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Excited States and Nonadiabatic Dynamics
CyberTraining School/Workshop 2022

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July 4, 2022

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Fundamentals of DVR with Libra

Wavefunction is discretized on a grid

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Wavefunction is discretized on a grid

$$\langle r|\Psi\rangle = \Psi(r,t) = \sum_{\substack{i\in grid,\\ a}} \Psi_a(r_i,t)\delta(r-r_i)|a\rangle$$

$$\text{PSI\_dia} = \left\{ \begin{pmatrix} \Psi_0(r_0) \\ \cdots \\ \Psi_{N-1}(r_0) \end{pmatrix}, \begin{pmatrix} \Psi_0(r_1) \\ \cdots \\ \Psi_{N-1}(r_1) \end{pmatrix}, \ldots, \begin{pmatrix} \Psi_0(r_{Npts-1}) \\ \cdots \\ \Psi_{N-1}(r_{Npts-1}) \end{pmatrix} \right\}$$

In Libra, any N-dimensional grid is “linearized” this way via a mapping function

This could be thought of as using the basis of grid-point functions $|i,a\rangle$: $\langle r|\Psi\rangle = \delta(r-r_i)|a\rangle$

Overlaps

$$\langle\Psi|\Psi\rangle = \sum_{a,b,i,j} \int dr \Psi_a^*(r_i)\Psi_b(r_j)\delta(r-r_i)\delta(r-r_j)\langle a|b\rangle = \Delta r \sum_{a,i} \Psi_a^*(r_i)\Psi_a(r_i)$$

Matrix elements of operators

$$\langle\Psi|\hat{A}|\Psi\rangle = \sum_{a,b,i,j} \int dr \Psi_a^*(r_i)\Psi_b(r_j)\delta(r-r_i)\delta(r-r_j)A_{ab}(r) = \Delta r \sum_{a,b,i} \Psi_a^*(r_i)A_{ab}(r_i)\Psi_a(r_i)$$

Momentum representation

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Real-space (coordinate) wavefunction

$$\psi_a(\boldsymbol{r},t) = \int \tilde{\psi}_a(\boldsymbol{k},t) e^{2\pi i \boldsymbol{r}\boldsymbol{k}} d\boldsymbol{k}$$

Reciprocal-space (momentum) wavefunction

$$\tilde{\psi}_i(\boldsymbol{k},t) = \int \psi_i(\boldsymbol{r},t) e^{-2\pi i \boldsymbol{r}\boldsymbol{k}} d\boldsymbol{r}$$

$$\left\langle \psi_i(x) \middle| \left(-i\frac{\partial}{\partial x}\right)^n \middle| \psi_j(x) \right\rangle = \sum_{i,j} \int dx \left(\int \tilde{\psi}_i(k) e^{2\pi i x k} dk \right) \left(-i\frac{\partial}{\partial x}\right)^n \left(\int \tilde{\psi}_j(k') e^{2\pi i x k'} dk' \right)$$

$$= (-i)^n \sum_{i,j} \int dx \left(\int \tilde{\psi}_i(k) e^{2\pi i x k} dk \right)^* \left((2\pi i)^n \int k'^n \tilde{\psi}_j(k') e^{2\pi i x k'} dk' \right)$$

$$= (2\pi)^n \sum_{i,j} \int dx dk dk' \tilde{\psi}_i^*(k) e^{-2\pi i x k} (k')^n \tilde{\psi}_j(k') e^{2\pi i x k'}$$

$$= (2\pi)^n \sum_{i,j} \int dk dk' \tilde{\psi}_i^*(k) \delta(k-k') (k')^n \tilde{\psi}_j(k') = (2\pi)^n \sum_{i,j} \int dk \tilde{\psi}_i^*(k) k^n \tilde{\psi}_j(k)$$

$$\rightarrow (2\pi)^n \Delta k \sum_{i,j,m} \tilde{\psi}_i^*(k_m) k_m^n \tilde{\psi}_j(k_m)$$

Solution of the TD-SE

$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \hat{H}\Psi(r,t) = \left(\hat{T} + \hat{V}\right)\Psi(r,t)$$

Finite difference evaluation of the derivatives

$$\partial_t \Psi_i(\boldsymbol{r}_n, t_m) = \frac{1}{2\Delta t}\left[\Psi_i(\boldsymbol{r}_n, t_{m+1}) - \Psi_i(\boldsymbol{r}_n, t_{m-1})\right]$$

$$\nabla_{\boldsymbol{r}_\alpha} \Psi_i(x_n, t_m) = \frac{1}{2\Delta r_\alpha}\left[\Psi_i\left(\boldsymbol{r}_{\alpha,n+1}, t_m\right) - \Psi_i\left(\boldsymbol{r}_{\alpha,n-1}, t_m\right)\right]$$

$$\nabla^2_{\boldsymbol{r}_\alpha} \Psi_i(x_n, t_m) = \frac{1}{4\Delta \boldsymbol{r}^2_\alpha}\left[\Psi_i\left(\boldsymbol{r}_{\alpha,n+2}, t_m\right) - \Psi_i(\boldsymbol{r}_n, t_m) - \left[\Psi_i(\boldsymbol{r}_n, t_m) - \Psi_i\left(\boldsymbol{r}_{\alpha,n-2}, t_m\right)\right]\right] = \frac{1}{4\Delta r^2_\alpha}\left[\Psi_i\left(\boldsymbol{r}_{\alpha,n+2}, t_m\right) - 2\Psi_i(\boldsymbol{r}_n, t_m) + \Psi_i\left(\boldsymbol{r}_{\alpha,n-2}, t_m\right)\right]$$

Solution of the TD-SE

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$$i\hbar \frac{\partial|\Psi(t)\rangle}{\partial t} = \hat{H}|\Psi(t)\rangle = \left(\hat{T} + \hat{V}\right)|\Psi(t)\rangle$$

Split-operator method (Kosloff & Kosloff)

$$|\Psi(t+\Delta t)\rangle = \exp\left(-\frac{i\Delta t}{\hbar}\hat{H}\right)|\Psi(t)\rangle = \exp\left(-\frac{i\Delta t}{\hbar}\left(\hat{T}+\hat{V}\right)\right)|\Psi(t)\rangle \approx \exp\left(-\frac{i\Delta t}{2\hbar}\hat{V}\right)\exp\left(-\frac{i\Delta t}{\hbar}\hat{T}\right)\exp\left(-\frac{i\Delta t}{2\hbar}\hat{V}\right)|\Psi(t)\rangle$$

$$\Psi_a(r_i,t') = \langle r_i, a|\exp\left(-\frac{i\Delta t}{2\hbar}\hat{V}\right)|\Psi(t)\rangle = \langle r_i|\exp\left(-\frac{i\Delta t}{2\hbar}\hat{V}\right)\sum_{j,b}|r_j,b\rangle\langle r_j,b|\Psi(t)\rangle = \sum_{j,b}\left\langle r_i,a\middle|\exp\left(-\frac{i\Delta t}{2\hbar}\hat{V}\right)\middle|r_j,b\right\rangle\langle r_j,b|\Psi(t)\rangle$$

$$= \sum_{j,b}\left\langle a\middle|\exp\left(-\frac{i\Delta t}{2\hbar}V\,(r_i)\right)\middle|b\right\rangle\delta_{ij}\Psi_b(r_j,t) = \sum_b\left[\exp\left(-\frac{i\Delta t}{2\hbar}V\,(r_i)\right)\right]_{ab}\Psi_b(r_i,t)$$

$$\tilde{\Psi}_{\mathrm{a}}(k_i,t'') = \langle k_i,a|\exp\left(-\frac{i\Delta t}{\hbar}\hat{T}\right)|\Psi(t)\rangle = \langle k_i,a|\exp\left(-\frac{i\Delta t}{\hbar}\hat{T}\right)\sum_{j,b}|k_j,b\rangle\langle k_j,b|\Psi(t)\rangle$$

$$= \sum_{j,b}\left\langle k_i,a\middle|\exp\left(-\frac{i\Delta t}{2\hbar}\hat{T}\right)\middle|k_j,b\right\rangle\langle k_j,b|\Psi(t)\rangle = \sum_{j,b}\exp\left(-\frac{i\Delta t}{2\hbar}\frac{k_i^2}{2m}\right)\delta_{ij}\delta_{ab}\tilde{\Psi}_b(t) = \exp\left(-\frac{i\Delta t}{2\hbar}\frac{k_i^2}{2m}\right)\tilde{\Psi}_a(t)$$

Fundamentals of HEOM with Libra

See here

https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2021/files/Jain-HEOM.pdf