Libra Summer School and Workshop 2024

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Exact quantum dynamics on grid with Libra

Solution of the TD-SE: Direct methods (finite differences)

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

These are essentially the wavefunction amplitudes at those points in space and time

Finite difference evaluation of the derivatives

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

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

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

$$\frac{i\hbar}{2\Delta t}[\Psi_i(\boldsymbol{r}_n, t_{m+1}) - \Psi_i(\boldsymbol{r}_n, t_{m-1})] = -\sum_\alpha \frac{\hbar^2}{8 m_\alpha \Delta r_\alpha^2}\left[\Psi_i(\boldsymbol{r}_{\alpha,n+2}, t_m) - 2\Psi_i(\boldsymbol{r}_n, t_m) + \Psi_i(\boldsymbol{r}_{\alpha,n-2}, t_m)\right] + \sum_j V_{ij}(r_n)\Psi_j(\mathrm{r_n}, \mathrm{t_m})$$

$$\Psi_i(\boldsymbol{r}_n, t_{m+1}) = \Psi_i(\boldsymbol{r}_n, t_{m-1}) + \sum_\alpha \frac{i\Delta t\hbar}{4 m_\alpha \Delta r_\alpha^2}\left[\Psi_i(\boldsymbol{r}_{\alpha,n+2}, t_m) - 2\Psi_i(\boldsymbol{r}_n, t_m) + \Psi_i(\boldsymbol{r}_{\alpha,n-2}, t_m)\right] - \frac{2i\Delta t}{\hbar}\sum_j V_{ij}(r_n)\Psi_j(\mathrm{r_n}, \mathrm{t_m})$$

Wavefunction is discretized on a grid

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Wavefunction is discretized on a grid

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

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

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 $|r_i,a\rangle$: $\langle r_i,a|r_j,b\rangle = \delta_{ij}\delta_{ab}$

Overlaps

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

Matrix elements of operators

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

$$A_{ab}(r_i,r_j) = \langle r_i,a|\hat{A}|r_j,b\rangle$$

That is in the **coordinate representation, the operators that depend only on coordinate have block-diagonal form!**

Operators in the grid basis: Real space

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Potential energy, $\hat{V}$ (aka diabatic Hamiltonian)

$$V_{ab}(r_i, r_j) = \langle r_i, a|\hat{V}|r_j, b\rangle = \langle a|\hat{V}|b\rangle(r_i)\delta_{ij} = V_{ab}(r_i)\delta_{ij}$$

Electronic state index

Grid point index

		$j = 0$		$j = 1$		$j = 2$	
		$b = 0$	$b = 1$	$b = 0$	$b = 1$	$b = 0$	$b = 1$
$i = 0$	$a = 0$	$V_{00}(r_0)$	$V_{01}(r_0)$				
	$a = 1$	$V_{10}(r_0)$	$V_{11}(r_0)$				
$i = 1$	$a = 0$			$V_{00}(r_1)$	$V_{01}(r_1)$		
	$a = 1$			$V_{10}(r_1)$	$V_{11}(r_1)$		
$i = 2$	$a = 0$					$V_{00}(r_2)$	$V_{01}(r_2)$
	$a = 1$					$V_{10}(r_2)$	$V_{11}(r_2)$

Momentum representation

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Real-space (coordinate) wavefunction

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

Reciprocal-space (momentum) wavefunction

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

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

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

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

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

That is in the **momentum representation, the kinetic energy and NAC** operators **have block-diagonal form!**

Operators in the grid basis: Real space

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Nuclear kinetic energy, $\hat{T}$

$$T_{ab}(k_i, k_j) = \langle k_i, a|\hat{T}|k_j, b\rangle = \sum_n \frac{4\pi^2 k_{i,n}^2}{2m_n}\,\delta_{ij}\delta_{ab}$$

Electronic state index

		$j = 0$		$j = 1$		$j = 2$	
		$b = 0$	$b = 1$	$b = 0$	$b = 1$	$b = 0$	$b = 1$
$i = 0$	$a = 0$	$\sum_n \frac{4\pi^2 k_{0,n}^2}{2m_n}$					
	$a = 1$		$\sum_n \frac{4\pi^2 k_{0,n}^2}{2m_n}$				
$i = 1$	$a = 0$			$\sum_n \frac{4\pi^2 k_{1,n}^2}{2m_n}$			
	$a = 1$				$\sum_n \frac{4\pi^2 k_{1,n}^2}{2m_n}$		
$i = 2$	$a = 0$					$\sum_n \frac{4\pi^2 k_{2,n}^2}{2m_n}$	
	$a = 1$						$\sum_n \frac{4\pi^2 k_{2,n}^2}{2m_n}$

Grid point index

Solution of the TD-SE: Split-Operator Fourier Transform (SOFT)

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Kosloff, D.; Kosloff, R. A F *Journal of Computational Physics* **1983**, *52*, 35–53.

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

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

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

$$\tilde{\Psi}_{\mathrm{a}}(k_i,t'') = \langle k_i,a|\exp\left(-\frac{i\Delta t}{\hbar}\hat{T}\right)|\Psi(t)\rangle = \langle k_i,a|\exp\left(-\frac{i\Delta t}{\hbar}\hat{T}\right)\sum_{j,b}|k_j,b\rangle\langle k_j,b|\Psi(t)\rangle$$
$$= \sum_{j,b}\left\langle k_i,a\middle|\exp\left(-\frac{i\Delta t}{2\hbar}\hat{T}\right)\middle|k_j,b\right\rangle\langle k_j,b|\Psi(t)\rangle = \sum_{j,b}\exp\left(-\frac{i\Delta t}{2\hbar}\frac{k_i^2}{2m}\right)\delta_{ij}\delta_{ab}\tilde{\Psi}_b(t) = \exp\left(-\frac{i\Delta t}{2\hbar}\frac{k_i^2}{2m}\right)\tilde{\Psi}_a(t)$$

Solution of the TD-SE: Colbert-Miller

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Colbert, D. T.; Miller, W. H. A *The Journal of Chemical Physics* **1992**, *96*, 1982–1991.

DVR grid points: $x_i = a + \frac{b-a}{N} i, i = 1,2, \ldots N-1$

Associated DVR functions: $\phi_n(x) = \sqrt{\frac{2}{b-a}} \sin\left(\frac{\pi n(x-a)}{b-a}\right)$ $, n = 1,2, \ldots N-1$ – particle-in-the-box eigenfunctions

Boundary conditions: $\phi_n(x_0 = a) = \phi_n(x_N = b) = 0$

$$T_{i,j} = -\frac{\hbar^2}{2m}\Delta x \sum_{n=1}^{N-1} \phi_n(x_i)\phi_n''(x_j) = \frac{\hbar^2}{2m}\left(\frac{2}{b-a}\right)^2 \frac{2}{N}\sum_{n=1}^{N-1} n^2 \sin\left(\frac{n\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right) = \begin{cases} \frac{\hbar^2}{2m}\frac{(-1)^{i-j}}{(b-a)^2}\frac{\pi^2}{2}\left\{\frac{1}{\sin^2(\pi(i-j)/2N)} - \frac{1}{\sin^2(\pi(i+j)/2N)}\right\}, i \neq j \\ \frac{\hbar^2}{2m}\frac{1}{(b-a)^2}\frac{\pi^2}{2}\left\{(2N^2+1)/3 - \frac{1}{\sin^2(\pi i/2N)}\right\}, i = j \end{cases}$$

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T = wfc.operator_T(Py2Cpp_int([1]), masses, 1.0+0.0j)
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Then special cases are considered:

bc_type = 0: (a, b) - finite boundaries

bc_type = 1: $(-\infty, +\infty)$ - assume finite boundaries

bc_type = 2: $(0, +\infty)$ -e.g. for radial grids

This is the default for 1D case
In principle, need a more general implementation
BC can be different for each DOF