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① Numerical methods for 1D differential eqs.

Ⓐ Finite-difference method (aka grid-based method)

Ⓑ Basis-set method (aka spectral method including finite-element method)

② Schrödinger eq. and atomic units and amu

$e = 1$ a.u. (the best units ever invented by men)

$\hbar = 1$ a.u.

H atom:

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)\psi = E\psi$$

$m_e = 1$ a.u.

$4\pi\varepsilon_0 = 1$ a.u.

$$E = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} = -\frac{1}{2}\ \text{a.u.}$$

As diff eqs. describe virtually all phys., chem., bio, economics, etc., knowing how to solve them numerically (in addition to or more than analytically) makes you useful.

$$\downarrow$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\psi = E\psi \qquad E = -\frac{1}{2}$$

1 a.u. of energy = 1 E_h = 1 Hartree $= \frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2} = 27.211\ \text{eV} = 627.51\ \text{kcal/mol}$

1 a.u. of length = 1 a_0 = 1 Bohr $= \frac{\hbar^2}{(4\pi\varepsilon_0)m_e e^2} = 0.529177\ \text{Å}$

1 a.u. of time $= 1\frac{\hbar}{E_h} = 2.419\times10^{-17}\ \text{s}$

Atomic mass unit (u)

one ^{12}C atom weighs 12 u

$$1\,u = \frac{1\,g}{6.022\times10^{23}} = 1.661\times10^{-24}\,g = 1.661\times10^{-27}\,kg$$

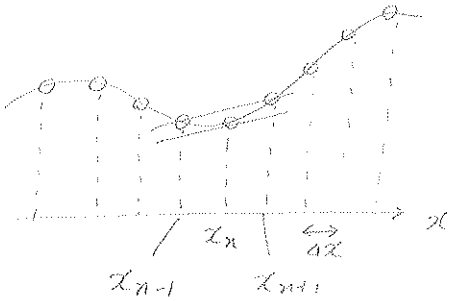
$$1\,m_e = 9.109\times10^{-31}\,kg$$

$$1\,u = 1823\,m_e = 1823\ \text{a.u.}$$

③ FD method

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\varphi(x) = E\,\varphi(x)$$

i) Represent $\varphi(x)$ by its numerical values on an (evenly spaced) grid.



$$\varphi(x) \longleftrightarrow \varphi(x_1), \varphi(x_2), \cdots \varphi(x_N)$$

(outside the grid, $\varphi = 0$)

→ boundary condition (implicit)

ii) Approximate $\varphi'(x)$, $\varphi''(x)$ by finite differences

$$\left.\frac{\partial \varphi}{\partial x}\right|_{x=x_n} \approx \frac{\varphi(x_{n+1}) - \varphi(x_{n-1})}{2\Delta x} \qquad (\text{exact at } \Delta x \to 0)$$

$$\left.\frac{\partial^2 \varphi}{\partial x^2}\right|_{x=x_n} \approx \frac{\frac{\varphi(x_{n+1})-\varphi(x_n)}{\Delta x} - \frac{\varphi(x_n)-\varphi(x_{n-1})}{\Delta x}}{\Delta x} = \frac{\varphi(x_{n+1}) + \varphi(x_{n-1}) - 2\varphi(x_n)}{\Delta x^2}$$

$$V(x)\varphi(x)\Big|_{x=x_n} = V(x_n)\,\varphi(x_n)$$

iii) Differential eq. → matrix eq.

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\varphi(x)\Big|_{x=x_n} \approx -\frac{1}{2m}\frac{\varphi(x_{n+1}) + \varphi(x_{n-1}) - 2\varphi(x_n)}{\Delta x^2} + V(x_n)\varphi(x_n)$$

$$\begin{pmatrix} a_1 & b_1 & & & 0 \\ b_2 & \ddots & \ddots & & \\ & \ddots & a_n & b_n & \\ & & b_n & \ddots & b_{N-1} \\ 0 & & & b_{N-1} & a_N \end{pmatrix} \begin{pmatrix} \varphi(x_1) \\ \vdots \\ \varphi(x_{n-1}) \\ \varphi(x_n) \\ \varphi(x_{n+1}) \\ \vdots \\ \varphi(x_N) \end{pmatrix} = E \begin{pmatrix} \varphi(x_1) \\ \vdots \\ \varphi(x_n) \\ \\ \varphi(x_N) \end{pmatrix}$$

$$\Leftrightarrow \quad b_n\varphi(x_{n-1}) + a_n\varphi(x_n) + b_n\varphi(x_{n+1}) = E\varphi(x_n)$$

$$\left(0 + a_1\varphi(x_1) + b_1\varphi(x_2) = E\varphi(x_1)\right) \Leftrightarrow \varphi(x_0) = 0$$

$$a_n = -\frac{1}{2m}\frac{-2}{\Delta x^2} + V(x_n) = \frac{1}{m\Delta x^2} + V(x_n)$$

$$b_n = -\frac{1}{2m}\frac{1}{\Delta x^2}$$

$N \times N$ symmetric matrix has N eigenvectors and (real) eigenvalues

$$H c_i = E_i c_i \quad (i = 1, \cdots, N)$$

$$H_{nn} = a_n$$

$$H_{n,n+1} = H_{n+1,n} = b_n$$

otherwise $H_{pq} = 0$

$$\downarrow$$

$$H(\underbrace{c_1 c_2 \cdots c_N}_{C}) = (c_1 c_2 \cdots c_N)E \quad \text{note the order}$$

$$E_{pq} = \underbrace{\delta_{pq} E_p}_{\text{diagonal}}$$

Kronecker's delta $\delta_{pq} = \begin{cases} 1, & p = q \\ 0, & p \neq q \end{cases}$

adjoint $HC = CE$

$C^\dagger H C = E$ where $C^\dagger C = 1$ $(C^{-1} = C^\dagger)$

diagonalization

(H is a symmetric matrix. Its eigenfunctions are orthogonal. An orthogonal → orthogonal basis transformation is represented by a unitary matrix which satisfies $U^\dagger U = 1$)

- Jacobi
- Householder
- QL
- ⋮

cf. Numerical Recipes in Fortran/c
BLAS, LAPACK, LINPACK
Davidson's method

$$(C^\dagger)_{ij} = c_{ij}^*$$

$\langle i|j\rangle = \delta_{ij}$, $\sum_i |i\rangle\langle i| = 1$

$\langle \alpha|\beta\rangle = \delta_{\alpha\beta}$, $\sum_\alpha |\alpha\rangle\langle\alpha| = 1$

→ two orthonormal, complete bases

$$|\alpha\rangle = \sum_i |i\rangle \underbrace{\langle i|\alpha\rangle}_{U_{i\alpha}} = \sum_i |i\rangle \underbrace{U_{i\alpha}}_{\text{transform. matrix}}$$

$$\delta_{\alpha\beta} = \langle\alpha|\beta\rangle = \sum_{i,j} U_{i\alpha}^* \langle i|j\rangle U_{j\beta}$$

$$= \sum_i (U^\dagger)_{\alpha i} (U)_{i\beta} = (U^\dagger U)_{\alpha\beta}$$

$$U^\dagger U = 1$$

④ Basis-set method

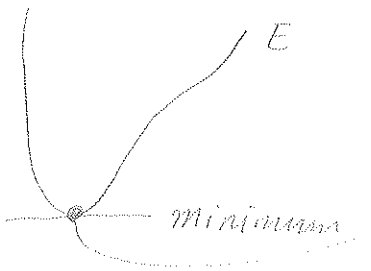
$$\psi(x) = \sum_{n=1}^{N} c_n \underbrace{\eta_n(x)}_{\text{basis function}}$$

i) Unconstrained optimization

$$|\psi\rangle = c_A|A\rangle + c_B|B\rangle$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{c_A^2\langle A|\hat{H}|A\rangle + c_B^2\langle B|\hat{H}|B\rangle + 2c_Ac_B\langle A|\hat{H}|B\rangle}{c_A^2\langle A|A\rangle + c_B^2\langle B|B\rangle + 2c_Ac_B\langle A|B\rangle}$$

Minimize E by varying c_A, c_B (no constraint)



$$\frac{\partial E}{\partial c_A} = \frac{\partial E}{\partial c_B} = 0$$

$$0 = \frac{\partial E}{\partial c_A} = \frac{\partial}{\partial c_A}\frac{num.}{den.} = \frac{\frac{\partial(num.)}{\partial c_A}den. - \frac{\partial(den.)}{\partial c_A}num.}{(den.)^2}$$

$$\rightarrow \frac{\partial(num.)}{\partial c_A} = \left(\frac{num.}{den.}\right)\frac{\partial(den.)}{\partial c_A}$$

$\frac{num.}{den.} = E$

$$\left(2c_A\langle A|\hat{H}|A\rangle + 2c_B\langle A|\hat{H}|B\rangle\right) = E\left(2c_A\langle A|A\rangle + 2c_B\langle A|B\rangle\right)$$

$$0 = \frac{\partial E}{\partial c_B} \rightarrow 2c_A\langle A|\hat{H}|B\rangle + 2c_B\langle B|\hat{H}|B\rangle = E\left(2c_A\langle A|B\rangle + 2c_B\langle B|B\rangle\right)$$

$$\begin{pmatrix}\langle A|\hat{H}|A\rangle & \langle A|\hat{H}|B\rangle \\ \langle B|\hat{H}|A\rangle & \langle B|\hat{H}|B\rangle\end{pmatrix}\begin{pmatrix}c_A \\ c_B\end{pmatrix} = E\begin{pmatrix}\langle A|A\rangle & \langle A|B\rangle \\ \langle B|A\rangle & \langle B|B\rangle\end{pmatrix}\begin{pmatrix}c_A \\ c_B\end{pmatrix}$$

H ← Hamiltonian matrix; $\mathbb{C}$ = E (energy) $\mathbb{S}$ $\mathbb{C}$; $\mathbb{S}$ ← overlap matrix; $\mathbb{C}$ ← HO, etc.

ii) Lagrange's undetermined multiplier

The versatile method for constrained optimization.

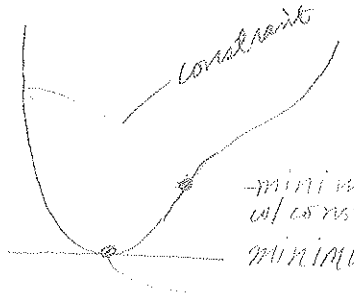
1) variational theorem

$$|\Psi\rangle = c_A|A\rangle + c_B|B\rangle$$

$$E = \langle\Psi|\hat{H}|\Psi\rangle = c_A^2\langle A|\hat{H}|A\rangle + c_B^2\langle B|\hat{H}|B\rangle + 2c_Ac_B\langle A|\hat{H}|B\rangle$$

Minimize E by varying c_A, c_B with constraint (not always possible to eliminate as in previous page)

$$1 = \langle\Psi|\Psi\rangle = c_A^2\langle A|A\rangle + c_B^2\langle B|B\rangle + 2c_Ac_B\langle A|B\rangle$$



$\rightarrow \frac{\partial E}{\partial c_A} = \frac{\partial E}{\partial c_B} = 0$?? How do we ensure $1 = \langle\Psi|\Psi\rangle$?

2) Lagrange's method

$$\underbrace{\frac{\partial\{E - \lambda(\langle\Psi|\Psi\rangle - 1)\}}{\partial c_A}}_{①} = \underbrace{\frac{\partial\{E - \lambda(\langle\Psi|\Psi\rangle - 1)\}}{\partial c_B}}_{②} = \underbrace{\frac{\partial\{E - \lambda(\langle\Psi|\Psi\rangle - 1)\}}{\partial \lambda}}_{③} = 0 \qquad (=\mathcal{L})$$

(X) two conditions $\begin{cases} \text{minimize } E \\ \text{constraint } \langle\Psi|\Psi\rangle = 1 \end{cases}$ with two params, c_A, c_B

$\Downarrow$ Lagrange

(Y) one condition $\frac{\partial\mathcal{L}}{\partial(\text{param})} = 0$ with three params. $c_A, c_B, \underline{\lambda}$

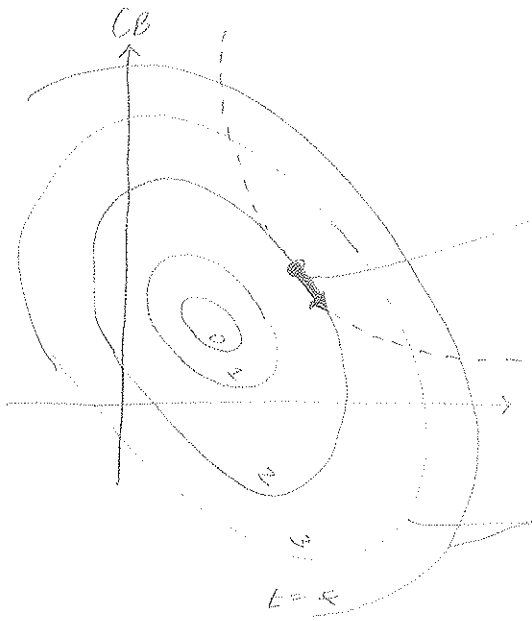
undetermined multiplier

Justification I (why (X) = (Y)) : if ③ then $\langle\Psi|\Psi\rangle = 1$

if $\langle\Psi|\Psi\rangle = 1$ then ①, ② become

$$\frac{\partial E}{\partial c_A} = \frac{\partial E}{\partial c_B} = 0 \quad (\text{with } \langle\Psi|\Psi\rangle = 1)$$

Justification II



minimum point of E that satisfies $\langle\Psi|\Psi\rangle = 1$

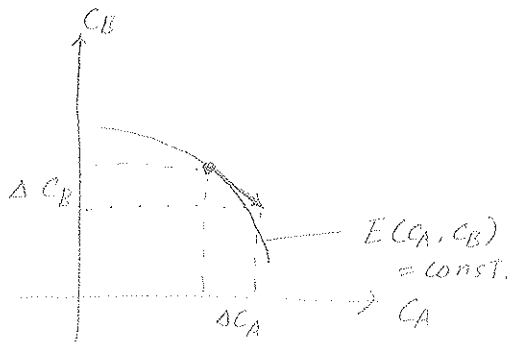
Note: tangent vectors of E-const., $\langle\Psi|\Psi\rangle=1$ are parallel

$\langle\Psi|\Psi\rangle = 1$ $\left(C_A^2\langle A|A\rangle + C_B^2\langle B|B\rangle + 2C_AC_B\langle A|B\rangle = 1 \right)$

contours of E

Lagrange eq. can be rewritten as

$$\begin{pmatrix} \Delta C_A \\ \Delta C_B \end{pmatrix} \propto \begin{pmatrix} \frac{\partial E}{\partial C_B} \\ -\frac{\partial E}{\partial C_A} \end{pmatrix} = \lambda \begin{pmatrix} \frac{\partial(\langle\Psi|\Psi\rangle - 1)}{\partial C_B} \\ -\frac{\partial(\langle\Psi|\Psi\rangle - 1)}{\partial C_A} \end{pmatrix} \quad (\neq 0)$$



Signifies ⇔

tangents of E-const and $\langle\Psi|\Psi\rangle = 1$ are parallel

$$\Delta C_A \frac{\partial E}{\partial C_A} + \Delta C_B \frac{\partial E}{\partial C_B} = 0$$

for $(\Delta C_A, \Delta C_B)$ which is tangent to the E=const contour!

$$\frac{\partial(E - \lambda(\langle\Psi|\Psi\rangle - 1))}{\partial C_A} = 0 \rightarrow 2C_A\langle A|\hat{H}|A\rangle + 2C_B\langle A|\hat{H}|B\rangle = 2\lambda\left(C_A\langle A|A\rangle + C_B\langle A|B\rangle\right)$$

$$\frac{\eta}{\partial C_B} = 0 \rightarrow 2C_A\langle A|\hat{H}|B\rangle + 2C_B\langle B|\hat{H}|B\rangle = 2\lambda\left(C_A\langle A|B\rangle + C_B\langle B|B\rangle\right)$$

$$\begin{pmatrix} \langle A|\hat{H}|A\rangle & \langle A|\hat{H}|B\rangle \\ \langle B|\hat{H}|A\rangle & \langle B|\hat{H}|B\rangle \end{pmatrix}\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \lambda \begin{pmatrix} \langle A|A\rangle & \langle A|B\rangle \\ \langle B|A\rangle & \langle B|B\rangle \end{pmatrix}\begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

$$H\,C = \lambda\, S\,C$$

H: Hamiltonian matrix; λ: energy; S: overlap matrix; C: MO, etc.