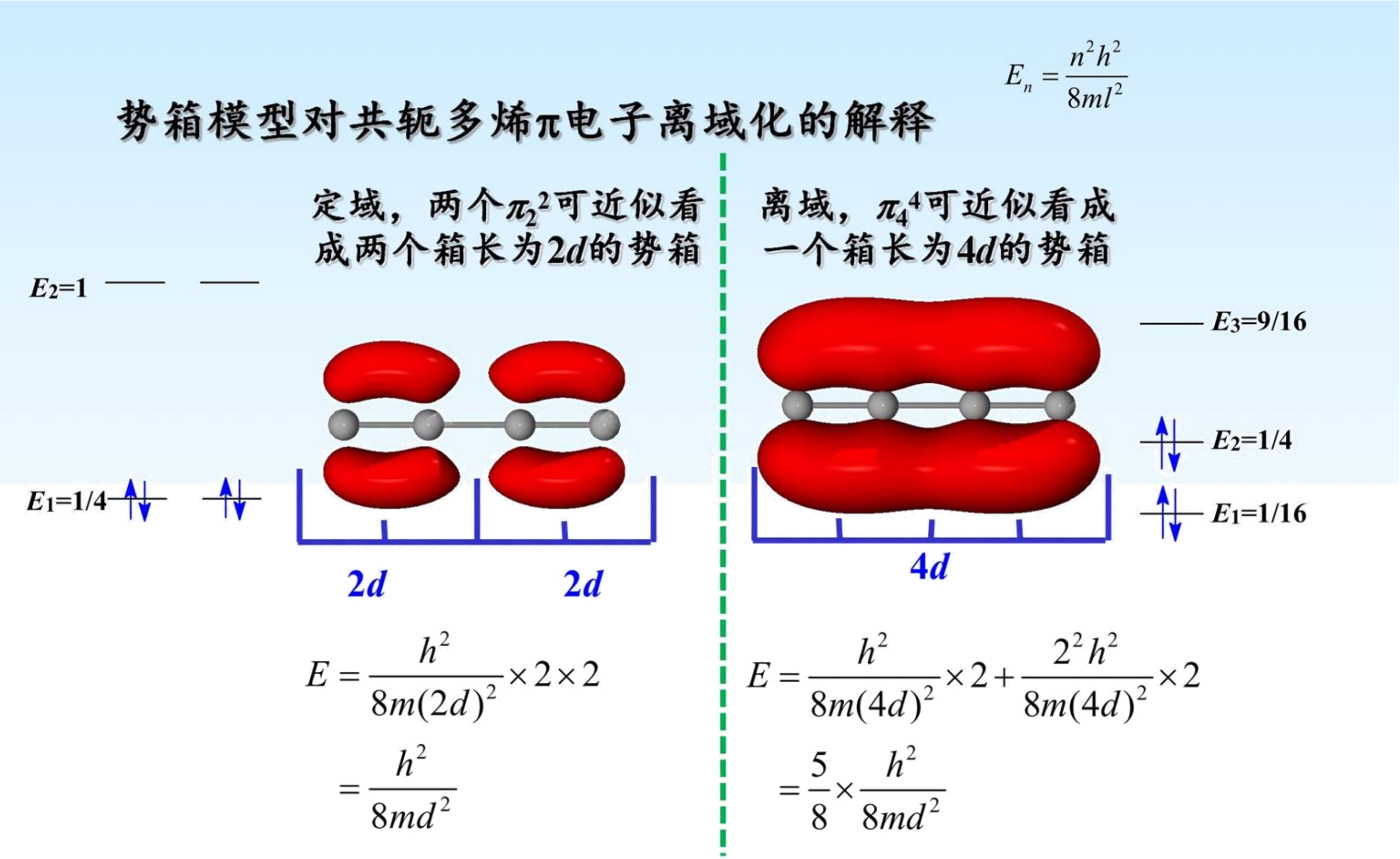
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

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

Infinite Well: Interpretation

- *n* is the quantum number indicating eigenstates.
  - For odd *n*s, the solutions are “even”, vice versa.
  - The energy spectrum is proportional to n^2.
  - Gaps between same states is proportional to $1/m$ and $1/a^2$.

Infinite Well: A coarse approximation for conjugate olefins



离域形成大π 键要比定域的小π 键能量低

Infinite Well: A coarse approximation for conjugate olefins

直链共轭多烯的电子吸收光谱的波长随链长的增加

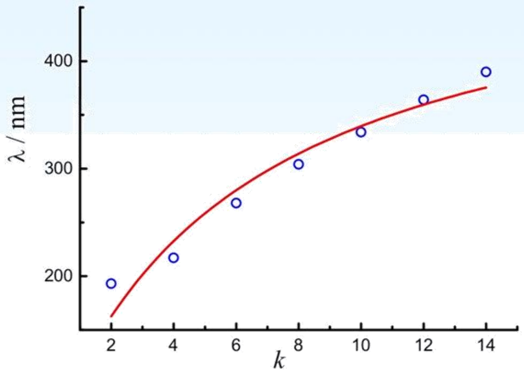
n(分子)	2	4	6	8	10	12	14
吸收波长(nm)	193	217	268	304	334	364	390

- 共轭C原子数为$2k$的直链共轭多烯，箱长为$2kd$
- 电子数为$2k$
- HOMO为第k个π轨道
- LUMO为第$k+1$个π轨道

$$\frac{hc}{\lambda} = \frac{h^2}{8m(2k)^2d^2}\left[(k+1)^2 - k^2\right] = \frac{(2k+1)h^2}{8m(2k)^2d^2}$$

$$\lambda = \frac{8m(2k)^2d^2c}{(2k+1)h}$$

***k*增加，*λ*增加**



考虑键长交替修正后模型

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Infinite Well: 3D occasion

三维无限深正方体势阱中粒子的简并态