Electron-ion entanglement and decoherence dynamics in trans-polyacetylene oligomers

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Outline

Correlated electron-ion dynamics

- Jordan-Wigner transform and exact diagonalization in Fock-Space
- Electron-ion correlation in trans-polyacetylene oligomers (SSH chains)

Electron-ion coupling: system-bath perspective

- Electrons vs. ions: Who is causing decoherence for whom?
- Connection to stochastic Schrödinger equation

Bi-linear electron-ion coupling

- Perimetric coordinates, reference system
- Accuracy of bi-linear electron-ion coupling?

Fock-Space representation of Fermionic and Bosonic operators

Jordan-Wigner Transformation: Represent Fermionic operators with spin matrices

Anihilation Operators

$$\hat{c}_1 = 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes \sigma_+$$
$$\hat{c}_2 = 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes \sigma_+ \otimes \sigma_z$$
$$\hat{c}_3 = 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes \sigma_+ \otimes \sigma_z \otimes \sigma_z$$
$$\hat{c}_4 = 1_2 \otimes \cdots \otimes 1_2 \otimes \sigma_+ \otimes \sigma_z \otimes \sigma_z \otimes \sigma_z$$
$$\cdots$$

Creation Operators: Replace σ_+ by σ_-

The matrices constructed in this way obey the usual fermionic anti-commutation relations:

$$\{\hat{c}_i, \hat{c}_j\} = 0$$
$$\{\hat{c}_i^\dagger, \hat{c}_j^\dagger\} = 0$$
$$\{\hat{c}_i, \hat{c}_j^\dagger\} = \delta_{i,j}$$

Fock-Space representation of Fermionic and Bosonic operators

Bosonic operators

$$b_s = \begin{bmatrix} 0 & \sqrt{1} & 0 & \cdots & 0 \\ 0 & 0 & \sqrt{2} & \cdots & 0 \\ \cdots & & & & \cdots \\ 0 & 0 & 0 & \cdots & \sqrt{s-1} \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix} \quad b_s^\dagger = \begin{bmatrix} 0 & \cdots & 0 & 0 & 0 \\ \sqrt{1} & \cdots & 0 & 0 & 0 \\ \cdots & & & & \cdots \\ 0 & \cdots & \sqrt{s-2} & 0 & 0 \\ 0 & \cdots & 0 & \sqrt{s-1} & 0 \end{bmatrix}$$

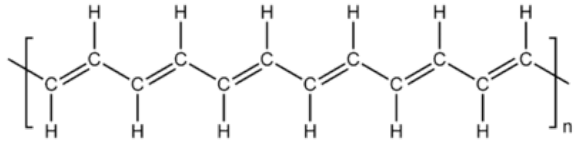
Operators in the combined space: Tensor product!

$$\hat{c}_1^\dagger = 1_s \otimes \cdots 1_s \otimes 1_s \otimes 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes \sigma_-$$
$$\hat{c}_2^\dagger = 1_s \otimes \cdots 1_s \otimes 1_s \otimes 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes \sigma_- \otimes \sigma_z$$
$$\cdots$$

$$\hat{b}_1^\dagger = 1_s \otimes \cdots 1_s \otimes b_s^\dagger \otimes 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2$$
$$\hat{b}_2^\dagger = 1_s \otimes \cdots b_s^\dagger \otimes 1_s \otimes 1_2 \otimes \cdots \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2 \otimes 1_2$$
$$\cdots$$

Su-Schrieffer-Heeger Hamiltonians for polyacetylene oligomers

Trans-polyacetylene



Su-Schrieffer-Heeger Hamiltonian

$$\hat{H}_{\mathrm{elec}} = \sum_{n=1}^{N-1} \sum_{\sigma=\pm 1} -t_0 (\hat{c}^{\dagger}_{n+1,\sigma} \hat{c}_{n,\sigma} + \hat{c}^{\dagger}_{n,\sigma} \hat{c}_{n+1,\sigma})$$

$$\hat{H}_{\mathrm{ph}} = \sum_{n=2}^{N-1} \frac{p_n^2}{2M} + \frac{K}{2} \sum_{n=2}^{N-1} (u_{n+1} - u_n)^2$$

$$\hat{H}_{\mathrm{el-ph}} = \sum_{n=1}^{N-1} \sum_{\sigma=\pm 1} \alpha (u_{n+1} - u_n)(\hat{c}^{\dagger}_{n+1,\sigma} \hat{c}_{n,\sigma} + \hat{c}^{\dagger}_{n,\sigma} \hat{c}_{n+1,\sigma})$$

W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 16981701 (1979).

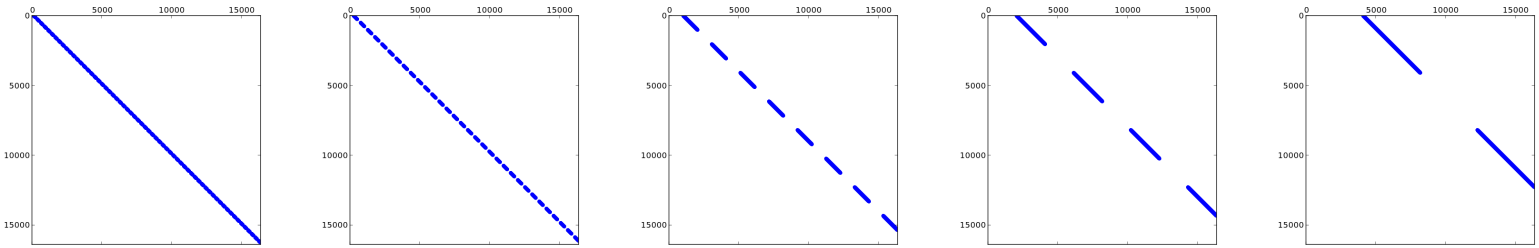
Typically solved with quantum-classical approaches.

In the following:

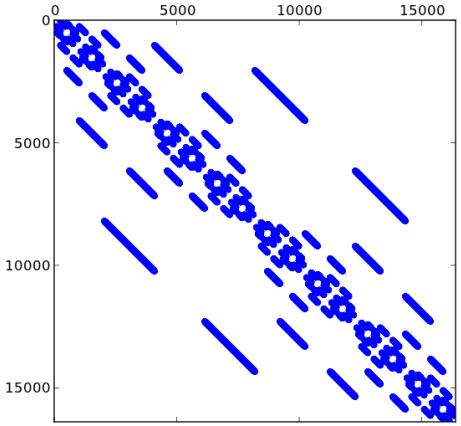
Fully quantum-mechanical SSH chains (small N) without Born-Oppenheimer approximation

Sparse Matrix representation of operators in Fock-Space

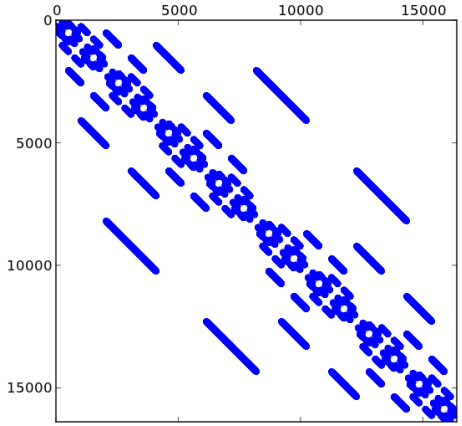
Fermionic creation operators



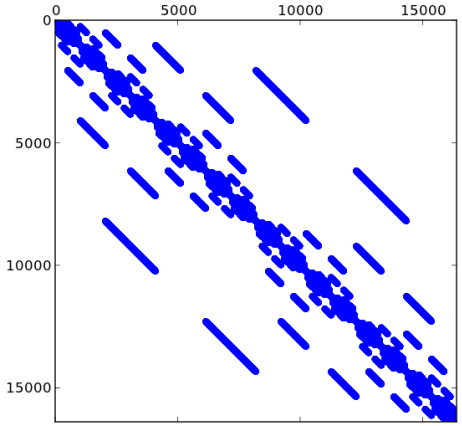
Fermion Hamiltonian



Fermion-Boson Interaction



Full Hamiltonian



Dimensions used in the plots: $4^4 \times 8^2 = 16384$ (4 Fermionic sites and 2 Bosonic sites with s=8)

Of course: exponential wall of many-body problem!

Su-Schrieffer-Heeger Hamiltonians for polyacetylene oligomers

Exact diagonalization of $\hat{H} = \hat{H}_{\mathrm{elec}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{el-ph}}$ in Fock space

$$\hat{H} \,|\, \psi_k \,\rangle = E_k \,|\, \psi_k \,\rangle$$

Fermionic N-body density matrix from eigenstates $|\, \psi_k \,\rangle$

$$\rho_F^k(t) = Tr_{\mathrm{Bosons}}(\,|\, \psi_k \,\rangle\langle\, \psi_k \,|\,)$$

(Note: can have different particle numbers (Fock space)) Bosonic N-body density matrix

$$\rho_B^k(t) = Tr_{\mathrm{Fermions}}(\,|\, \psi_k \,\rangle\langle\, \psi_k \,|\,)$$

Time-evolution of Fock space states from TDSE

$$i\partial_t \,|\, \psi(t) \,\rangle = \hat{H} \,|\, \psi(t) \,\rangle, \qquad |\, \psi(t=0) \,\rangle = |\, \psi_0 \,\rangle$$

Partial traces

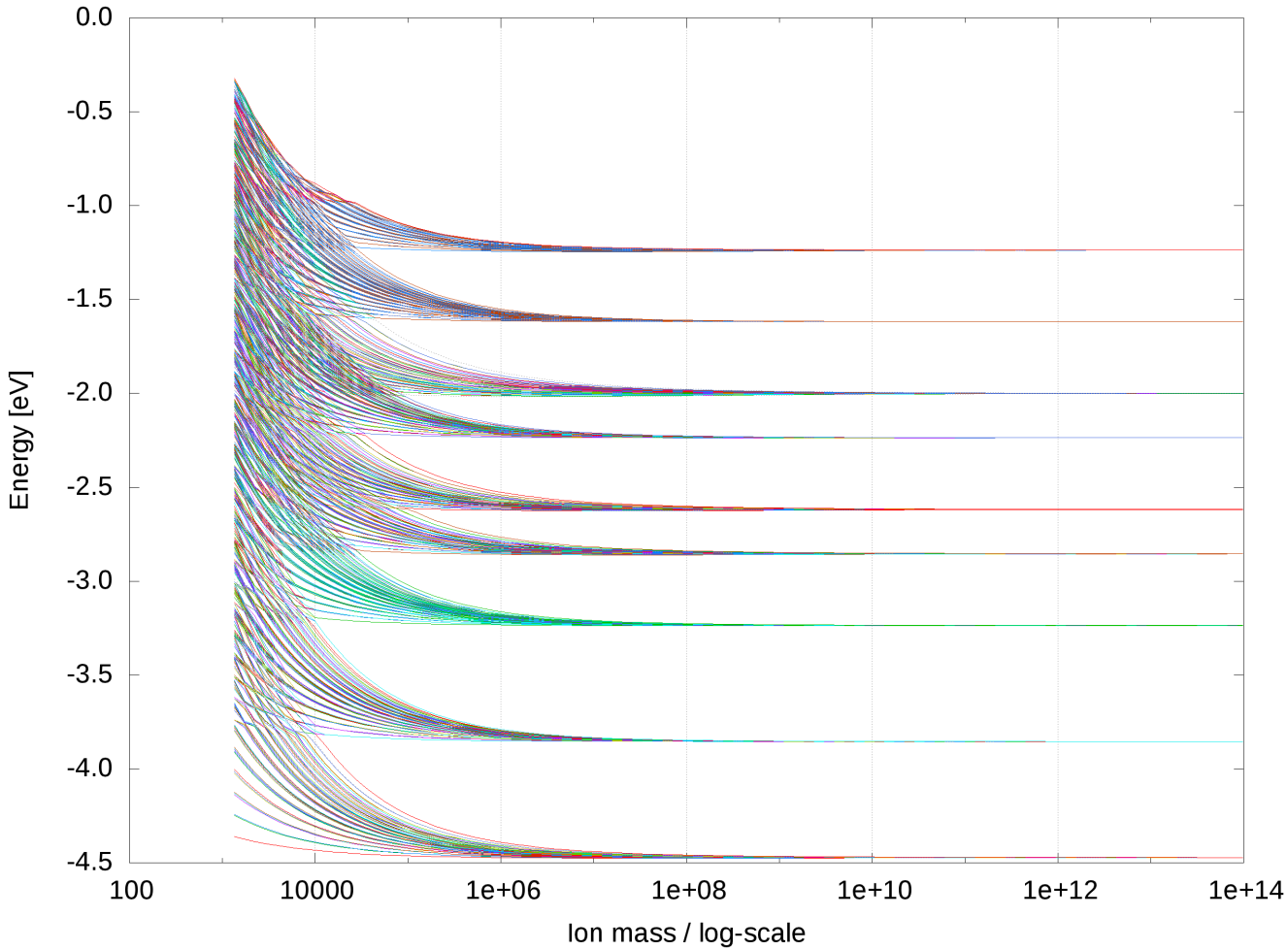
$$\rho_F(t) = Tr_{\mathrm{Bosons}}(\,|\, \psi(t) \,\rangle\langle\, \psi(t) \,|\,)$$
$$\rho_B(t) = Tr_{\mathrm{Fermions}}(\,|\, \psi(t) \,\rangle\langle\, \psi(t) \,|\,)$$

ELPA dense eigenvalue solver - http://elpa.rzg.mpg.de/

ScaLapack drop-in replacement, LGPL license

Dense-matrix diagonalization of up to 200.000 x 200.000 SSH chain matrices possible

Energy spectrum as function of ion mass



Lowest 4096 levels of the SSH Hamiltonian as function of the ion-mass

Carlson-Keller theorem - Phys. Rev. 121, 659

PHYSICAL REVIEW VOLUME 121, NUMBER 3 FEBRUARY 1, 1961

Eigenvalues of Density Matrices*

B. C. CARLSON AND JOSEPH M. KELLER
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
(Received September 8, 1960)

For a system of N identical particles in a pure bound state, the density matrices of positive orders p and $N-p$ have the same nonzero eigenvalues with the same multiplicities. If the number of nonzero eigenvalues is finite, these density matrices are unitarily equivalent.

$$\gamma_p(1,...,p;1',...,p') := \binom{N}{p} \int \Psi(1,\ldots,p,p+1,\ldots,N)\Psi^*(1',\ldots,p',(p+1),\ldots,N)\, d^3(p+1)\ldots d^3N$$

$\gamma_p(1,...,p;1',...,p')$ and $\gamma_{N-p}(1,...,N-p;1',...,N-p')$ have the same nonzero eigenvalues.

Carlson-Keller theorem for electron-ion wavefunctions

Identical particles:

$$\gamma_p(r_1,...,r_p;r'_1,...,r'_p) :=$$
$$\left(\begin{array}{c} N \\ p \end{array} \right) \int \Psi(r_1,\ldots,r_p,r_{p+1},\ldots,r_{N_\mathrm{e}})\Psi^*(r'_1,\ldots,r'_p,r_{(p+1)},\ldots,r_{N_\mathrm{e}})\, d^3r_{(p+1)}\ldots d^3r_{N_\mathrm{e}}$$

Electron-ion system:
Trace over ionic coordinates

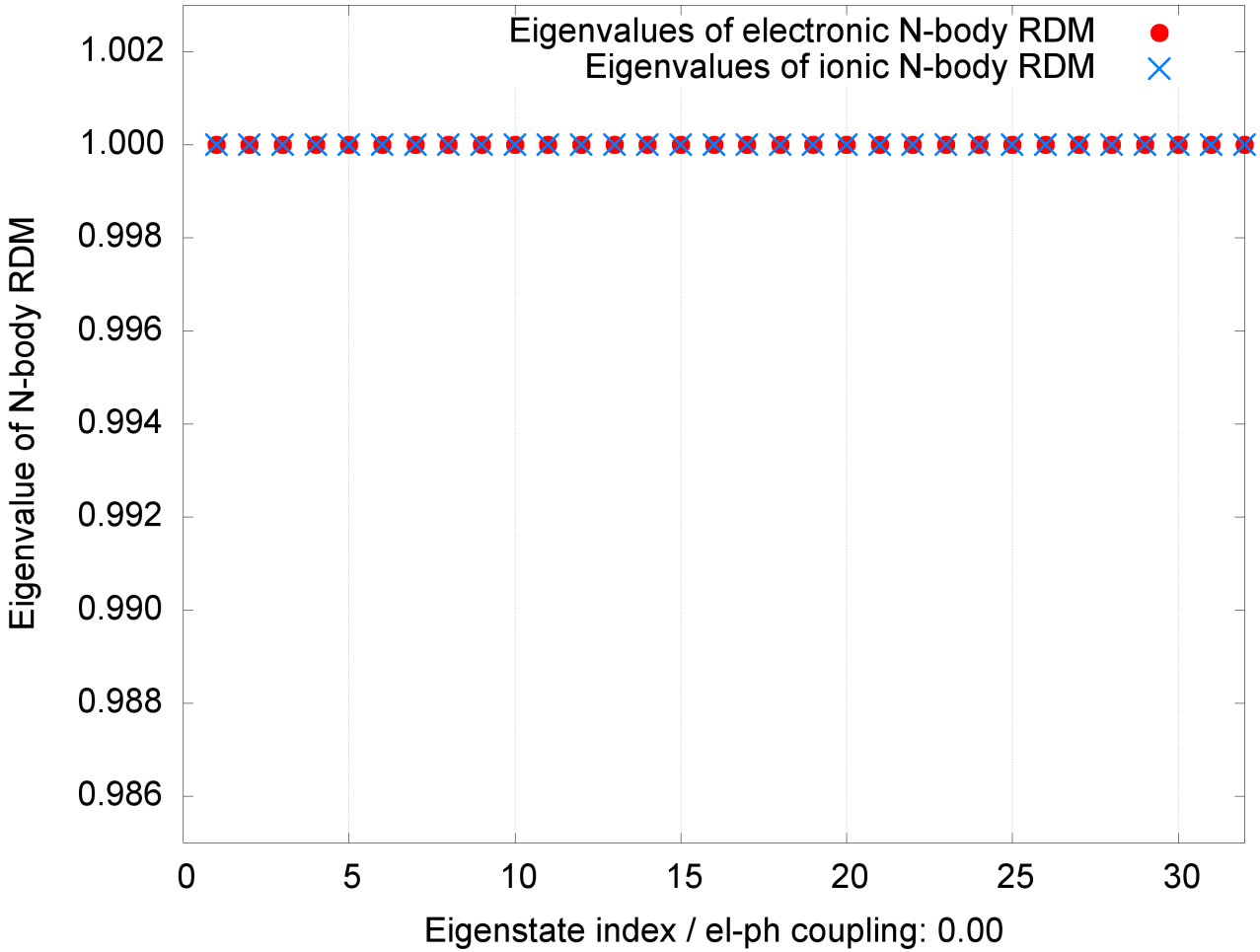
$$\gamma_p(r_1,...,r_{N_\mathrm{e}};r'_1,...,r'_{N_\mathrm{e}}) :=$$
$$\int \Psi(r_1,\ldots,r_{N_\mathrm{e}};R_1,\ldots,R_{N_\mathrm{n}})\Psi^*(r'_1,\ldots,r_{N_\mathrm{e}};R_1,\ldots,R_{N_\mathrm{n}})\, d^3R_1\ldots d^3R_{N_\mathrm{n}}$$

Trace over electronic coordinates

$$\gamma_q(R_1,...,R_{N_\mathrm{n}};R'_1,...,R'_{N_\mathrm{n}}) :=$$
$$\int \Psi(r_1,\ldots,r_p;R_1,\ldots,R_{N_\mathrm{n}})\Psi^*(r'_1,\ldots,r'_p;R_1,\ldots,R_{N_\mathrm{e}})\, d^3r_1\ldots d^3r_{N_\mathrm{e}}$$

Carlson-Keller theorem for correlated electron-ion states

The Carlson-Keller theorem seems to hold also for correlated electron-ion eigenstates of the combined electron-ion Hamiltonian.



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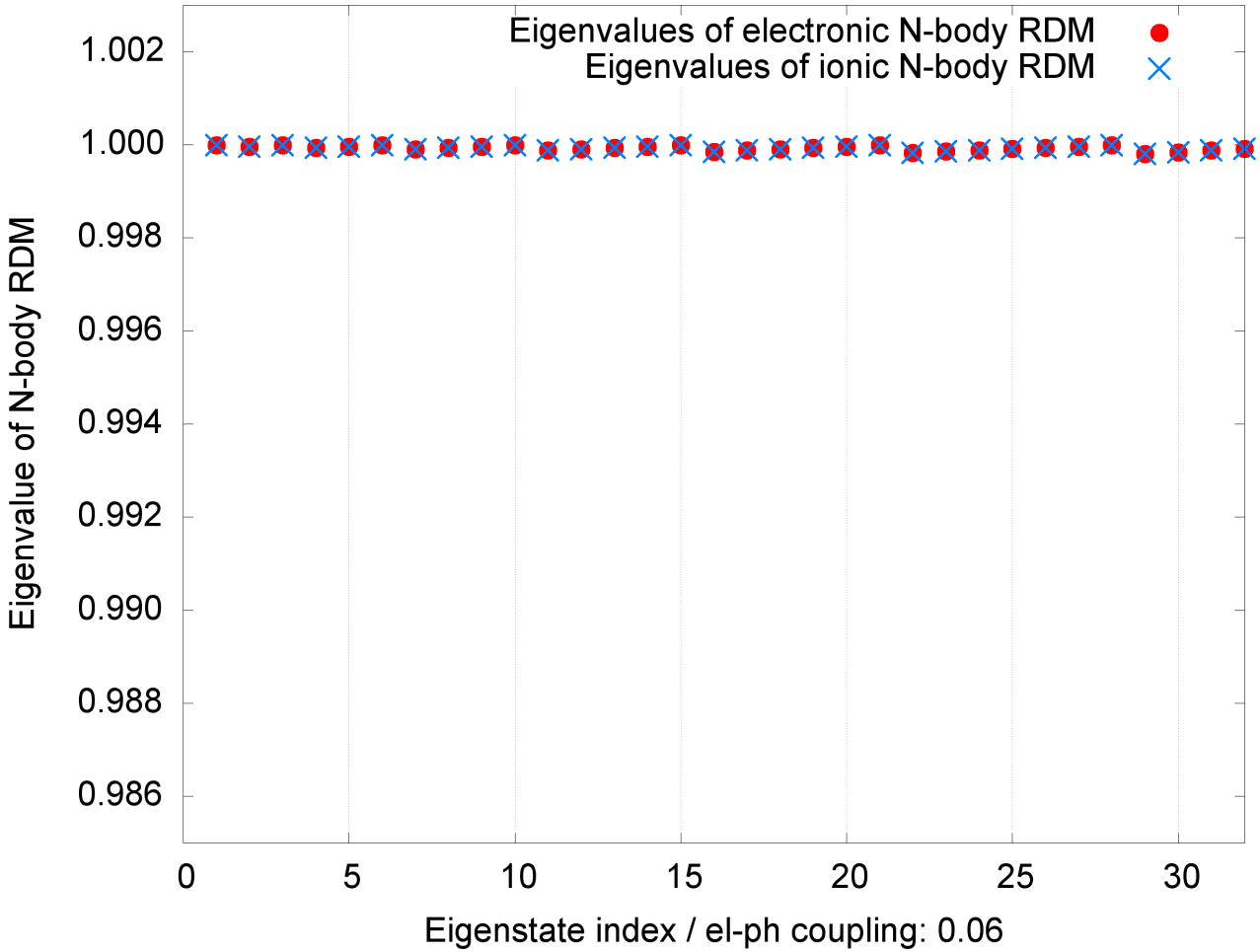

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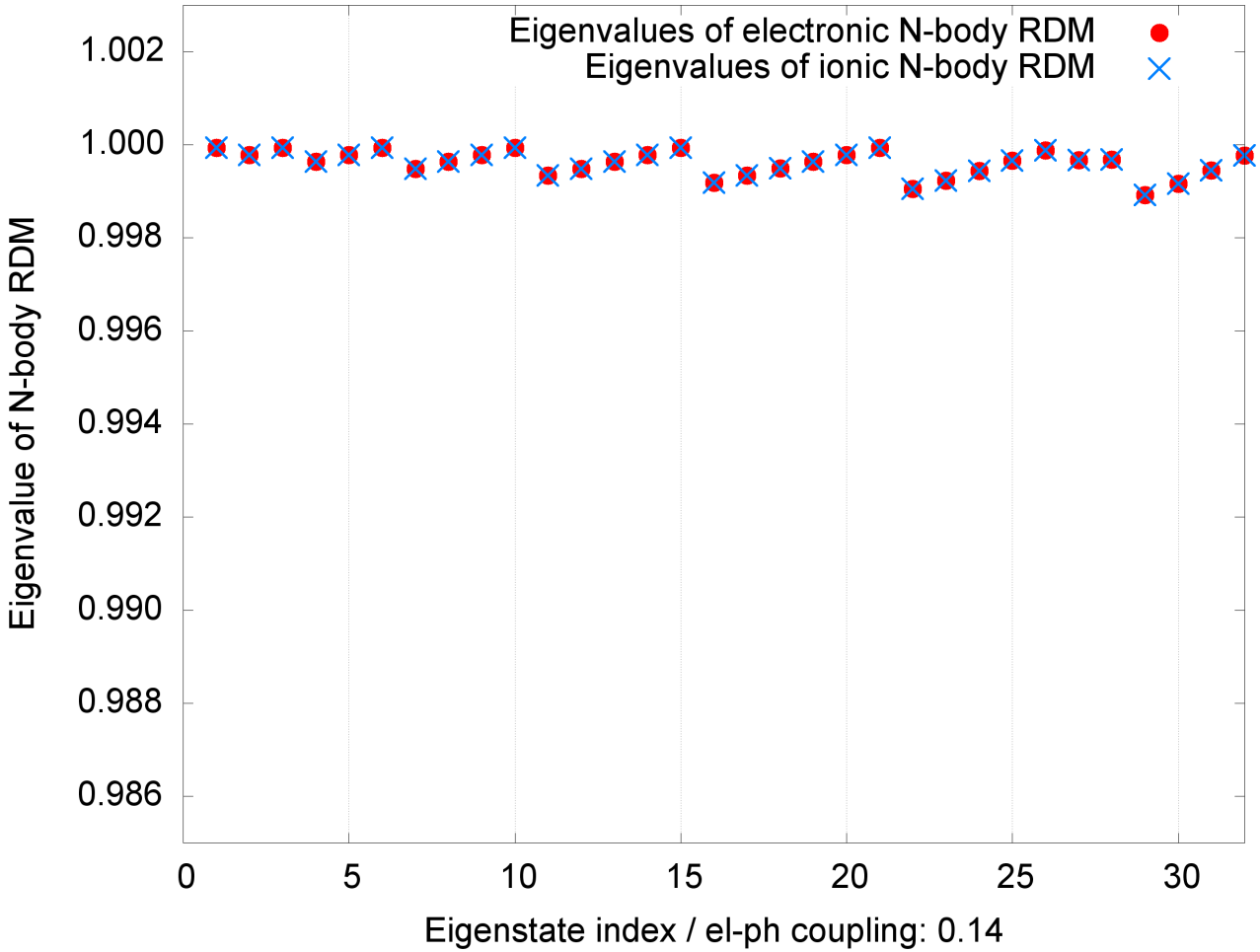

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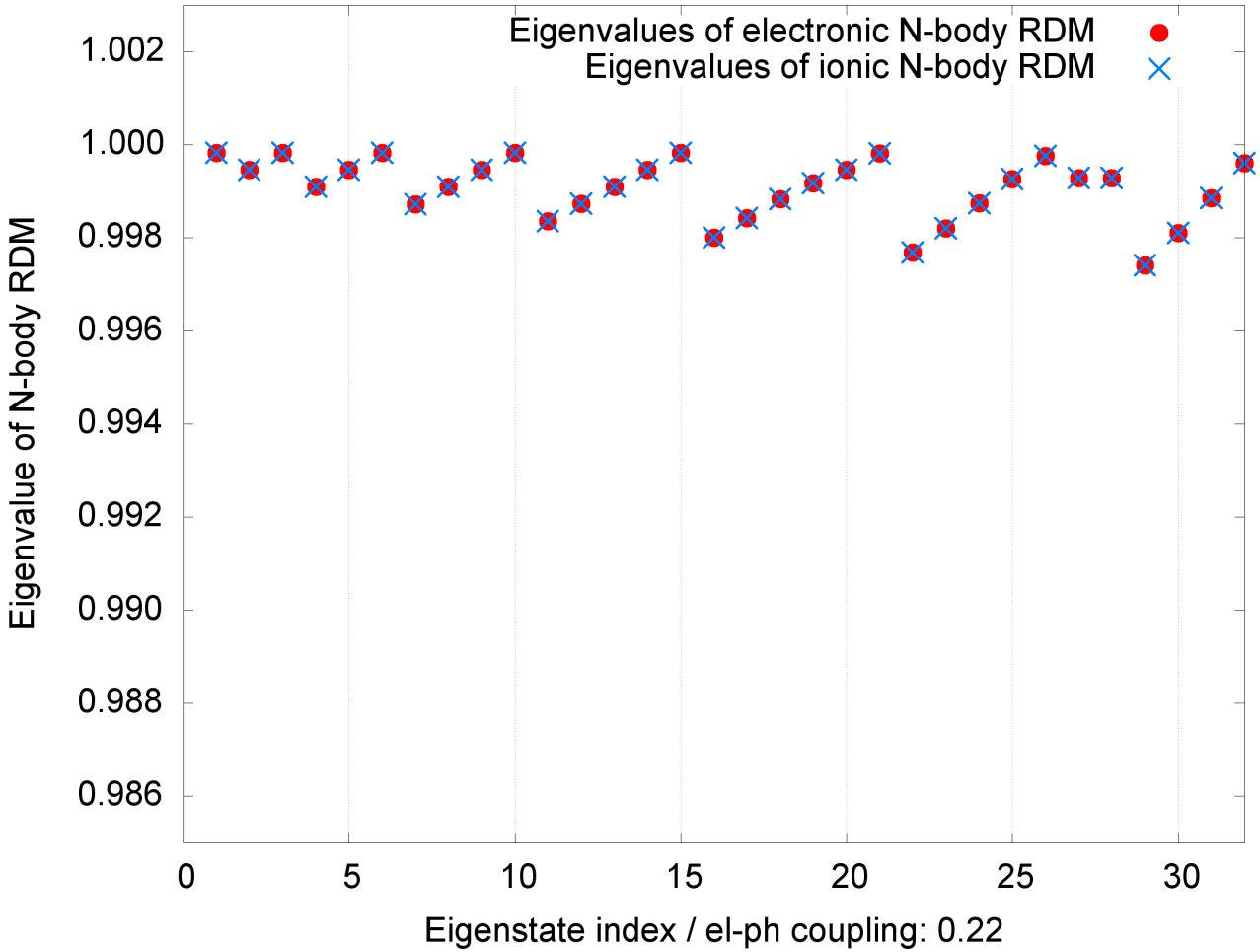

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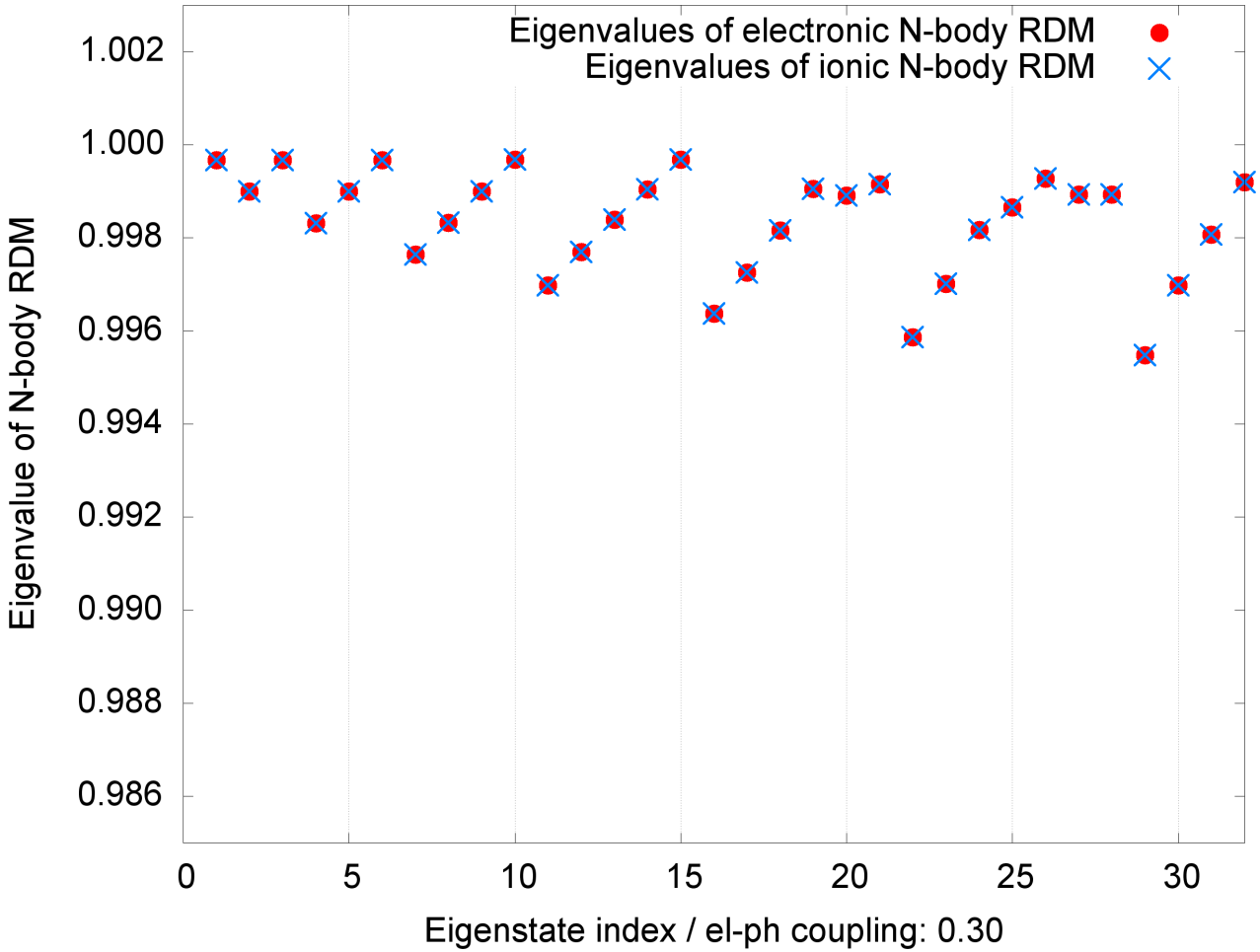

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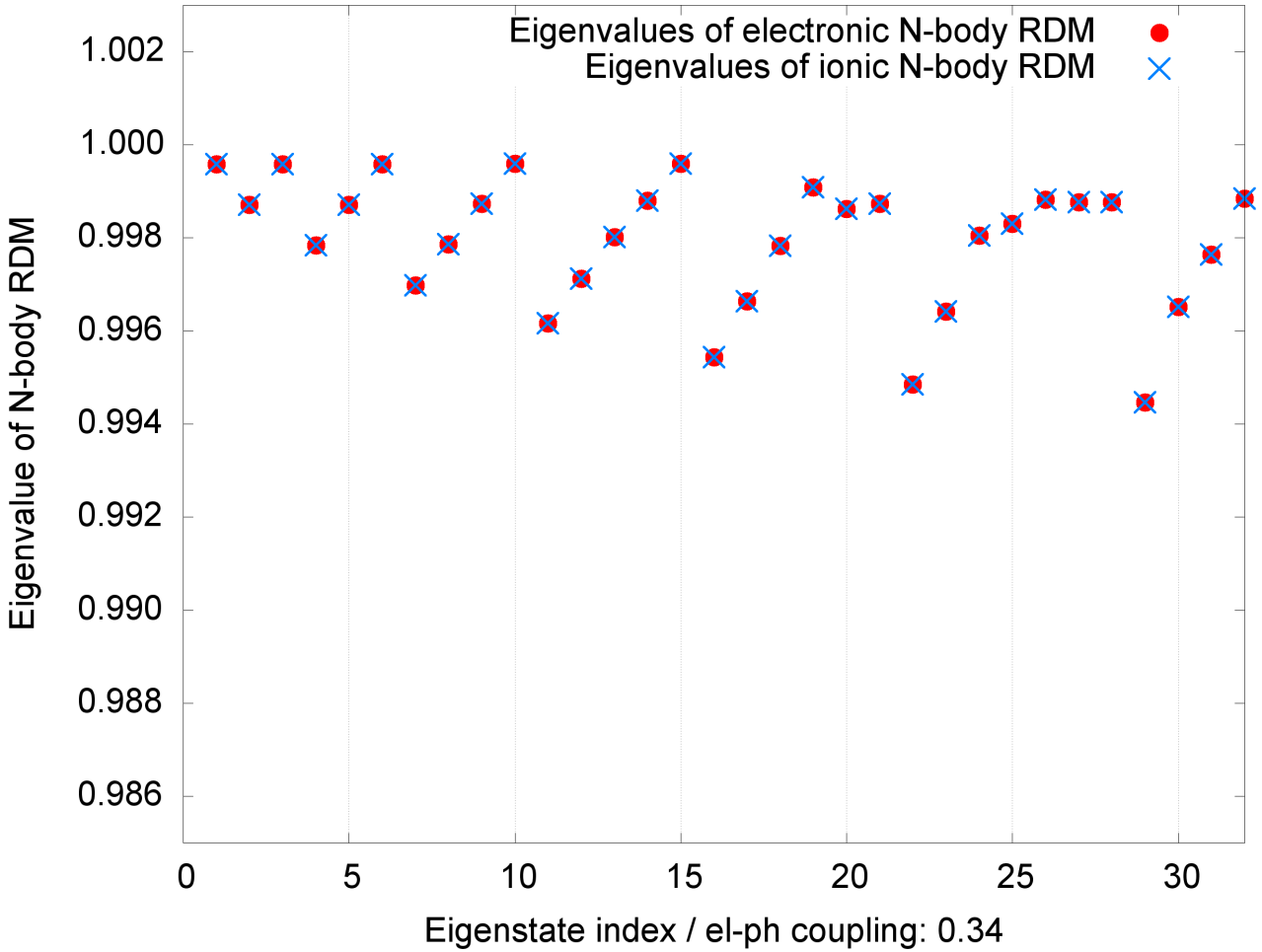

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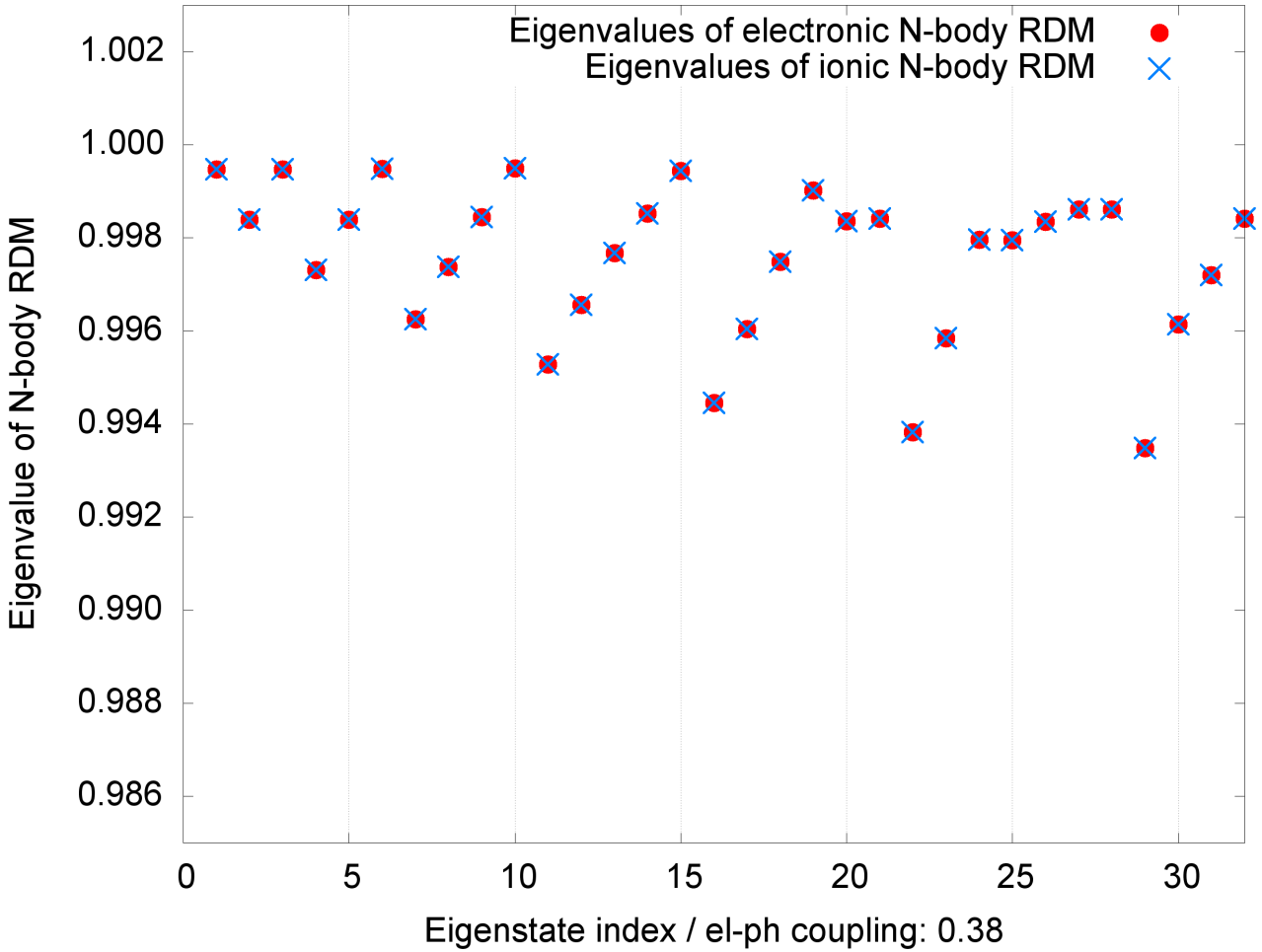

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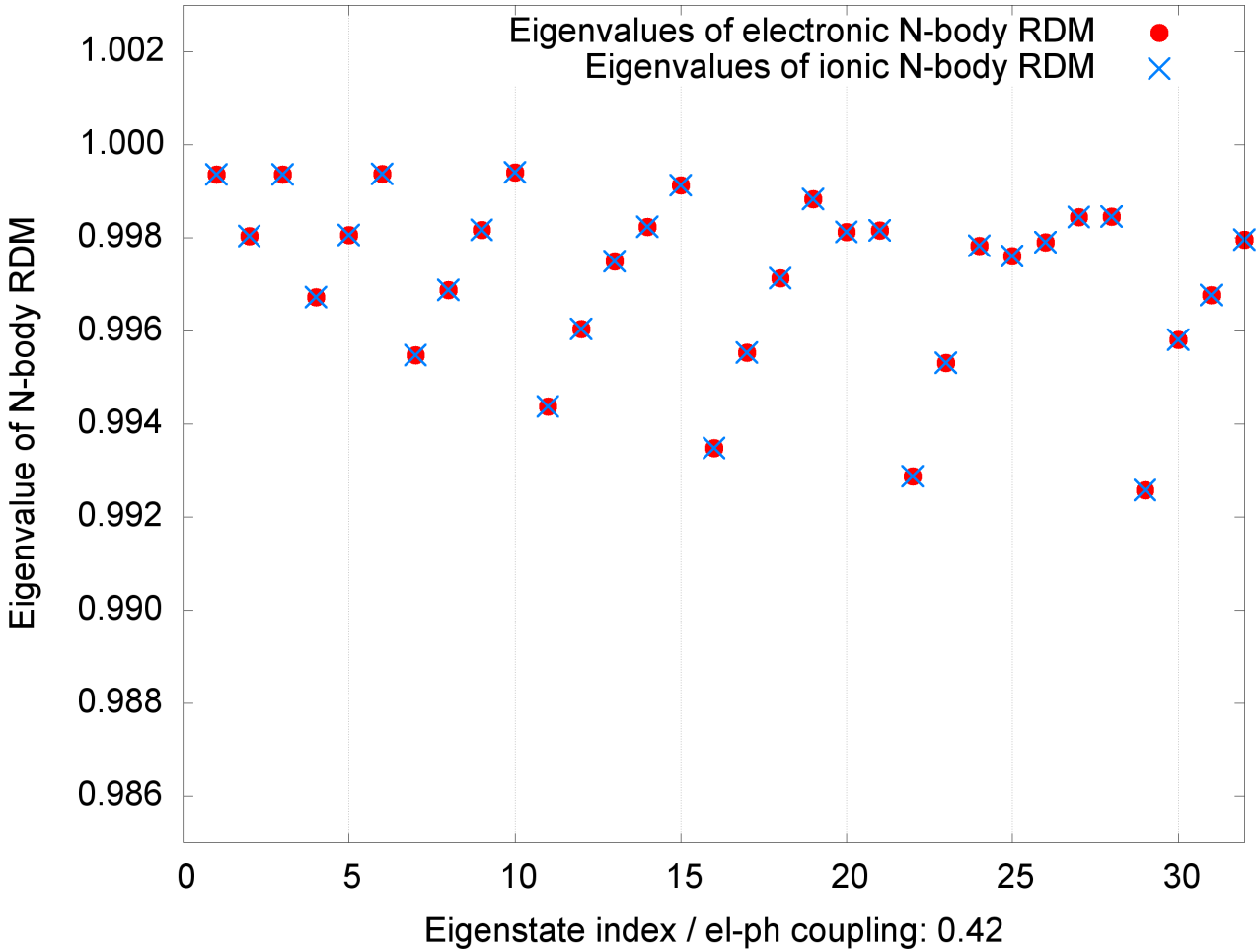

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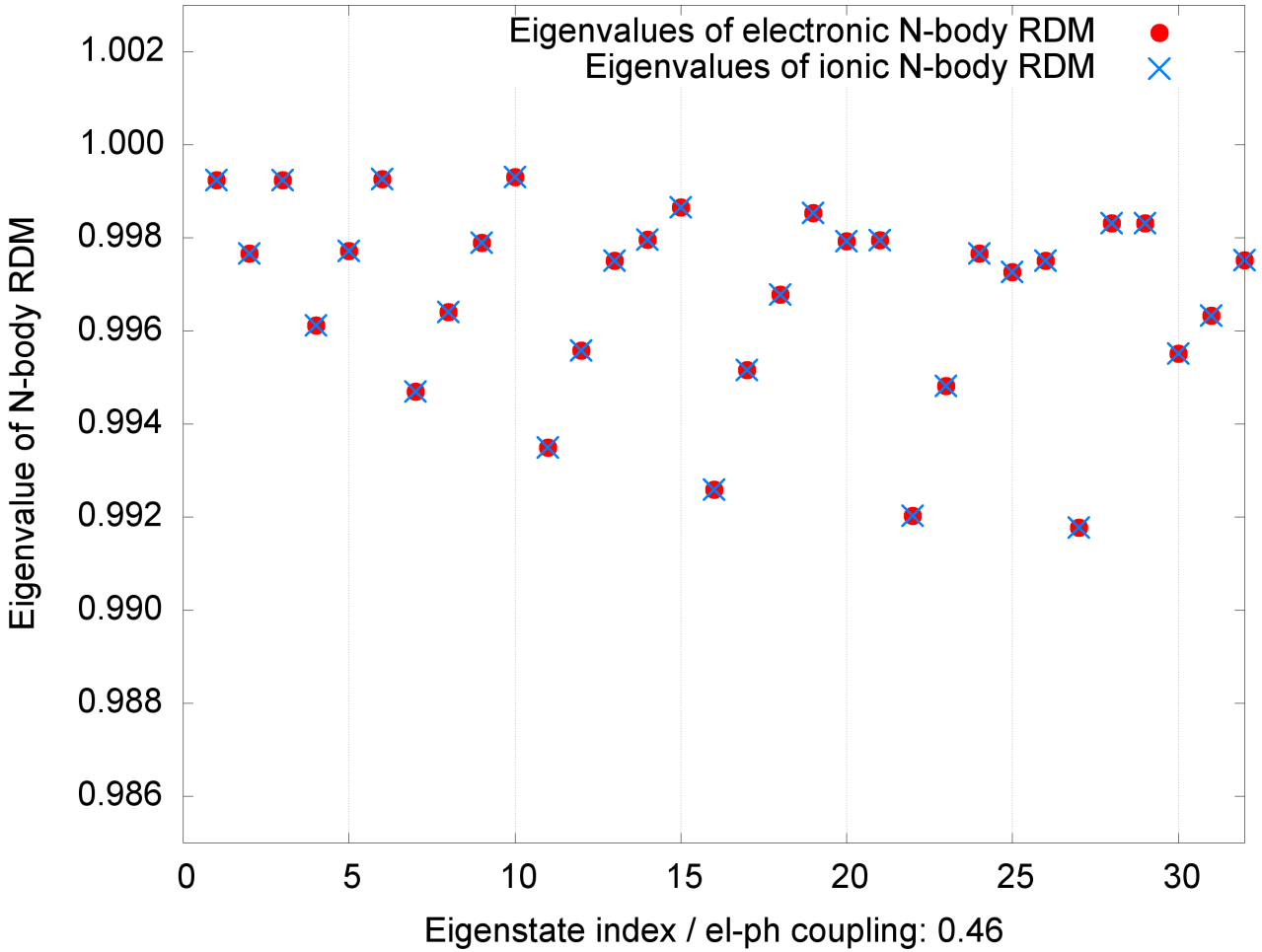

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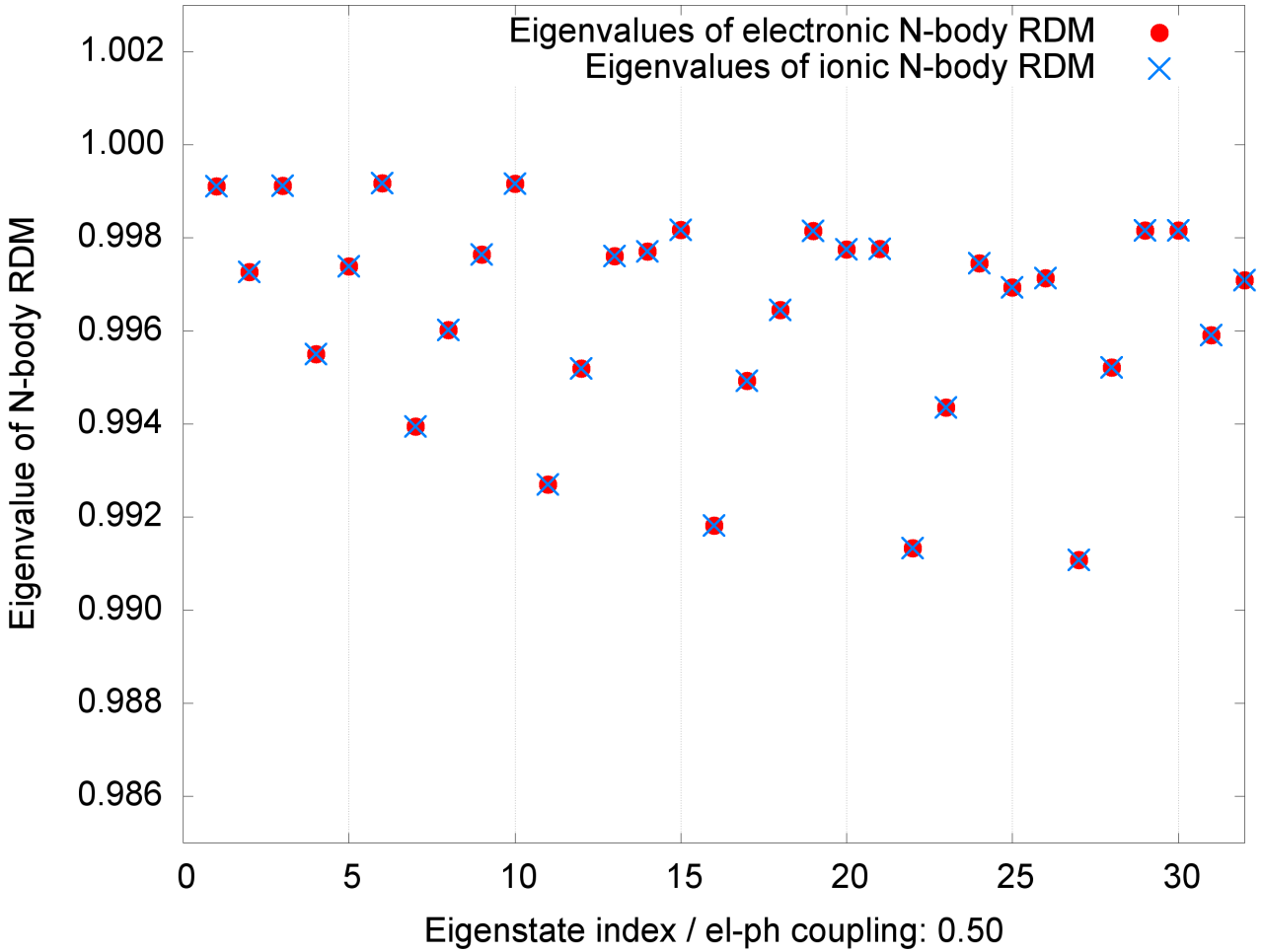

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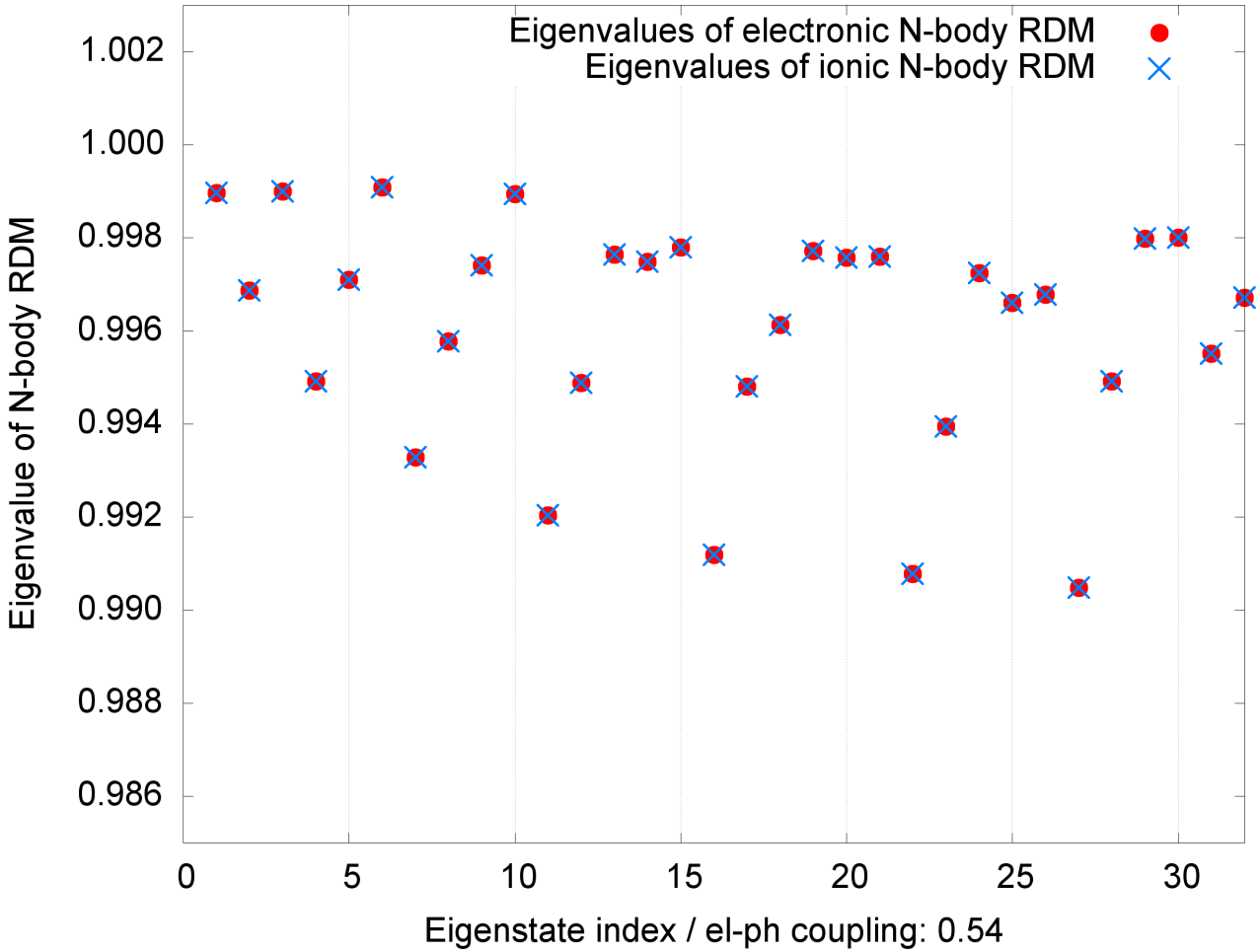

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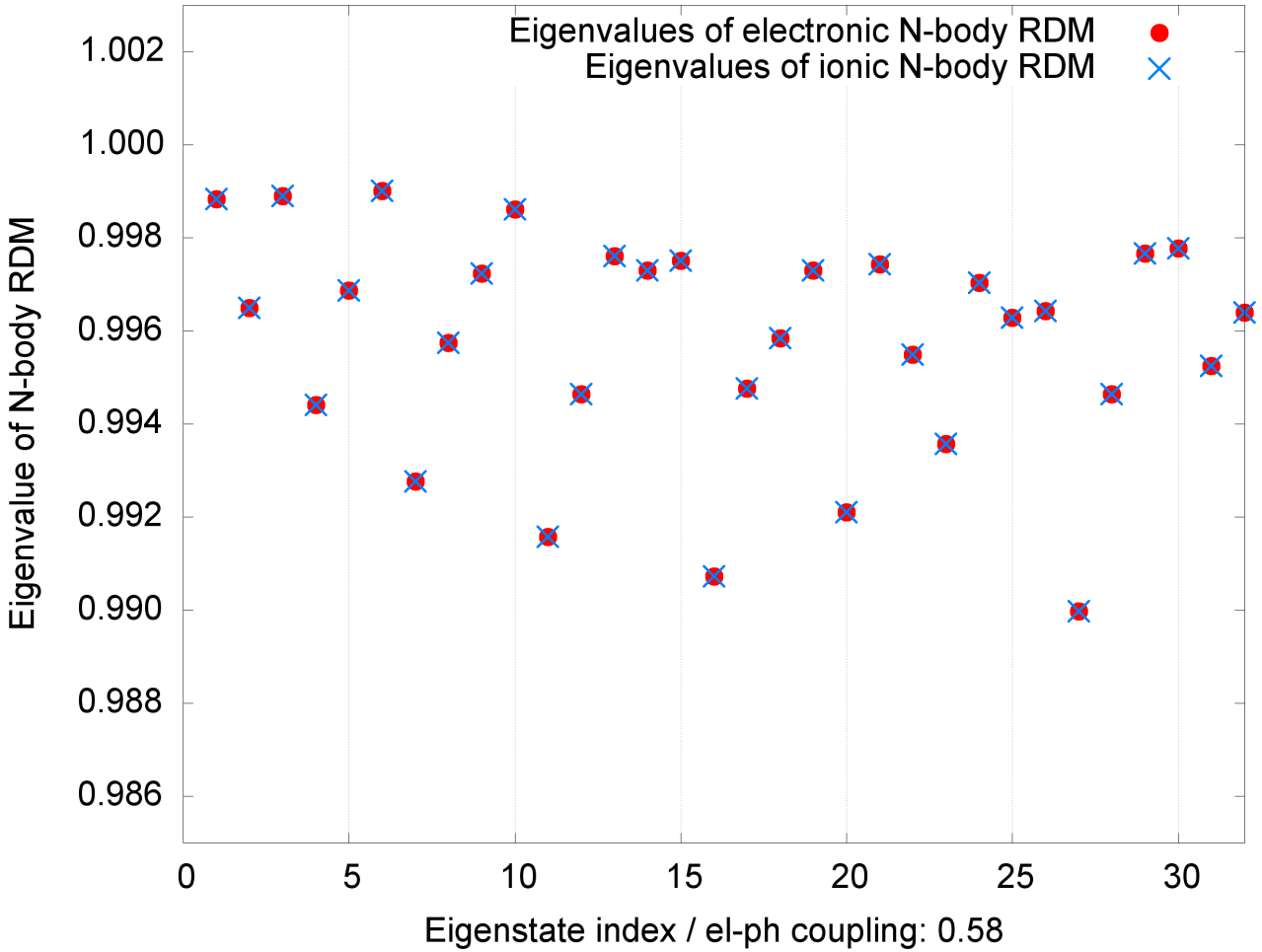

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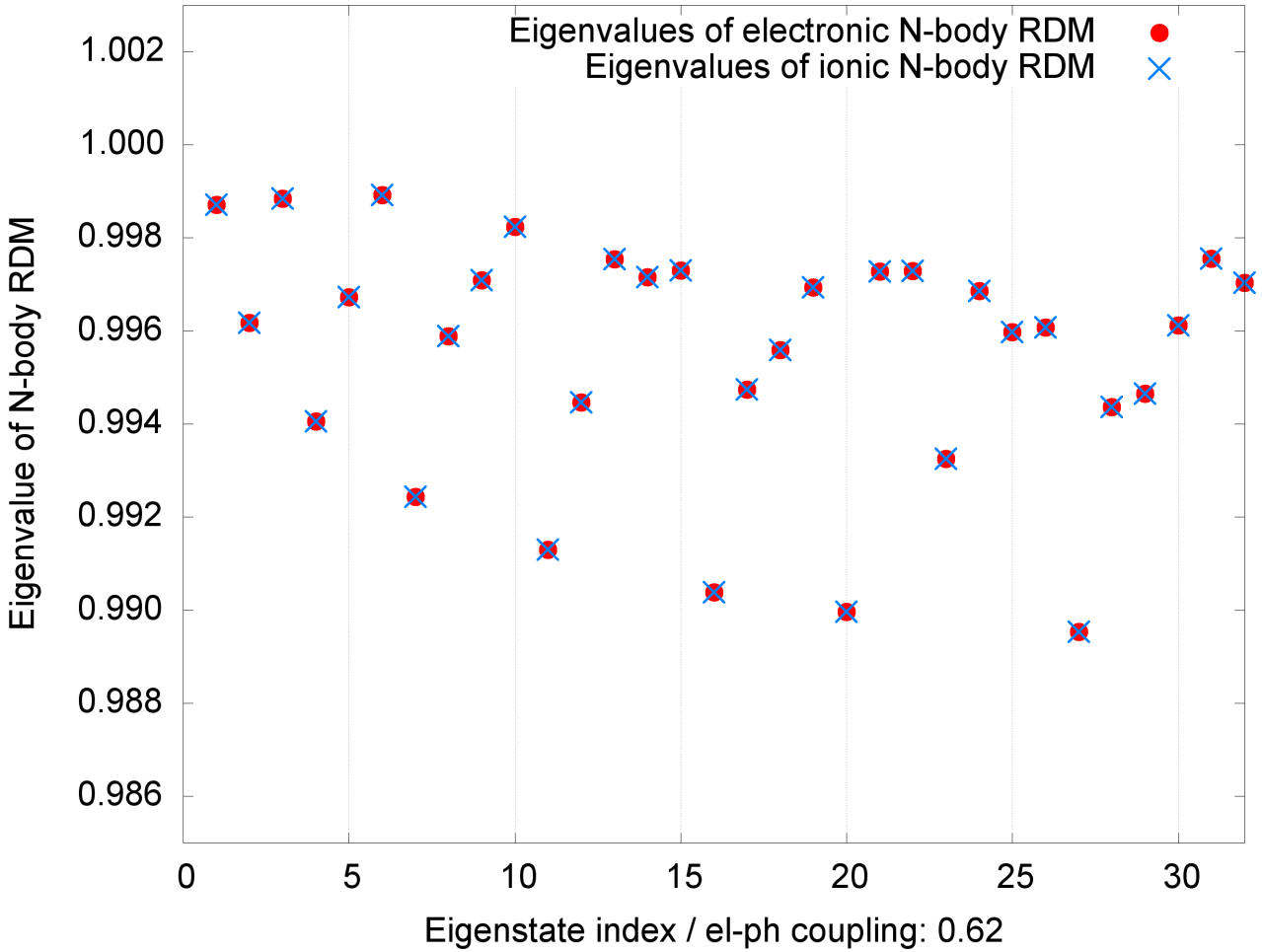

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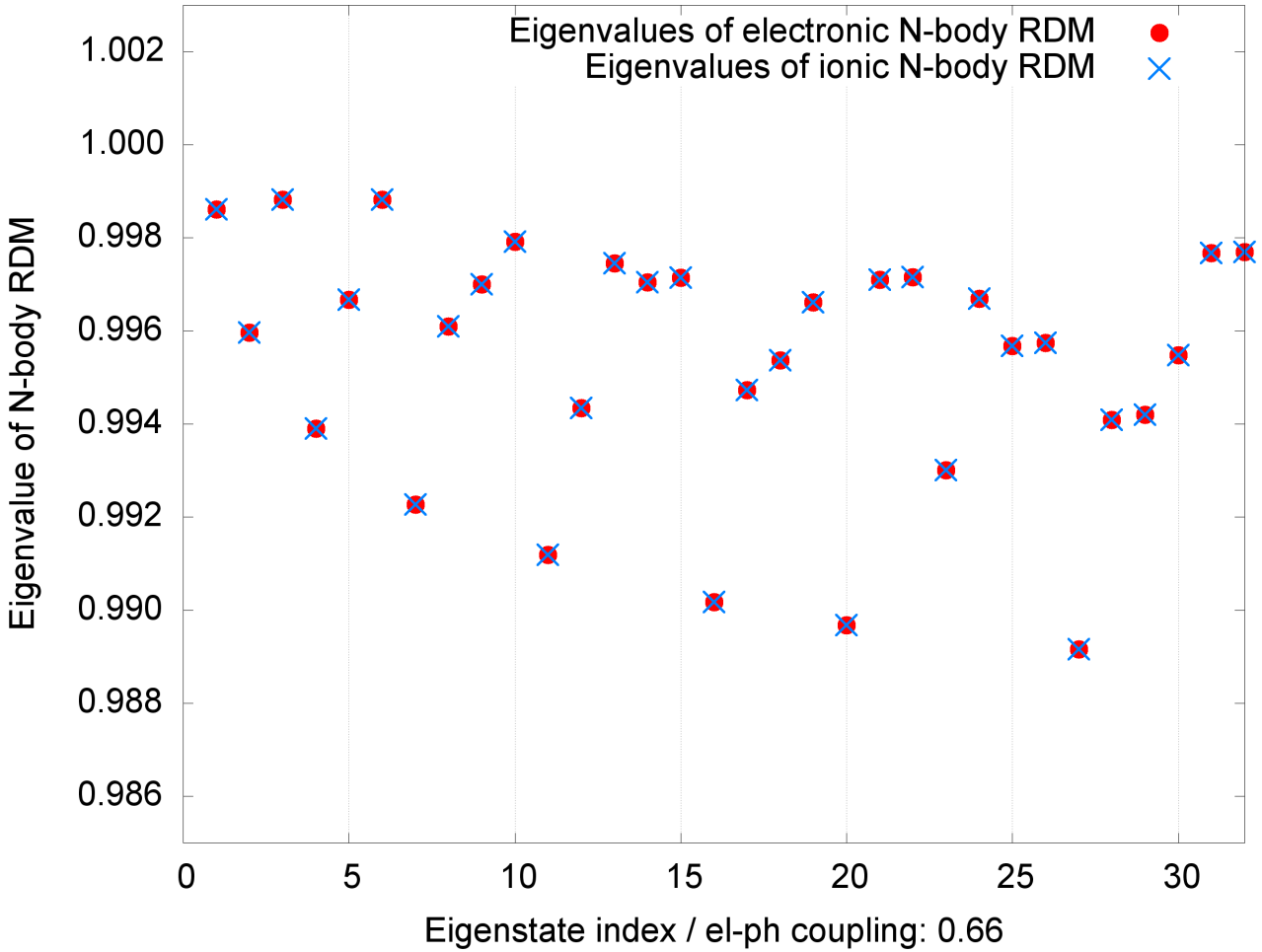

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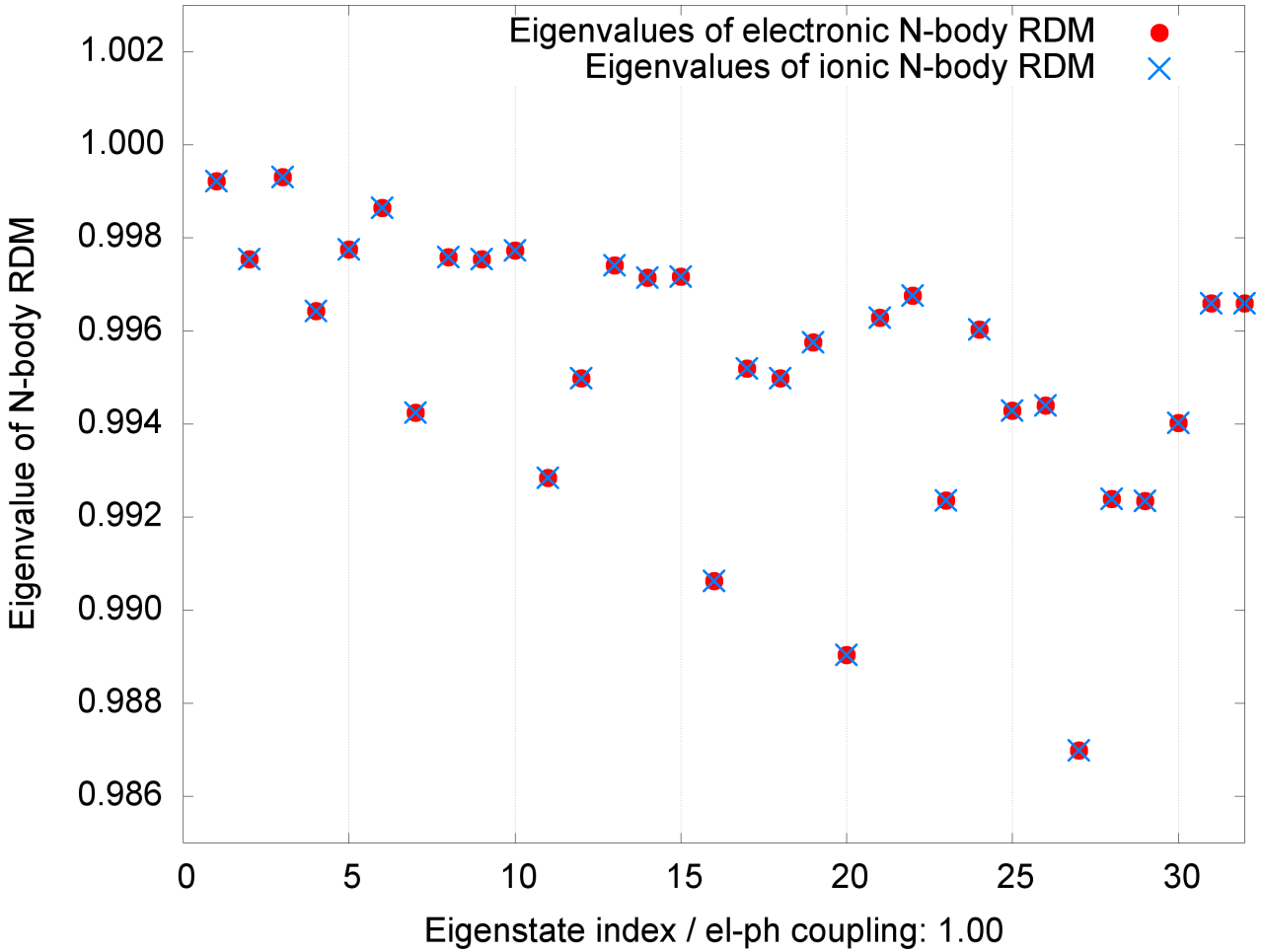
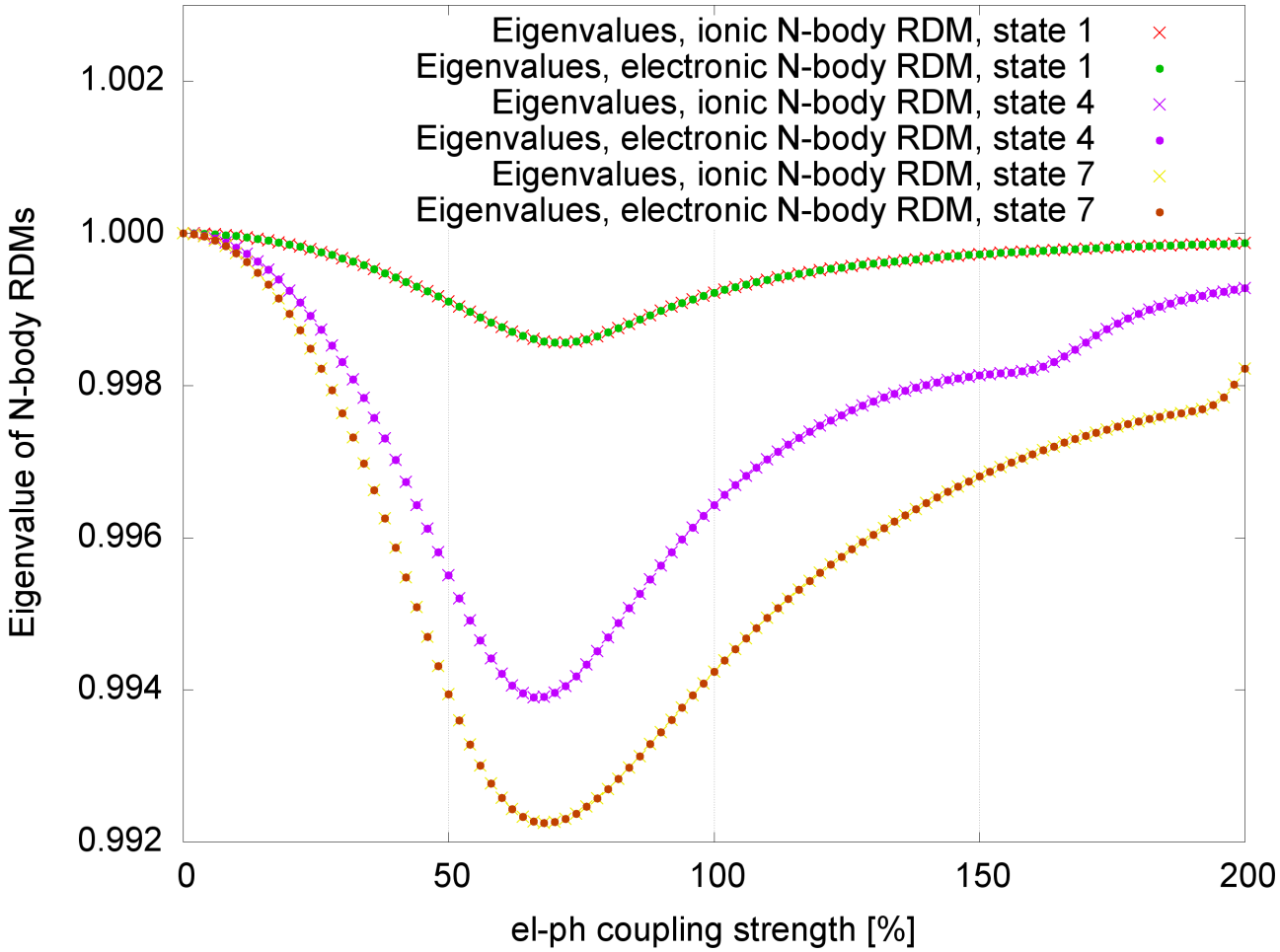


Occupation numbers of N-body RDM vs. el.-ph. coupling strength



Eigenvalues of the electronic N-body RDM of the SSH Hamiltonian as function of the electron-phonon coupling strength

Schmidt decomposition of electron-ion wavefunction

$$|\,\Psi(\underline{r},\underline{\underline{R}};t)\,\rangle = \sum_j \sqrt{\lambda_j(t)}\,|\,\Phi_j(\underline{r};t)\,\rangle\,|\,\chi_j(\underline{\underline{R}};t)\,\rangle$$

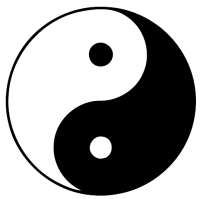
Note: no parametric dependence on $\underline{\underline{R}}$ for $\Phi_j(\underline{r};t)$

Tracing over nuclear coordinates of pure-state density matrix

$$\begin{aligned}\hat{\rho}_F(\underline{r};t) &= Tr_{\underline{R}}(\,|\,\Psi(\underline{r},\underline{\underline{R}};t)\,\rangle\langle\,\Psi(\underline{r},\underline{\underline{R}};t)\,|\,)\\ &= \sum_j \lambda_j(t)\,|\,\Phi_j(\underline{r};t)\,\rangle\langle\,\Phi_j(\underline{r};t)\,|\end{aligned}$$

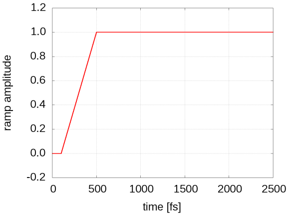
Tracing over electronic coordinates of pure-state density matrix

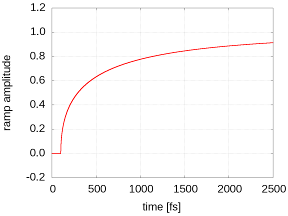
$$\begin{aligned}\hat{\rho}_B(\underline{\underline{R}};t) &= Tr_{\underline{r}}(\,|\,\Psi(\underline{r},\underline{\underline{R}};t)\,\rangle\langle\,\Psi(\underline{r},\underline{\underline{R}};t)\,|\,)\\ &= \sum_j \lambda_j(t)\,|\,\chi_j(\underline{\underline{R}};t)\,\rangle\langle\,\chi_j(\underline{\underline{R}};t)\,|\end{aligned}$$

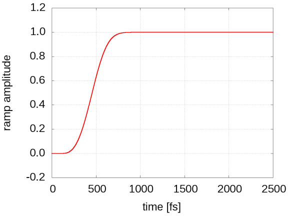


Ramp shapes for time-dependent perturbations

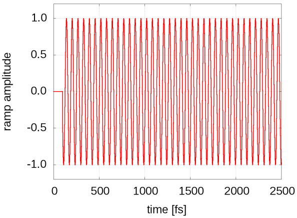
TD ramps for switch-on

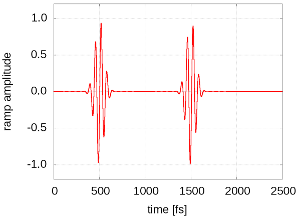




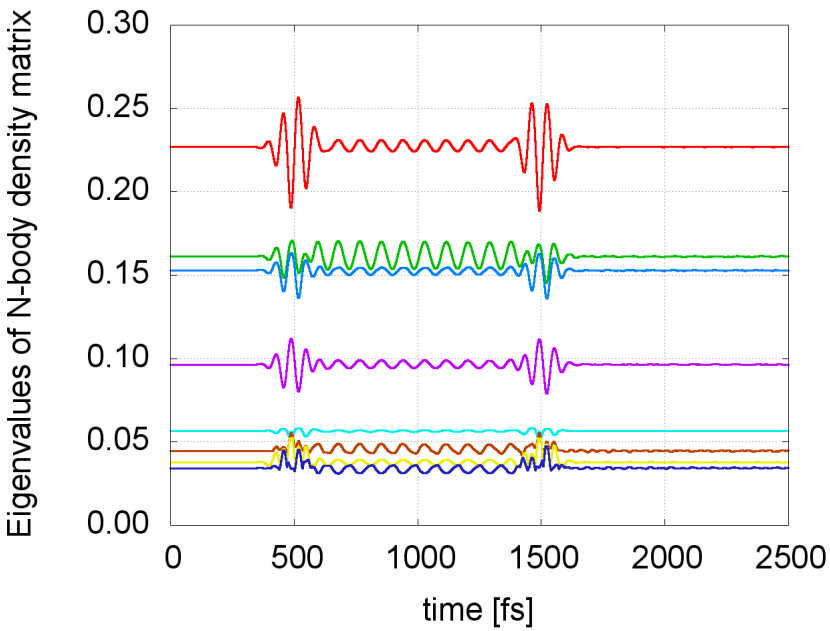


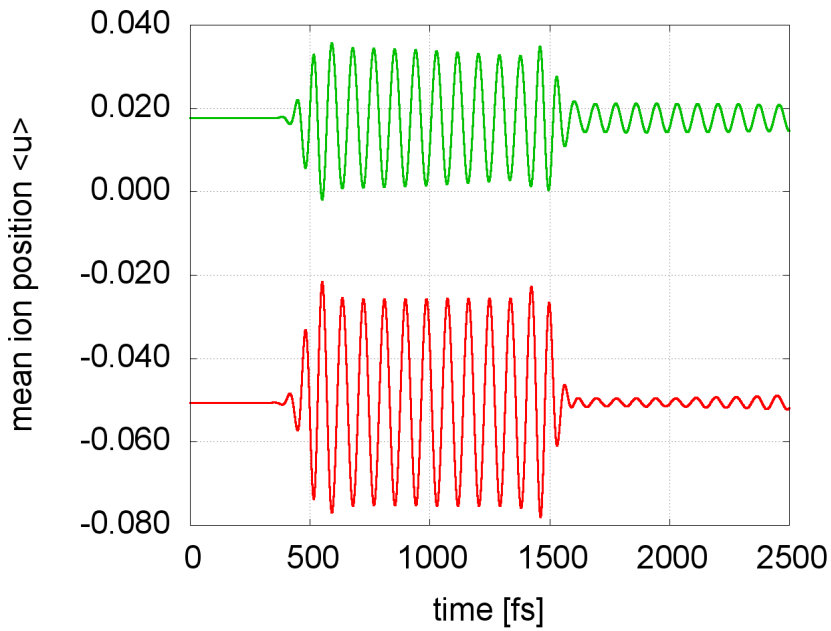
TD pulses





Some Examples - Electron Dipole Forcing

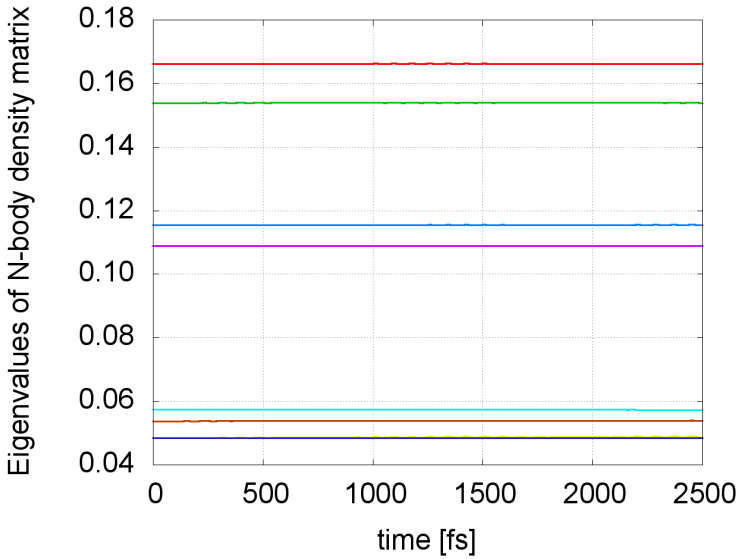


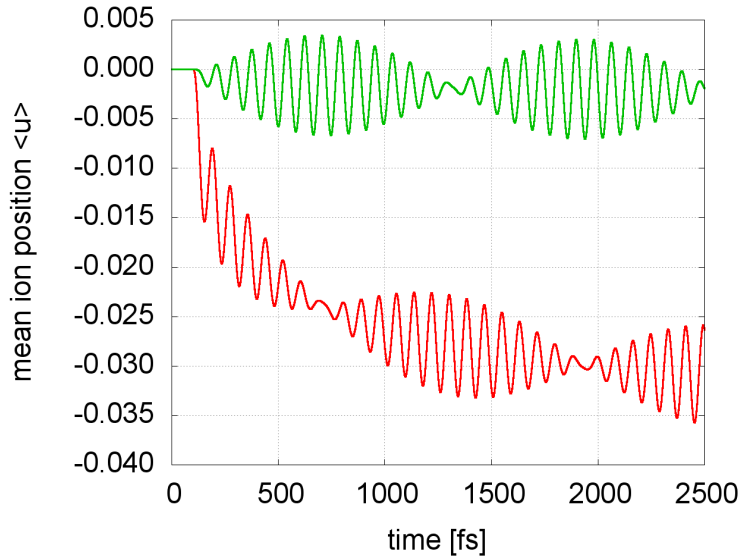


Control of Electron-Ion entanglement?

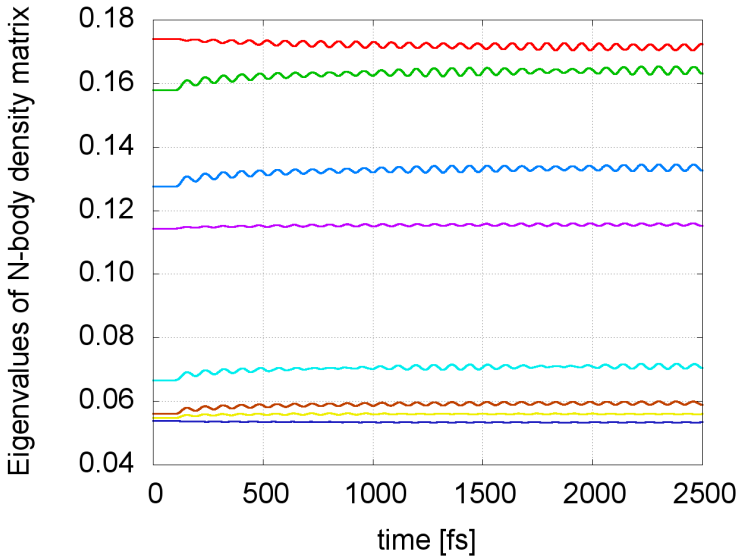
Some Examples - Ion kick

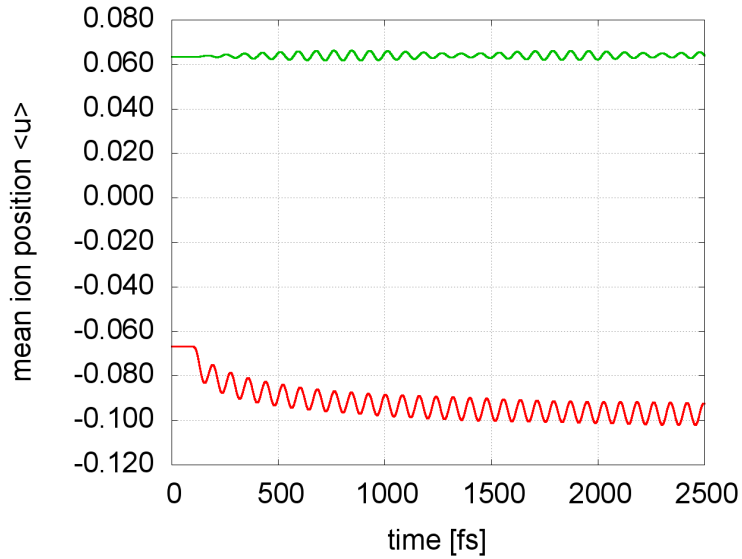
Electron-phonon interaction $\alpha = 0.0$, Hubbard $U = 1$





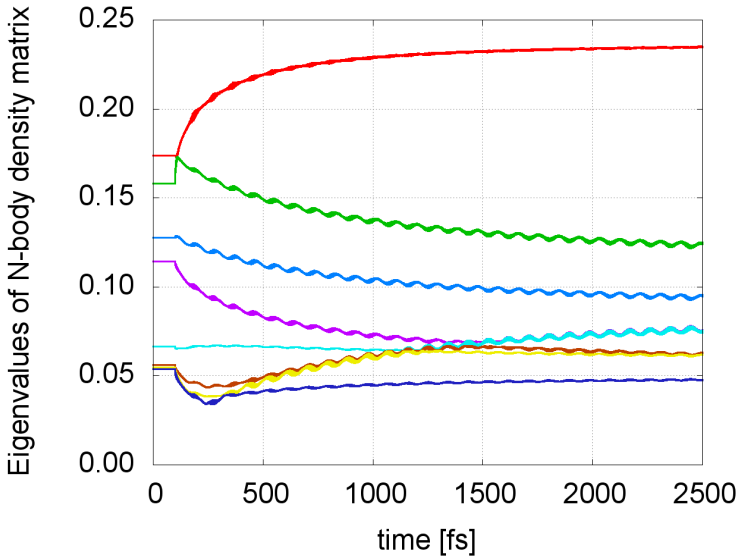
Electron-phonon interaction $\alpha = 1.0$, Hubbard $U = 1$

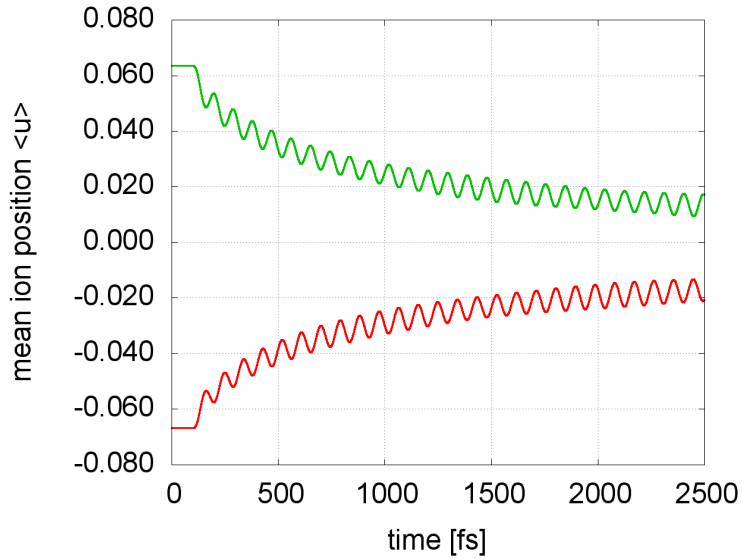




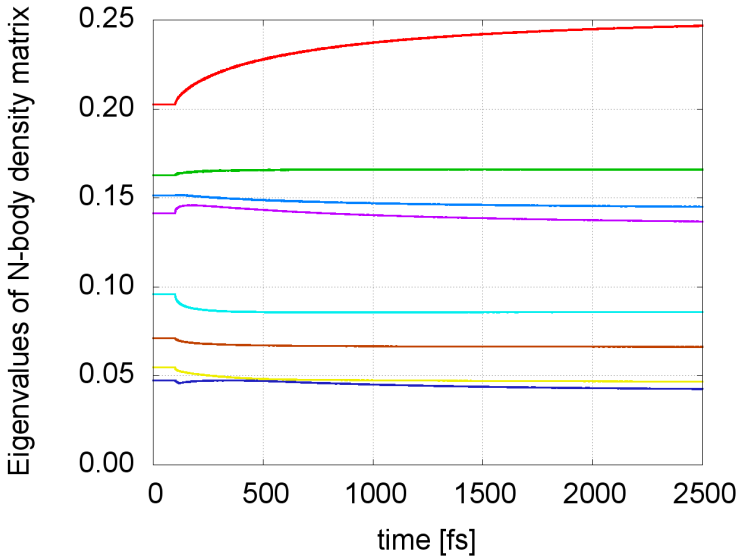
Some Examples - Electron Dipole Forcing

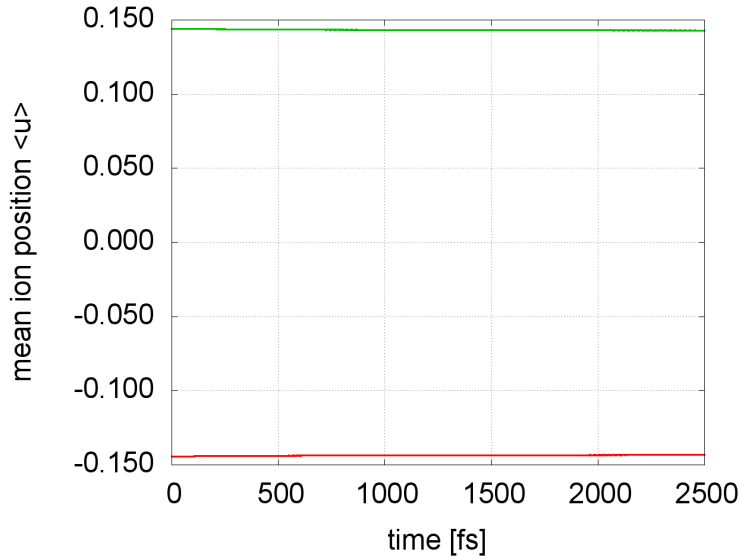
Electron-phonon interaction $\alpha = 0.5$, Hubbard $U = 1$





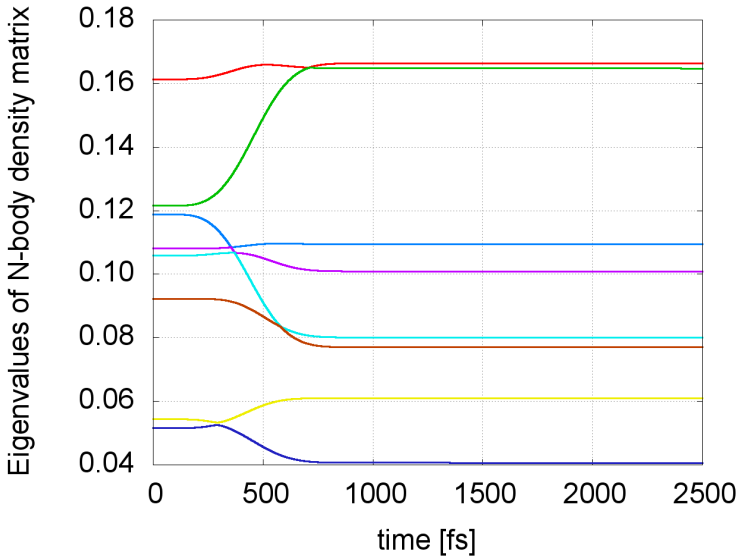
Electron-phonon interaction $\alpha = 1.5$, Hubbard $U = 1$

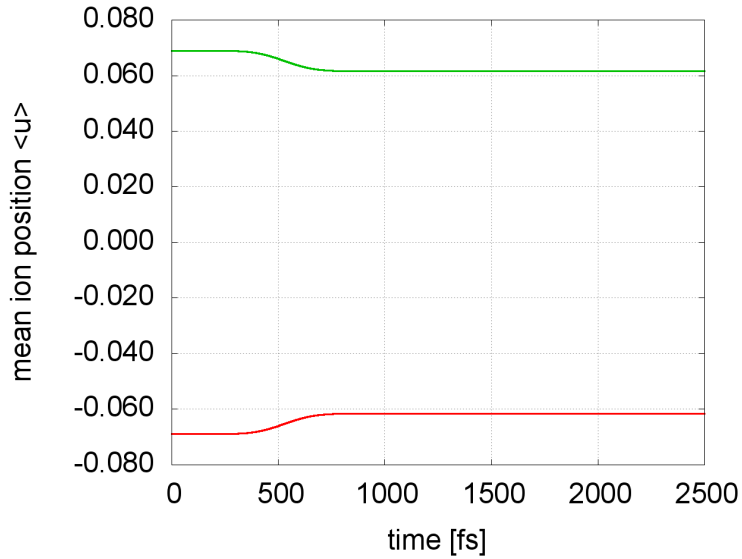




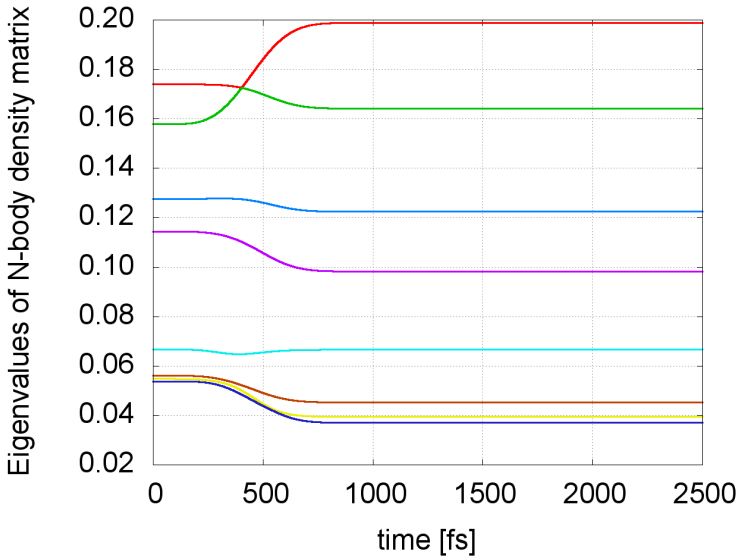
Some Examples - Electron Dipole Forcing

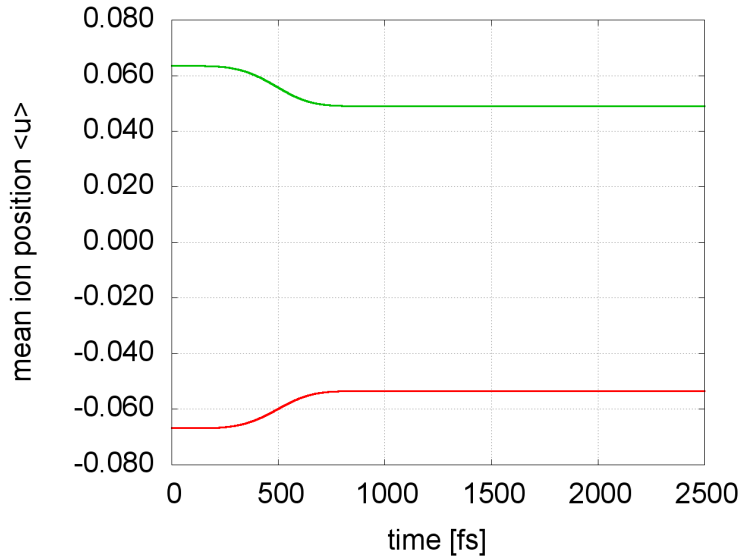
Non-interacting electrons





Hubbard $U = 1$





Outline

Correlated electron-ion dynamics

- Jordan-Wigner transform and exact diagonalization in Fock-Space
- Electron-ion correlation in trans-polyacetylene oligomers (SSH chains)

Electron-ion coupling: system-bath perspective

- Electrons vs. ions: Who is causing decoherence for whom?
- Connection to stochastic Schrödinger equation

Bi-linear electron-ion coupling

- Perimetric coordinates, reference system
- Accuracy of bi-linear electron-ion coupling?

Decoherence and dissipation in coupled electron-ion systems

Ions coupled to a bath of electrons?

- Surface hopping

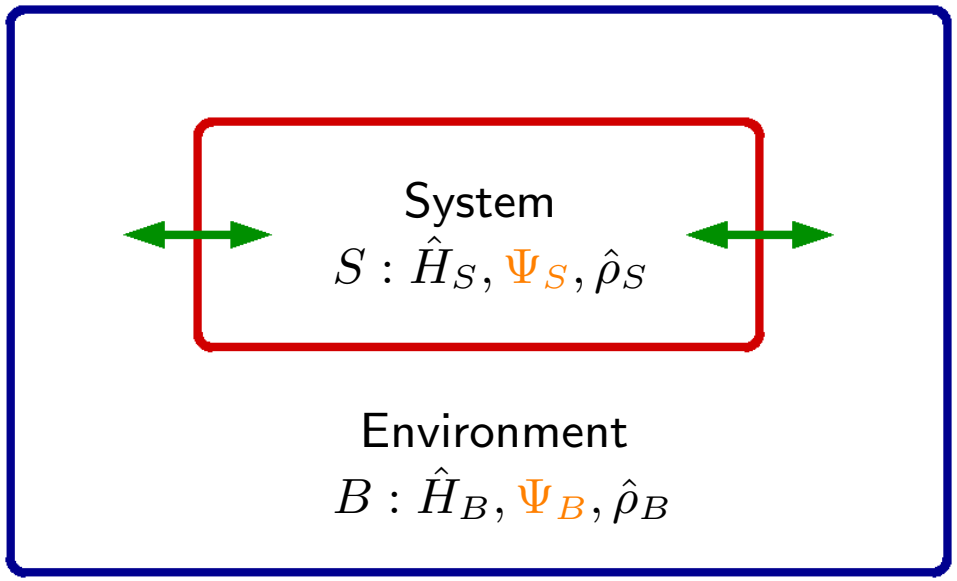
Electrons coupled to a vibronic bath?

- Molecular systems

Who is causing dephasing (and dissipation) for whom?

Reduced system dynamics

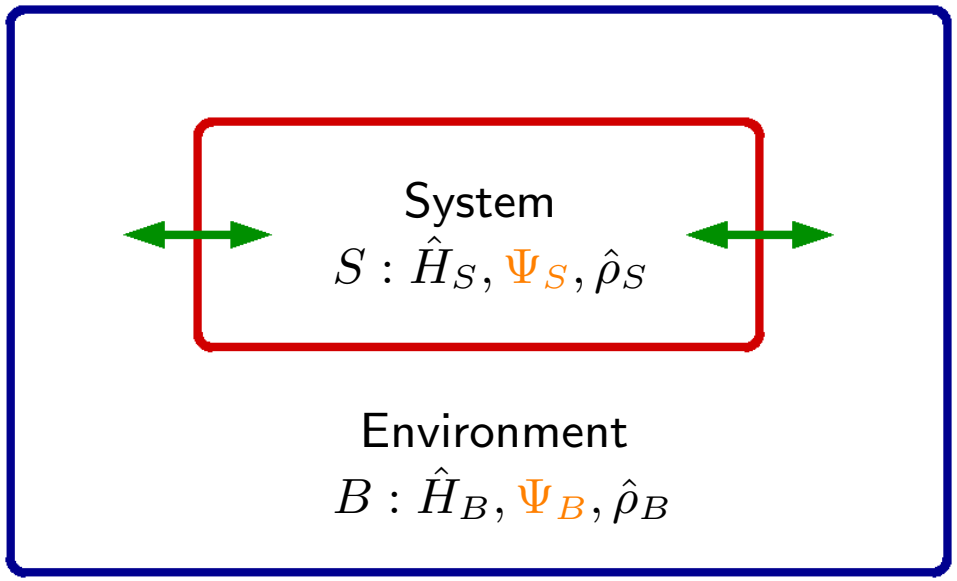
$$S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho}$$



$\Longrightarrow$ Use state vector Ψ_S

Reduced system dynamics

$$S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho}$$



$$\Longrightarrow \text{Use state vector } \Psi_S$$

- Can trace out bath directly on the level of state vectors

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha \sum_j \hat{S}_j \otimes \hat{B}_j, \qquad H_B \chi_n(x_B) = \varepsilon_n \chi_n(x_B)$$

Feshbach Projection-Operator Method

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Expand total wavefunction in arbitrary complete and orthonormal basis of the bath

$$\Psi(x_S, x_B; t) = \sum_n \phi_n(x_S; t) \chi_n(x_B)$$

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Projection Operators

$$\hat{P}_n := \hat{I}_S \otimes |\, \chi_n \,\rangle\langle\, \chi_n \,| \qquad \hat{Q}_n := \hat{I}_S \otimes \sum_{j \neq n} |\, \chi_j \,\rangle\langle\, \chi_j \,|$$

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha \sum_j \hat{S}_j \otimes \hat{B}_j, \qquad H_B \chi_n(x_B) = \varepsilon_n \chi_n(x_B)$$

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Apply to TDSE

$$i\partial_t \hat{P}_n \Psi(t) = \hat{P}_n \hat{H} \hat{P}_n \Psi(t) + \hat{P}_n \hat{H} \hat{Q}_n \Psi(t)$$
$$i\partial_t \hat{Q}_n \Psi(t) = \hat{Q}_n \hat{H} \hat{Q}_n \Psi(t) + \hat{Q}_n \hat{H} \hat{P}_n \Psi(t)$$

P. Gaspard, M. Nagaoka, JCP, **111**, 5676 (1999).

Feshbach Projection-Operator Method

Effective equation for $\hat{P}\,\Psi$ (still fully coherent)

$$i\partial_t \hat{P}\Psi(t) = (\hat{P}\hat{H}\hat{P})\hat{P}\Psi(t) + \overbrace{\hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(t_0)}^{\text{Source Term}}$$
$$\underbrace{-i\int_{t_0}^{t} d\tau \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}(t-\tau)}\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)}_{\text{Memory Term}}$$

Feshbach Projection-Operator Method

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Choice of initial condition

$$\Psi(x_S, x_B; t_0) = \psi(x_S; t_0)\sum_m \sqrt{\frac{e^{-\beta\epsilon_m}}{Z_B}} e^{i\theta_m}\chi_m(x_B)$$

$e^{i\theta_m}$ - random phases, $\beta = 1/k_B T$ - inverse temperature, Z_B - bath partition function

Non-Markovian Stochastic Schrödinger equation

Non-Markovian Stochastic Schrödinger equation

- perturbative expansion to second order in αH_{SB}
- random phases, dense bath spectrum, bath in statistical equilibrium

$$i\partial_t\psi(t) = \hat{H}_S\psi(t) + \alpha\sum_\alpha \eta_\alpha(t)\hat{S}_\alpha\psi(t) - i\alpha^2\int_{t_0}^{t} d\tau \sum_{\alpha\beta} \underbrace{C_{\alpha\beta}(t-\tau)}_{\text{Bath correlation functions}} \hat{S}_\alpha^\dagger e^{-i\hat{H}_S(t-\tau)}\hat{S}_\beta\psi(\tau) + \mathcal{O}(\alpha^3)$$

Markov-limit

$$C_{\alpha\beta}(t-\tau) = D_{\alpha\beta}\delta(t-\tau)$$

Stochastic Schrödinger equation in Born-Markov approximation

$$i\partial_t\psi(t) = \hat{H}_S\psi(t) + \alpha\sum_\alpha \eta_\alpha(t)\hat{S}_\alpha\psi(t) - i\alpha^2\sum_{\alpha\beta} D_{\alpha\beta}\hat{S}_\alpha^\dagger\hat{S}_\beta\psi(t) + \mathcal{O}(\alpha^3)$$

Stochastic TD Kohn-Sham equations for open quantum systems

M. Di Ventra, R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007), R. D'Agosta, M. Di Ventra, Phys. Rev. B **78**, 165105 (2008).

H. Appel, M. Di Ventra, Phys. Rev. B **80**, 212303 (2009), H. Appel, M. Di Ventra, Chem. Phys. **391**, 27 (2011).

Markovian Stochastic Schrödinger equation - Lindblad equation

Statistical average:

$$\hat{\rho}_S(t) = \frac{\overline{|\,\psi(t)\,\rangle\langle\,\psi(t)\,|}}{\overline{\langle\,\psi(t)\,|\,\psi(t)\,\rangle}}$$

Ito stochastic differential

$$d|\psi\rangle\langle\psi| = (d|\psi\rangle)\langle\psi| + |\psi\rangle(d\langle\psi|) + (d|\psi\rangle)(d\langle\psi|)$$

Leads in lowest order in dt to

$$d\hat{\rho}_S = -i\overline{\Big[\hat{H}_S, |\psi\rangle\langle\psi|\Big]}dt - \frac{1}{2}\overline{\Big\{\hat{S}^\dagger\hat{S}, |\psi\rangle\langle\psi|\Big\}}dt + \overline{\hat{S}|\psi\rangle\langle\psi|\hat{S}^\dagger}dt + O(dt^2)$$

For $\overline{\hat{H}[\,|\,\psi\rangle]} \neq \hat{H}[\overline{|\,\psi\rangle}]$, $\overline{\hat{S}[\,|\,\psi\rangle]} \neq \hat{S}[\overline{|\,\psi\rangle}]$ the EOM has closed form and can be written in the familiar Lindblad form

$$\frac{d}{dt}\hat{\rho}_S = -i\Big[\hat{H}_S, \hat{\rho}_S\Big] - \frac{1}{2}\Big\{\hat{S}^\dagger\hat{S}, \hat{\rho}_S\Big\} + \hat{S}\hat{\rho}_S\hat{S}^\dagger$$

Decoherence and dissipation in coupled electron-ion systems

Who is causing dephasing (and dissipation) for whom?

Choice of initial condition - generic system-bath form Choice of initial condition

$$\Psi(x_S, x_B; t_0) = \psi(x_S; t_0) \sum_m \sqrt{\frac{e^{-\beta\epsilon_m}}{Z_B}} e^{i\theta_m} \chi_m(x_B)$$

P. Gaspard, M. Nagaoka, JCP, **111**, 5676 (1999).

Choice of initial condition - ions as bath

$$\Psi(x_{\mathrm{el}}, x_{\mathrm{ion}}; t_0) = \psi(x_{\mathrm{el}}; t_0) \sum_m \sqrt{\frac{e^{-\beta\epsilon_m}}{Z_{\mathrm{ions}}}} e^{i\theta_m} \chi_m(x_{\mathrm{ions}})$$

Choice of initial condition - electrons as bath (as e.g. in surface hopping)

$$\Psi(x_{\mathrm{ions}}, x_{\mathrm{electrons}}; t_0) = \psi(x_{\mathrm{ions}}; t_0) \sum_m \sqrt{\frac{e^{-\beta\epsilon_m}}{Z_{\mathrm{electrons}}}} e^{i\theta_m} \chi_m(x_{\mathrm{electrons}})$$

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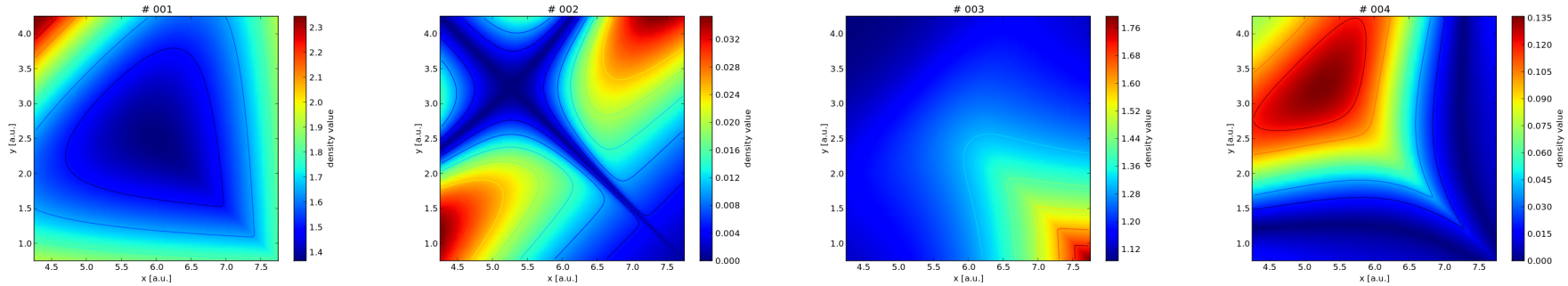
Bi-linear electron-ion coupling

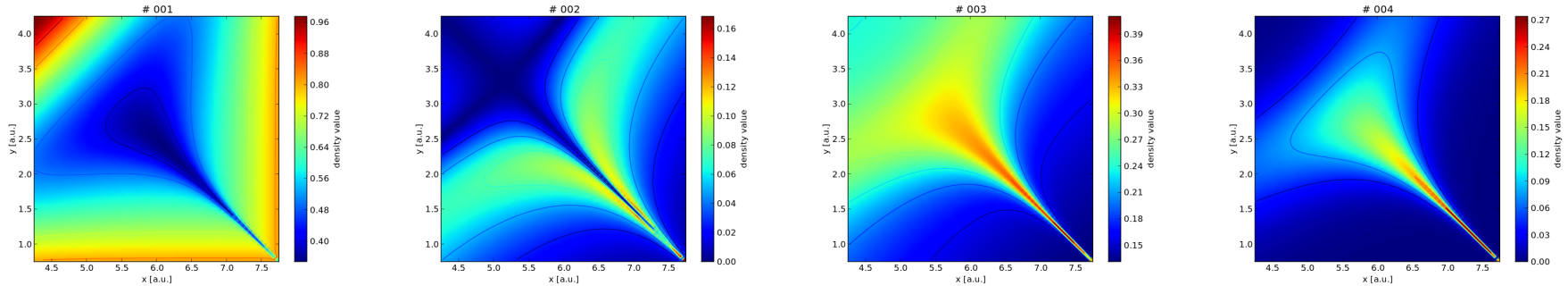
- Perimetric coordinates, reference system
- Accuracy of bi-linear electron-ion coupling?

Matrix elements from quantum chemistry

One-body terms



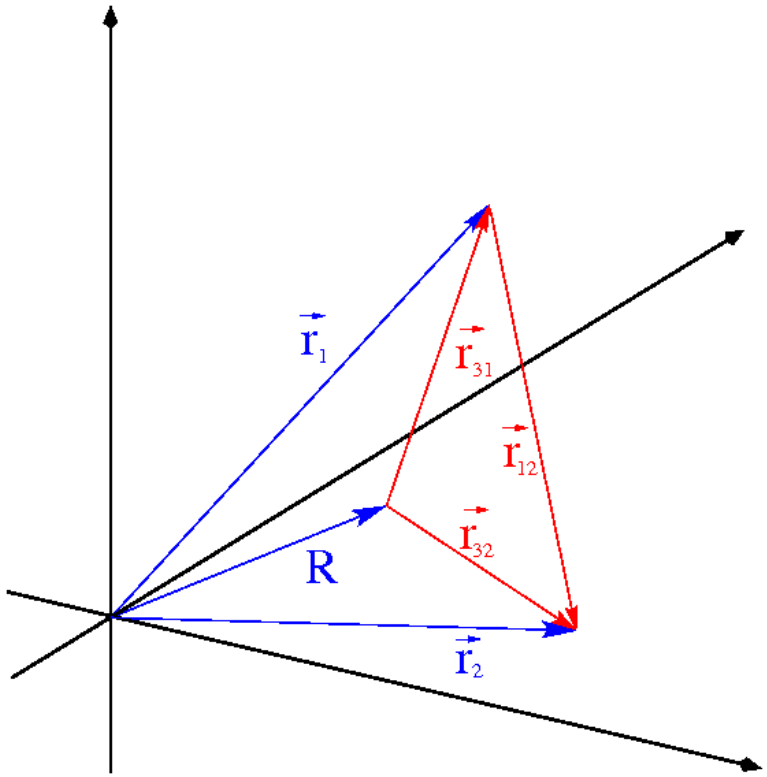
Two-body terms



Bi-linear electron ion coupling

$$\hat{H}_{\mathrm{el-ph}} = \sum_{n=1}^{N-1} \sum_{\sigma=\pm 1} \alpha(u_{n+1} - u_n)(\hat{c}^{\dagger}_{n+1,\sigma}\hat{c}_{n,\sigma} + \hat{c}^{\dagger}_{n,\sigma}\hat{c}_{n+1,\sigma})$$

3-body systems - Perimetric coordinates



Perimetric coordinates:

$$x = -|\vec{r}_{31}| + |\vec{r}_{32}| + |\vec{r}_{12}|$$
$$y = |\vec{r}_{31}| - |\vec{r}_{32}| + |\vec{r}_{12}|$$
$$z = |\vec{r}_{31}| + |\vec{r}_{32}| - |\vec{r}_{12}|$$

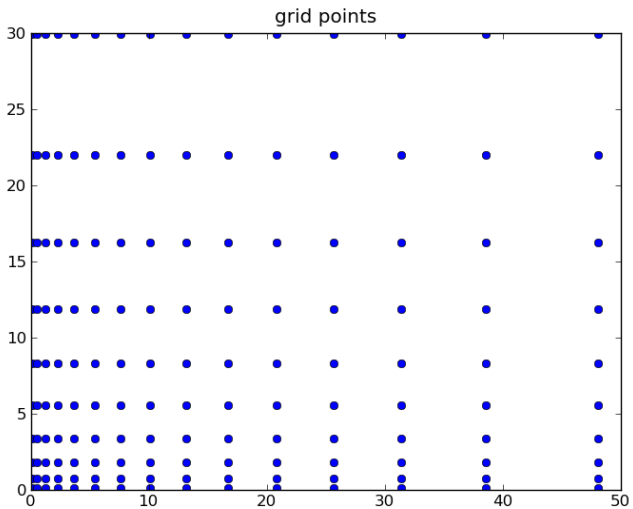
Laguerre-Lagrange basis-set

Expansion for three-body wavefunction

$$\Psi_{LM} = \sum_{K=-L}^{L} D_{KM}(\psi, \theta, \phi)\overline{\Phi}_K(R, \rho, \xi)$$

For S-states (L=M=K=0) the wavefunction becomes

$$\Psi_{00} = \overline{\Phi}_0^{(S)}(R, \rho, \xi) = \Phi_0^{(S)}(x, y, z)$$



Basis-set expansion in orthonormal Laguerre-Lagrange functions:

$$f_i(x) = (-1)^i x_i^{1/2} \frac{L_N(x)}{x - x_i} e^{-x/2}$$

Wavefunction

$$\Phi_0^{(S)}(x, y, z) = \sum_{i,j,k} C_{ijk}[f_i(x)f_j(y) + f_j(x)f_i(y)]f_k(z)$$

Accuracy of the Gauss-Laguerre mesh approach

Method		ground-state energy
Full CI - aug-cc-pVQZ	∞ mass	-2.9025335993384
Hylleras WF	∞ mass	-2.9037243770341
Laguerre mesh (this work)	∞ mass	-2.9037243770340
Hylleras WF	He core mass	-2.9033045555594
Laguerre mesh (this work)	He core mass	-2.9033045555592

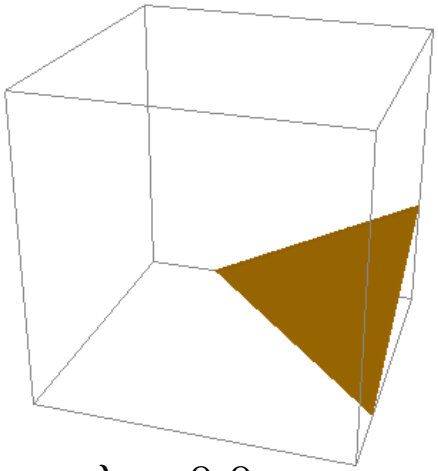
Full CI - aug-cc-pVQZ vs. "exact/Hylleras" $\Longrightarrow$ 32 meV

∞ mass vs. finite mass $\Longrightarrow$ 11 meV

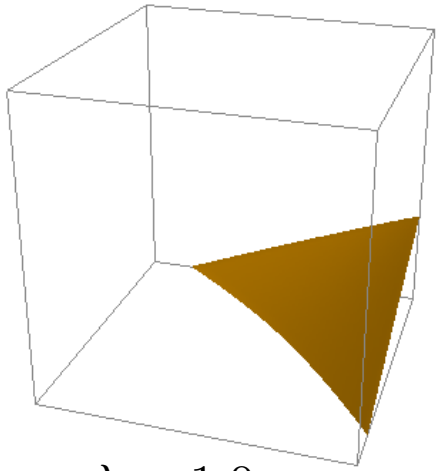
Pico Hartree accuracy with Gauss-Laguerre solver

Exact three body eigenfunctions

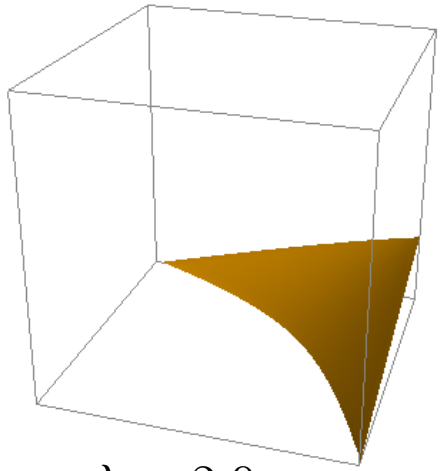
Helium



$\lambda = 0.0$

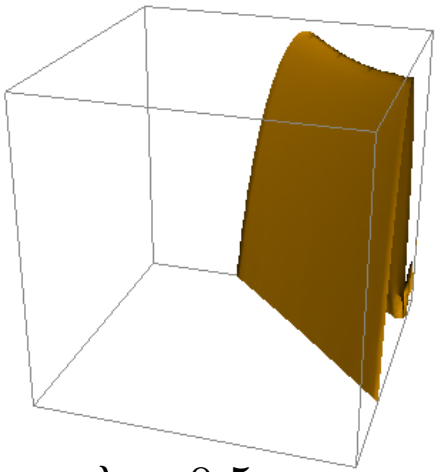


$\lambda = 1.0$

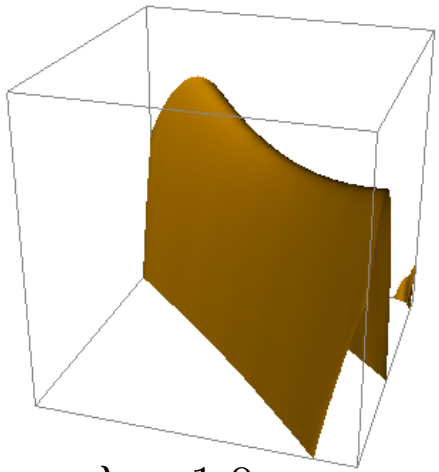


$\lambda = 2.0$

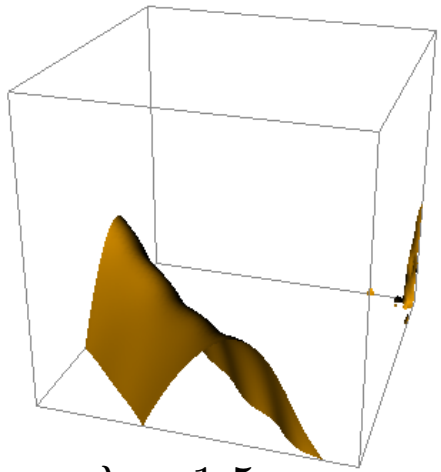
H_2^+



$\lambda = 0.5$



$\lambda = 1.0$



$\lambda = 1.5$

Accuracy of the Gauss-Laguerre mesh approach

H_2^+ molecule

(0, 0)	35	25	15	750	-0.597 139 063 07
(1, 0)	35	25	15	750	-0.587 155 677 6
(0, 1)	35	20	24	500	-0.596 873 738 82
(0, 1)K=0	35	20	12	600	-0.596 873 727 7546
(1, 1)	35	20	24	500	-0.586 904 321 0349

$dt\mu$ molecule

(0, 0)	15	15	15	3 375	-111.364 511 5131
(1, 0)	15	15	15	3 375	-100.916 562
(0, 1)	10	10	10	2 000	-108.179 543 781
(1, 1)	25	25	20	25 000	-99.660 676

Accuracy of bi-linear electron ion coupling

Standard Fröhlich electron-ion coupling

$$\hat{V}_{\mathrm{el-ph}} = \frac{1}{\mathcal{V}} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{q}\lambda} \sum_{\mathbf{G}} g_{\mathbf{G},\mathbf{q},\lambda}\ \hat{c}^{\dagger}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\sigma} c_{\mathbf{k},\sigma} \left(\hat{b}_{\mathbf{q},\lambda} + b^{\dagger}_{-\mathbf{q},\lambda}\right)$$

In textbooks derived from

$$V_{\mathrm{el-ion}} = \int d\mathbf{r}\ (-e)\rho_{\mathrm{el}}(\mathbf{r}) \sum_{j=1}^{N} V_{\mathrm{ion}}(\mathbf{r} - \mathbf{R}_j)$$

Involved approximations:

- Born-Oppenheimer approximation
- Hartree-type interaction, no electron-ion correlation potential
- Only static density $\rho_{\mathrm{el}}(\mathbf{r})$
- Taylor expansion up to first order

Conclusions

- Carlson-Keller theorem also holds for electron-ion wavefunctions

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- Importance of initial condition for decoherence in coupled quantum systems

Conclusions

- Carlson-Keller theorem also holds for electron-ion wavefunctions
- Importance of initial condition for decoherence in coupled quantum systems
- Numerically accurate three-body code for Coulombic systems in 3D

Thanks!

René Jestädt
Ignacio Franco
Angel Rubio

Thank you for your attention!

Connection to Lindblad equation

Ito stochastic differential

$$d|\psi\rangle\langle\psi| = (d|\psi\rangle)\langle\psi| + |\psi\rangle(d\langle\psi|) + (d|\psi\rangle)(d\langle\psi|)$$

Insert stochastic Schrödinger equation in Born-Markov limit

$$\begin{aligned}
d|\psi\rangle\langle\psi| = &- i\hat{S}|\psi\rangle\langle\psi|dW + \text{h.c.} \\
&- i\Big[\hat{H}_S, |\psi\rangle\langle\psi|\Big]dt - \frac{1}{2}\Big\{\hat{S}^\dagger\hat{S}, |\psi\rangle\langle\psi|\Big\}dt \\
&+ \hat{S}|\psi\rangle\langle\psi|\hat{S}^\dagger dW^\dagger dW \\
&+ \hat{S}|\psi\rangle\langle\psi|\hat{H}_S\, dW dt + \text{h.c.} \\
&+ \frac{i}{2}\hat{S}|\psi\rangle\langle\psi|\hat{S}^\dagger\hat{S}\, dW dt + \text{h.c.} \\
&+ \hat{H}_S|\psi\rangle\langle\psi|\hat{H}_S dt^2 + \frac{1}{4}\hat{S}^\dagger\hat{S}|\psi\rangle\langle\psi|\hat{S}^\dagger\hat{S}dt^2 \\
&+ \frac{i}{2}\Big\{\hat{H}_S, |\psi\rangle\langle\psi|\hat{S}^\dagger\hat{S}\Big\}dt^2
\end{aligned}$$

Connection to Lindblad equation

Ensemble average over Ito stochastic differential

$$d\hat{\rho}_S = d\overline{|\psi\rangle\langle\psi|} = \overline{(d|\psi\rangle)\langle\psi|} + \overline{|\psi\rangle(d\langle\psi|)} + \overline{(d|\psi\rangle)(d\langle\psi|)}$$

Properties of stochastic process

$$\overline{dW} = 0, \qquad \overline{dW^\dagger dW} = dt$$

Leads in lowest order in dt to

$$d\hat{\rho}_S = -i\overline{\Big[\hat{H}_S, |\psi\rangle\langle\psi|\Big]}dt - \frac{1}{2}\overline{\Big\{\hat{S}^\dagger\hat{S}, |\psi\rangle\langle\psi|\Big\}}dt + \overline{\hat{S}|\psi\rangle\langle\psi|\hat{S}^\dagger}dt + O(dt^2)$$

Only if we have not

$$\overline{\hat{H}[\,|\psi\rangle]} \neq \hat{H}[\overline{|\psi\rangle}], \qquad \overline{\hat{S}[\,|\psi\rangle]} \neq \hat{S}[\overline{|\psi\rangle}]$$

the EOM has closed form and can be written in the familiar Lindblad form

$$\frac{d}{dt}\hat{\rho}_S = -i\Big[\hat{H}_S, \hat{\rho}_S\Big] - \frac{1}{2}\Big\{\hat{S}^\dagger\hat{S}, \hat{\rho}_S\Big\} + \hat{S}\hat{\rho}_S\hat{S}^\dagger$$

Connection to Redfield master equation

Ito stochastic differential

$$d|\psi\rangle\langle\psi| = (d|\psi\rangle)\langle\psi| + |\psi\rangle(d\langle\psi|) + (d|\psi\rangle)(d\langle\psi|)$$

- Insert non-Markovian stochastic Schrödinger equation
- Perform ensemble average
- Consider average properties of stochastic process

In the long time limit this leads to Redfield-type master equations with slipped initial condition!

P. Gaspard, M. Nagaoka, JCP, **111**, 5668 (1999).

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