Advanced Laser and Photon Science
レーザー・光量子科学特論

First principles simulations
第一原理計算

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1. Two electron systems
2. Second quantization
3. Multiconfiguration time-dependent Hartree-Fock method

Time-dependent variational principle

$$S = \int_{t_1}^{t_2} \langle \Psi | (\hat{H} - i\partial_t) | \Psi \rangle$$

Action integral

$$\delta S = 0, \quad \text{for} \;\; \Psi \to \Psi' = \Psi + \delta\Psi$$

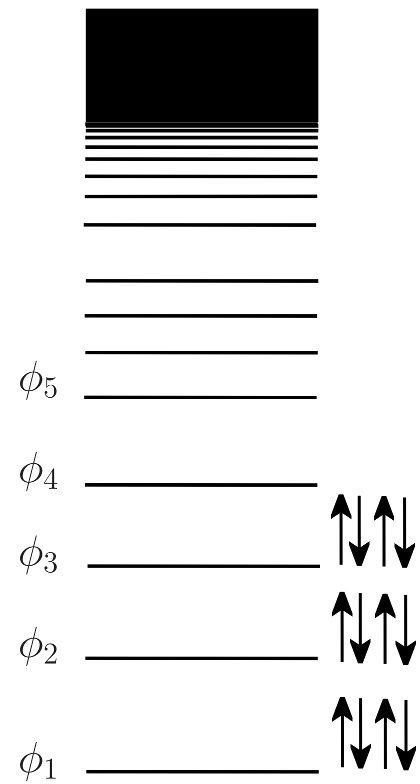
$$\delta\Psi(t_1) = \delta\Psi(t_2) = 0$$

$$\begin{array}{lccc} \text{Arbitrary} & \delta\Psi & \Longrightarrow & \text{TDSE} \\ \text{Approximate} & \delta\Psi & \Longrightarrow & \text{Variational EOMs} \end{array}$$

Example 1: Time-dependent Configuration Interaction

$$S = \int_{t_1}^{t_2} \langle \Psi | (\hat{H} - i\partial_t) | \Psi \rangle$$ Action integral

$$|\Psi(t)\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}(t) |\boldsymbol{n}\rangle,$$



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Configuration Interaction (CI) coefficients: Variational parameters

$$S = \sum_{\mathbf{n},\mathbf{m}} \int_{t_1}^{t_2} dt \left(C_{\mathbf{n}}^* C_{\mathbf{m}} \langle \mathbf{n} | \hat{H} | \mathbf{m} \rangle - i C_{\mathbf{n}}^* \langle \mathbf{n} | \mathbf{m} \rangle \dot{C}_{\mathbf{m}} \right)$$

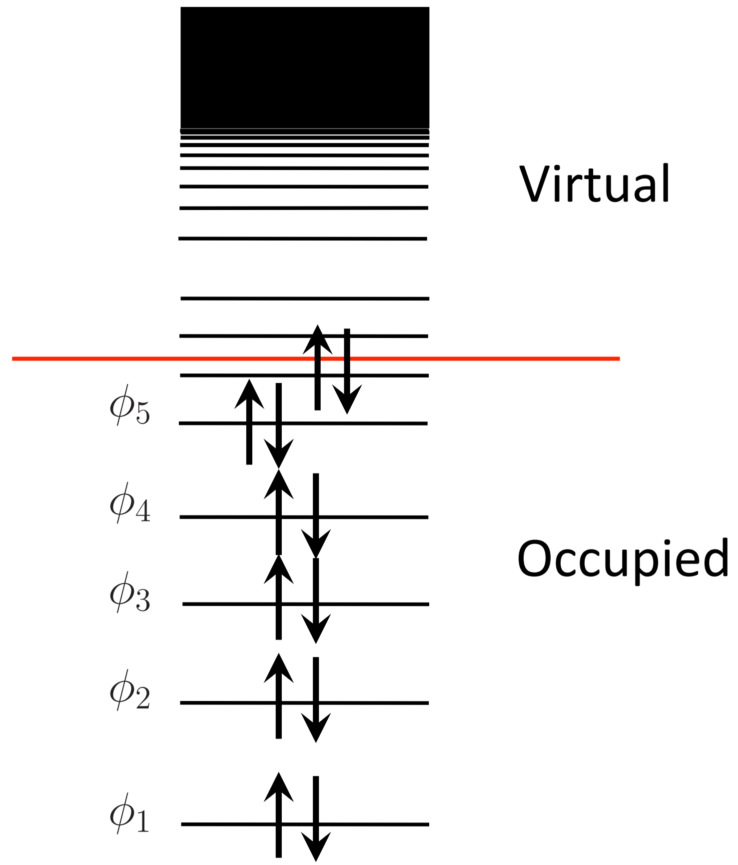
$$= \sum_{\mathbf{n},\mathbf{m}} \int_{t_1}^{t_2} dt \left(C_{\mathbf{n}}^* C_{\mathbf{m}} \langle \mathbf{n} | \hat{H} | \mathbf{m} \rangle - i C_{\mathbf{n}}^* \dot{C}_{\mathbf{n}} \delta_{\mathbf{nm}} \right)$$

$$\frac{\delta S}{\delta C_{\mathbf{n}}^*(t)} = \sum_{\mathbf{m}} \langle \mathbf{n} | \hat{H} | \mathbf{m} \rangle C_{\mathbf{m}} - i \dot{C}_{\mathbf{n}} = 0$$

$$i\dot{C}_{\mathbf{n}} = \sum_{\mathbf{m}} \langle \mathbf{n} | \hat{H} | \mathbf{m} \rangle C_{\mathbf{m}}$$

Example 2: Time-dependent Hartree-Fock

$$|\Psi(t)\rangle = |1_1 1_2 \cdots 1_N 000 \cdots\rangle \leftrightarrow \det\left[\phi_1 \phi_2 \cdots \phi_N\right]$$



Example 2: Time-dependent Hartree-Fock

$$|\Psi(t)\rangle = |1_1 1_2 \cdots 1_N 000\cdots\rangle \leftrightarrow \det\left[\phi_1\phi_2\cdots\phi_N\right]$$

Orbital functions: Variational parameters

$$S = \int_{t_1}^{t_2} dt \left[\sum_{i=1}^{N} \left(h_i^i - i\langle\phi_i|\dot{\phi}_i\rangle \right) + \frac{1}{2}\sum_{ij}^{N} \left(V_{ij}^{ij} - V_{ji}^{ij} \right) \right]$$

From Homework (2)

$$\frac{\delta S}{\delta \phi_i^*(t)} = \hat{h}\phi_i - i\dot{\phi}_i + \sum_{j=1}^{N} \left(\hat{W}_j^j \phi_i - \hat{W}_i^j \phi_j \right)$$

$$i\dot{\phi}_i = \hat{h}\phi_i + \sum_{j=1}^{N} \left(\hat{W}_j^j \phi_i - \hat{W}_i^j \phi_j \right)$$

$$W_j^i(\boldsymbol{r}_1) = \int dx_2 \frac{\phi_i^*(x_2)\phi_j(x_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

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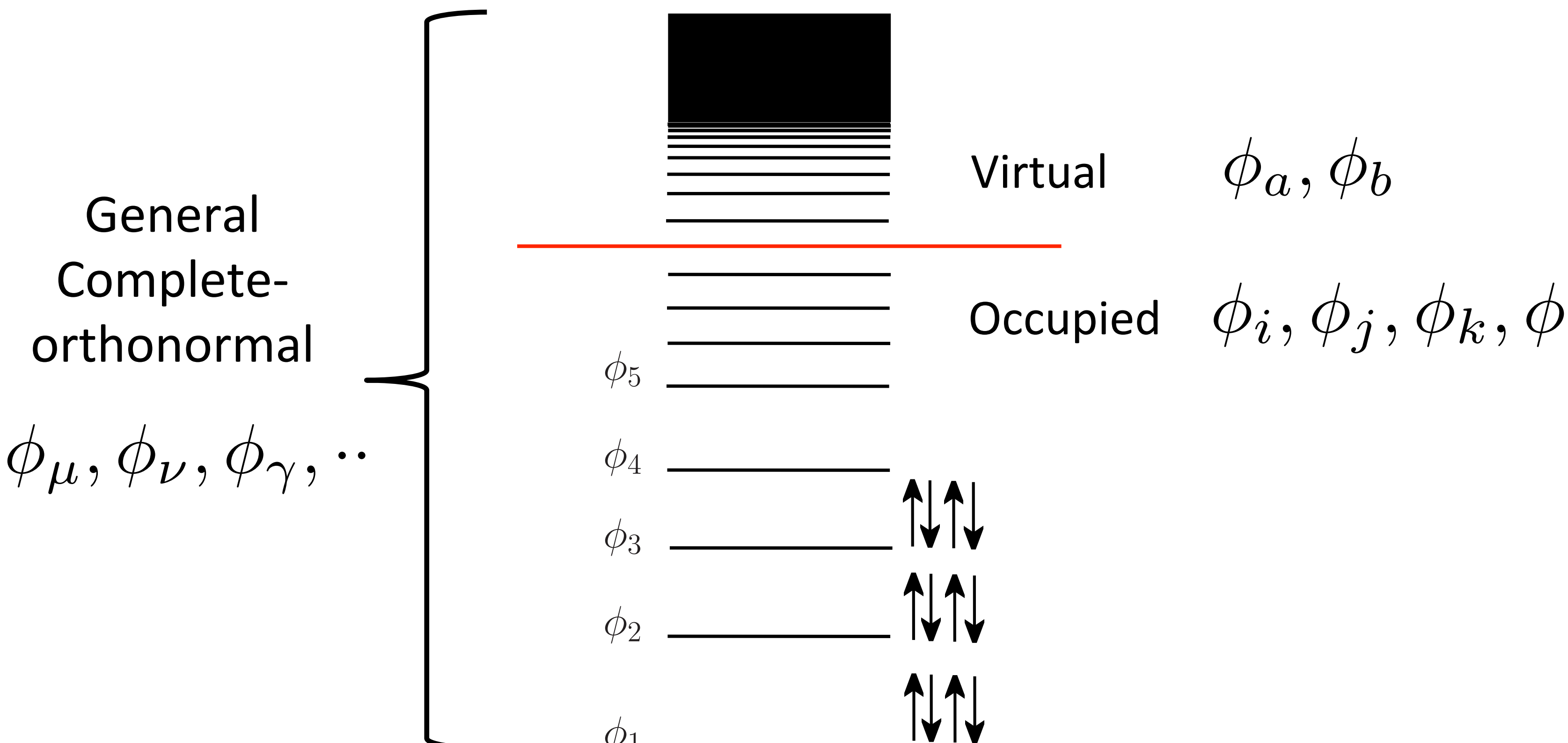
Multiconfiguration TD Hartree-Fock (MCTDHF)

$$|\Psi(t)\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}(t)|\boldsymbol{n}\rangle,$$

TD Configuration Interaction (CI) with given number of moving orbitals



Multiconfiguration TD Hartree-Fock (MCTDHF)

$$|\Psi(t)\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}(t)|\boldsymbol{n}\rangle,$$

Both CI coefficients & orbital functions: Variational parameters

Working with Slater determinant is, in general, extremely tedious:
Need techniques of second quantization

(1) Matrix (operator) exponential

$$\exp(A) \equiv \sum_{n=0}^{\infty} \frac{A^n}{n!}$$

$$\exp(A)^\dagger = \exp(A^\dagger), \quad B^{-1}\exp(A)B = \exp(B^{-1}AB)$$

$$\exp(A+B) = \exp(A)\exp(B) \Leftarrow [A,B] = 0$$

$$\exp(A)B\exp(-A) = B + [A,B] + \frac{1}{2!}[A,[A,B]] + \frac{1}{3!}[A,[A,[A,B]]] + \cdots$$

Baker-Campbell-Hausdorff (BCH) expansion

Multiconfiguration TD Hartree-Fock (MCTDHF)

(2) Exponential parameterization of unitary matrix (operator)

$$U = \exp(X)$$

$$U: \quad \text{unitary} \qquad U^\dagger U = UU^\dagger = 1$$

$$X: \quad \text{anti-Hermitian} \qquad X^\dagger = -X$$

Anti-Hermitian matrix can be parameterized more easily than unitary one

(3) Unitary transformation of orbitals

$$\phi_\mu(t) = \sum_\nu \phi_\nu(0) U_{\nu\mu} = \sum_\nu \phi_\nu(0) \exp(X)_{\nu\mu},$$

$$\Longleftrightarrow a^\dagger_\mu(t) = \sum_\nu a^\dagger_\nu(0) U_{\nu\mu} = \sum_\nu a^\dagger_\nu(0) \exp(X)_{\nu\mu}$$

$$a_\mu(t) = \sum_\nu a_\nu(0) U^*_{\nu\mu} = \sum_\nu a^\dagger_\nu(0) \exp(X)^*_{\nu\mu}$$

Multiconfiguration TD Hartree-Fock (MCTDHF)

(3) Unitary transformation of orbitals

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$$a_\mu(t) = \sum_\nu a_\nu(0) U^*_{\nu\mu} = \sum_\nu a^\dagger_\nu(0) \exp(X)^*_{\nu\mu}$$

$$\Longleftrightarrow a^\dagger_\mu(t) = \exp(\hat{X}) a^\dagger_\mu(0) \exp(-\hat{X})$$

$$a_\mu(t) = \exp(\hat{X}) a_\mu(0) \exp(-\hat{X})$$

$$\hat{X} = \sum_{\mu\nu} X^\mu_\nu a^\dagger_\mu(0) a_\nu(0)$$

Proof: From BCH expansion

Multiconfiguration TD Hartree-Fock (MCTDHF)

(4) Unitary transformation of Slater determinants

$$\phi_\mu(t) = \sum_\nu \phi_\nu(0) U_{\nu\mu} = \sum_\nu \phi_\nu(0) \exp(X)_{\nu\mu},$$

$$\Longleftrightarrow a^\dagger_\mu(t) = \exp(\hat{X}) a^\dagger_\mu(0) \exp(-\hat{X})$$

$$a_\mu(t) = \exp(\hat{X}) a_\mu(0) \exp(-\hat{X})$$

$$\hat{X} = \sum_{\mu\nu} X^\mu_\nu a^\dagger_\mu(0) a_\nu(0)$$

$$|\mathbf{n}(0)\rangle = a_1^{\dagger n_1}(0) a_2^{\dagger n_2}(0) a_3^{\dagger n_3}(0) \cdots |\rangle$$

$$|\mathbf{n}(t)\rangle = a_1^{\dagger n_1}(t) a_2^{\dagger n_2}(t) a_3^{\dagger n_3}(t) \cdots |\rangle$$

$$= \exp(\hat{X}) |\mathbf{n}(0)\rangle$$

Multiconfiguration TD Hartree-Fock (MCTDHF)

(5) Unitary transformation of total wave function

$$|\Psi(t)\rangle = \sum_{\mathbf{n}} C_{\mathbf{n}}(t)|\mathbf{n}(t)\rangle$$
$$= \exp(\hat{X}) \sum_{\mathbf{n}} C_{\mathbf{n}}(t)|\mathbf{n}(0)\rangle$$

(6) Variation and Time derivative of total wave function

$$|\delta\Psi(t)\rangle = \sum_{\mathbf{n}} \delta C_{\mathbf{n}}(t)|\mathbf{n}(t)\rangle + \sum_{\mu\nu} \delta X^{\mu}_{\nu} \hat{E}^{\mu}_{\nu}|\Psi(t)\rangle$$

$$|\dot{\Psi}(t)\rangle = \sum_{\mathbf{n}} \dot{C}_{\mathbf{n}}(t)|\mathbf{n}(t)\rangle + \sum_{\mu\nu} \dot{X}^{\mu}_{\nu} \hat{E}^{\mu}_{\nu}|\Psi(t)\rangle$$

$$\dot{X}^{\mu}_{\nu} = \langle \phi_\mu(t)|\dot{\phi}_\nu(t)\rangle \qquad (\hat{E}^{\mu}_{\nu} \equiv \hat{a}^{\dagger}_{\mu}\hat{a}_{\nu})$$

Multiconfiguration TD Hartree-Fock (MCTDHF)

$$|\Psi(t)\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}(t)|\boldsymbol{n}\rangle,$$

Both CI coefficients & orbital functions: Variational parameters

Insert previous results into TDVP and require

$$\delta S/\delta C^*_{\mathbf{n}}(t) = \delta S/\delta X_{\mu\nu}(t) = 0$$

$$i\dot{C}_{\mathbf{n}} = \sum_{\mathbf{m}} \langle \mathbf{n}| \left(\hat{H} - i\sum_{\mu\nu} \hat{E}^{\mu}_{\nu} \dot{X}^{\mu}_{\nu} \right) |\mathbf{m}\rangle C_{\mathbf{m}}$$

$$i\sum_{\gamma\lambda}\left[\langle\Psi|\hat{E}^{\mu}_{\nu}\left(1-\sum_{\mathbf{n}}|\mathbf{n}\rangle\langle\mathbf{n}|\right)\hat{E}^{\gamma}_{\lambda}|\Psi\rangle - \langle\Psi|\hat{E}^{\gamma}_{\lambda}\left(1-\sum_{\mathbf{n}}|\mathbf{n}\rangle\langle\mathbf{n}|\right)\hat{E}^{\mu}_{\nu}|\Psi\rangle\right]\dot{X}^{\gamma}_{\lambda}$$

$$= \langle\Psi|\hat{E}^{\mu}_{\nu}\left(1-\sum_{\mathbf{n}}|\mathbf{n}\rangle\langle\mathbf{n}|\right)\hat{H}|\Psi\rangle - \langle\Psi|\hat{H}\left(1-\sum_{\mathbf{n}}|\mathbf{n}\rangle\langle\mathbf{n}|\right)\hat{E}^{\mu}_{\nu}|\Psi\rangle$$

General equations of motion

Multiconfiguration TD Hartree-Fock (MCTDHF)

$$|\Psi(t)\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}(t)|\boldsymbol{n}\rangle,$$

In case of complete CI expansion within the given orbitals

$$i\dot{C}_{\mathbf{n}} = \sum_{\mathbf{m}} \langle \mathbf{n}| \left(\hat{H} - \sum_{ij} E^i_j R^i_j \right) |\mathbf{m}\rangle C_{\mathbf{m}}$$

$$i|\dot{\phi}_i\rangle = \hat{Q} \left(\hat{h}|\phi_i\rangle + \sum_{jklm}^{occ} (D^{-1})^i_m P^{mk}_{jl} \hat{W}^k_l |\phi_j\rangle \right) + \sum_j^{occ} |\phi_j\rangle R^j_i$$

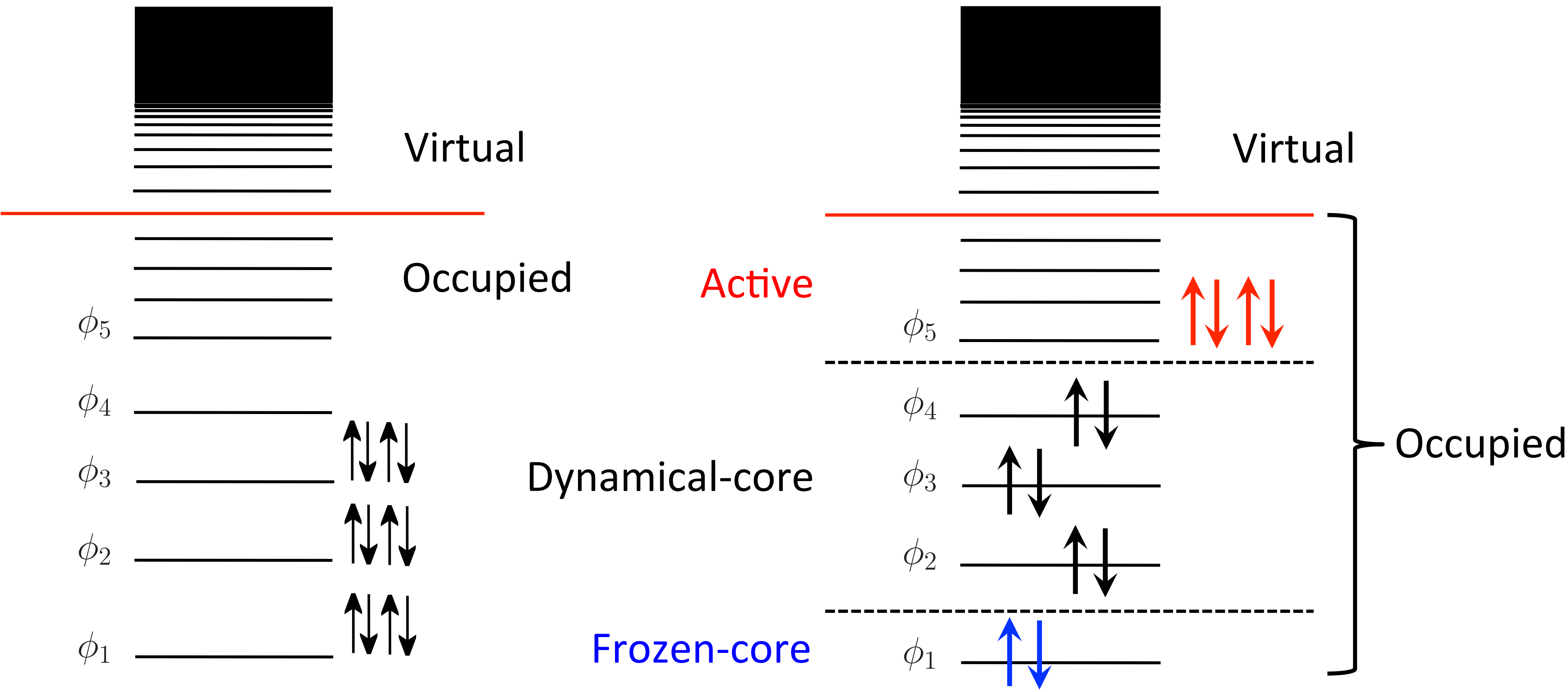
$$\hat{Q} = 1 - \sum_j^{occ} |\phi_j\rangle\langle\phi_j|$$

$$R^j_i \equiv i\langle\phi_j|\dot{\phi}_i\rangle : \quad \text{Arbitrary Hermitian matrix}$$

$$D^i_j = \langle\Psi|E^i_j|\Psi\rangle, P^{ik}_{jl} = \langle\Psi|E^{ik}_{jl}|\Psi\rangle \quad (\hat{E}^{ik}_{jl} = \hat{a}^\dagger_i \hat{a}^\dagger_k \hat{a}_l \hat{a}_j)$$

One (*D*) and two (*P*) particle reduced density matrices

Importance of non-complete CI expansions



MCTDHF

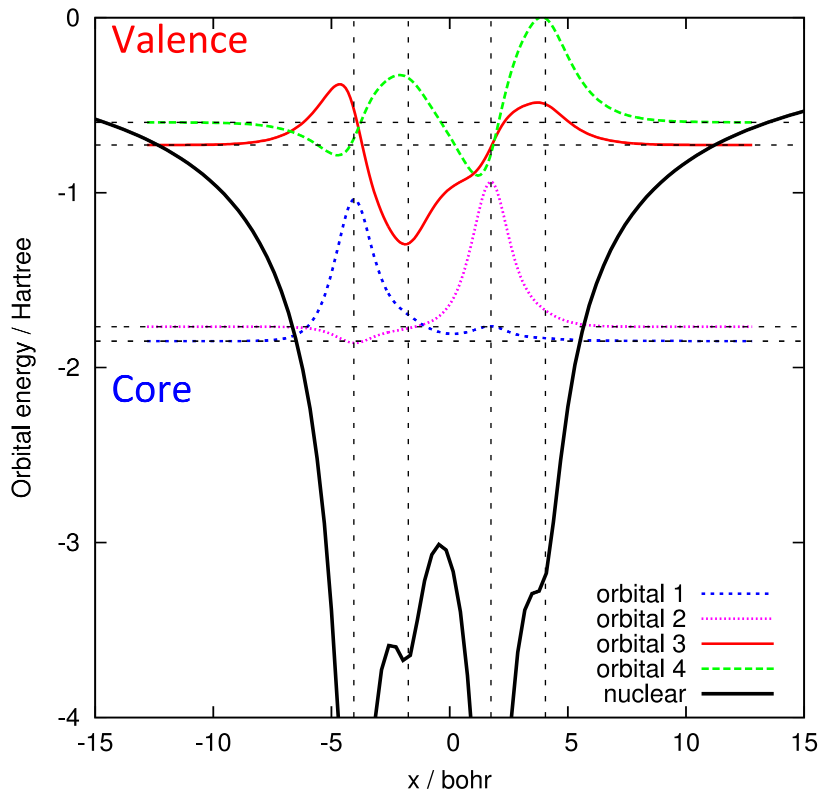
$N_{Det} = 784$

TD-CASSCF (complete-active-space self-consistent-field): core and active subspaces

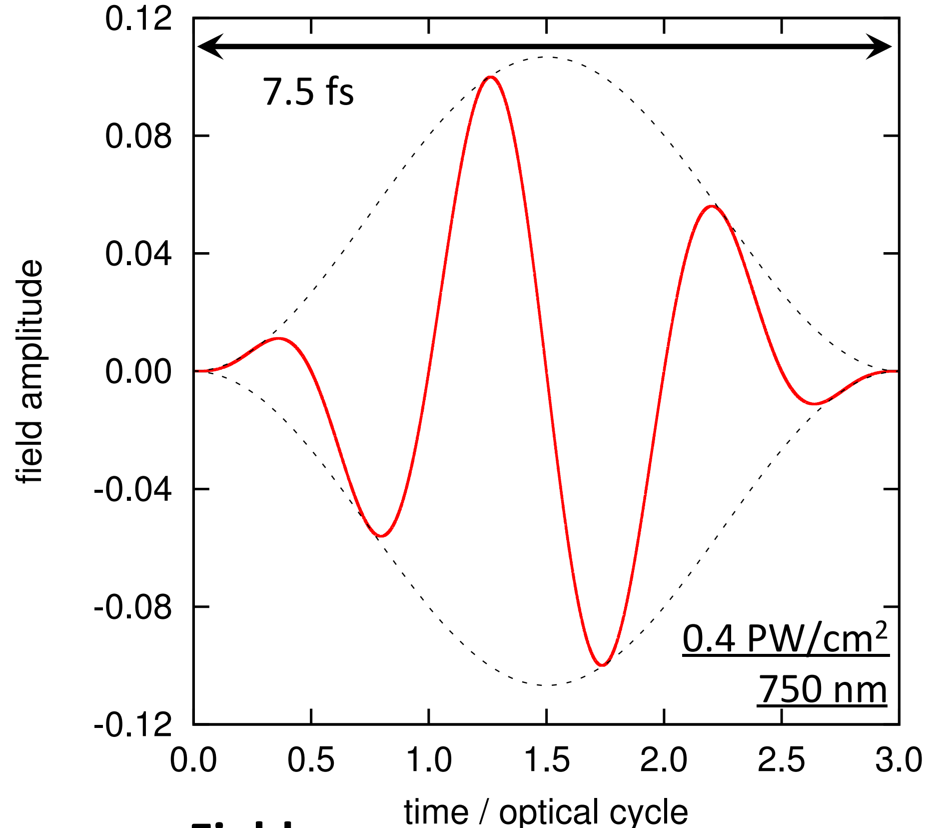
$N_{Det} = 36$

Applicaions

$$H = \sum_{i=1}^{N} \left\{ -\frac{1}{2}\frac{\partial^2}{\partial x_i^2} - \sum_{a=1}^{M} \frac{Z_a}{\sqrt{(x_i - X_a)^2 + c}} - x_i E(t) \right\} + \sum_{i>j}^{N} \frac{1}{\sqrt{(x_i - x_j)^2 + d}}$$



Ground-state



Field

1D "LiH dimer" 4 valence and 4 core electrons

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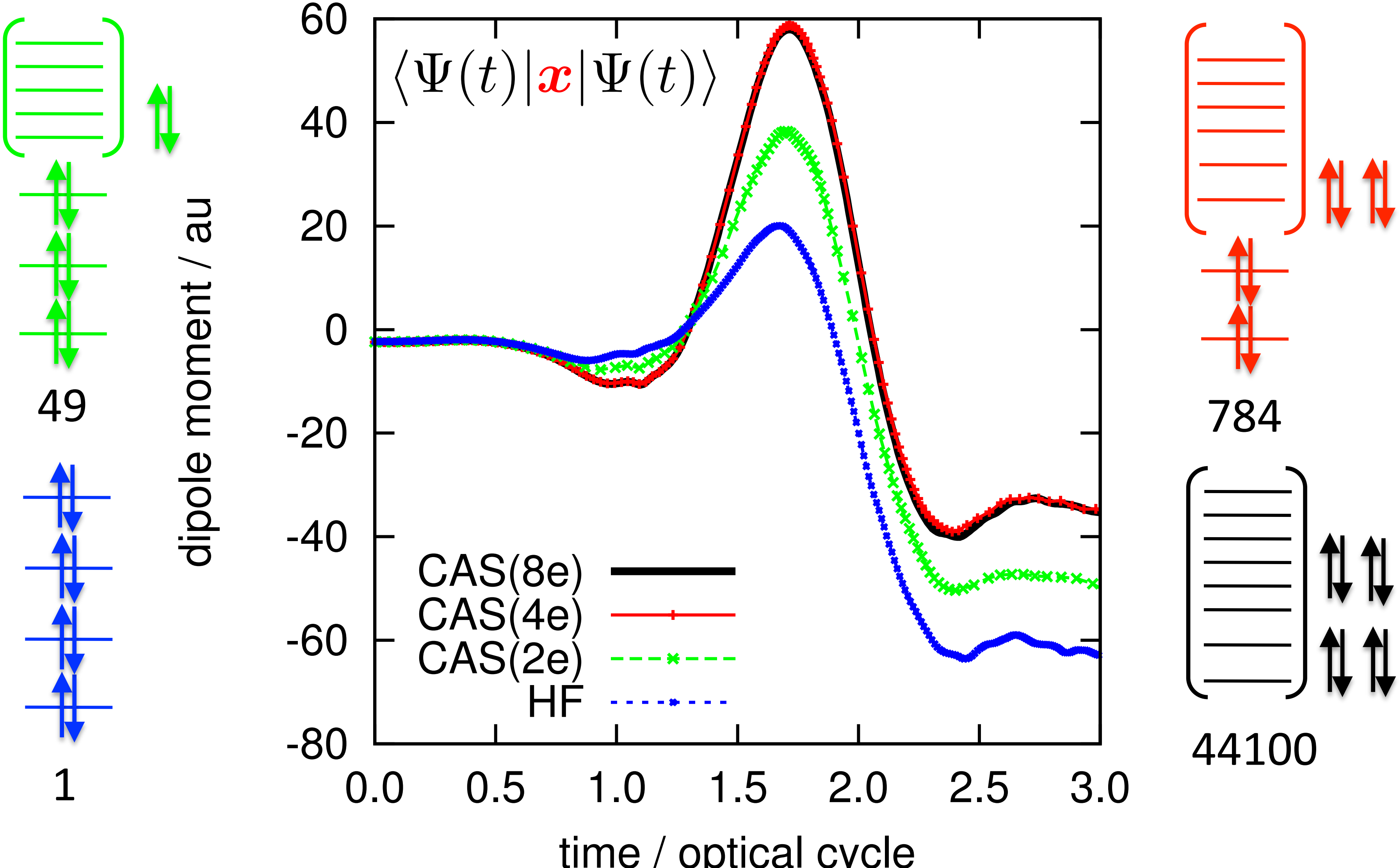
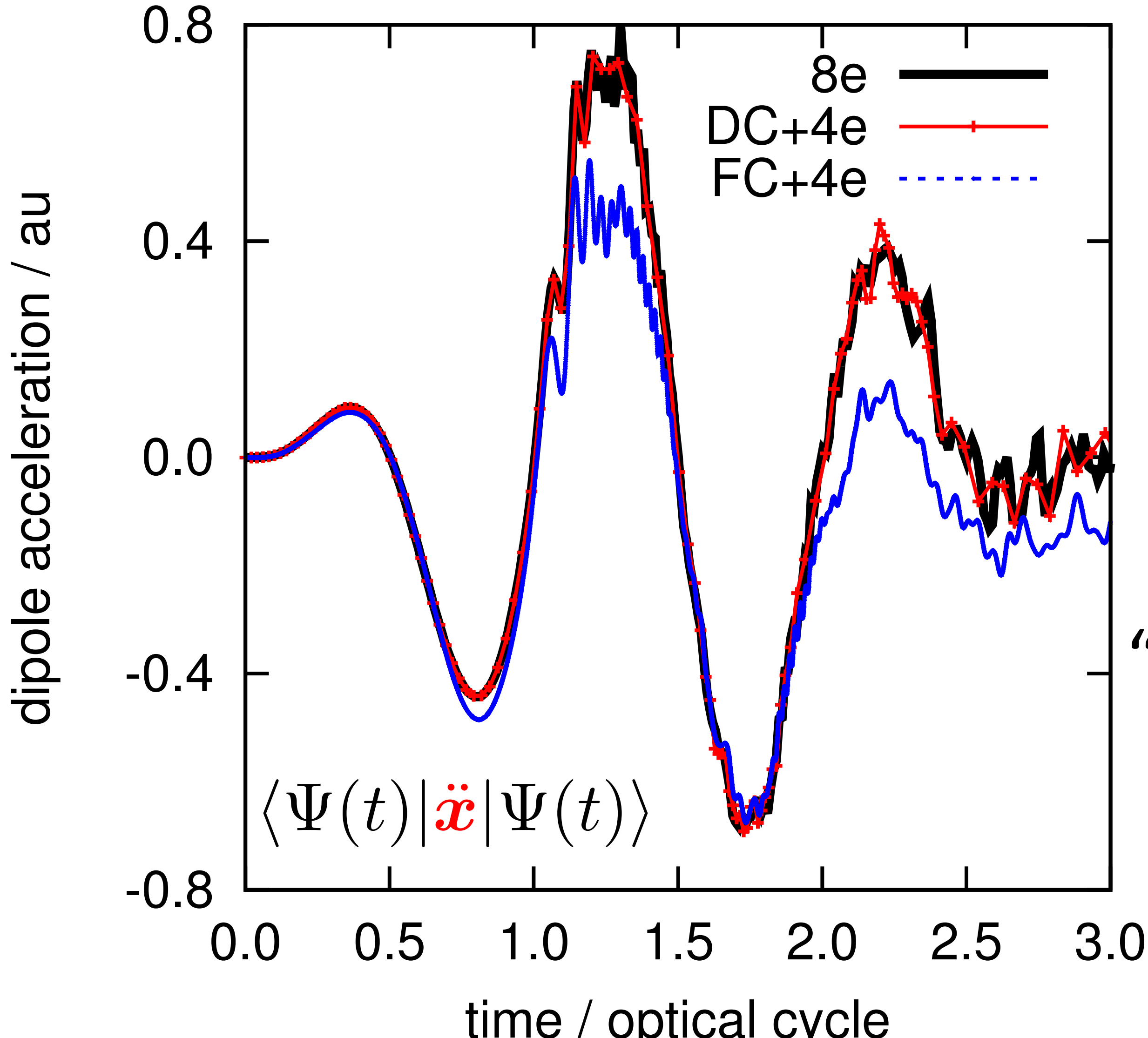
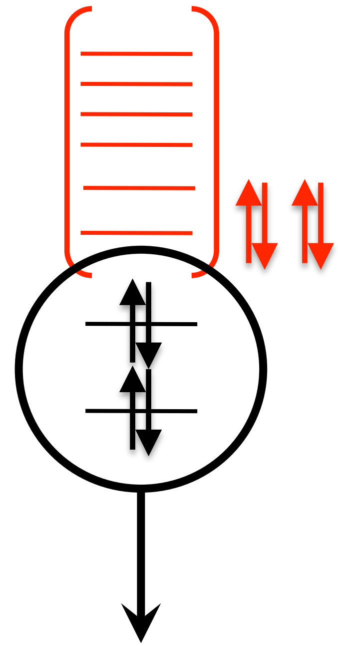
Applicaions



TD-CASSCF(4e, 8a) reproduces MCTDHF(8o, 10o)

Applicaions

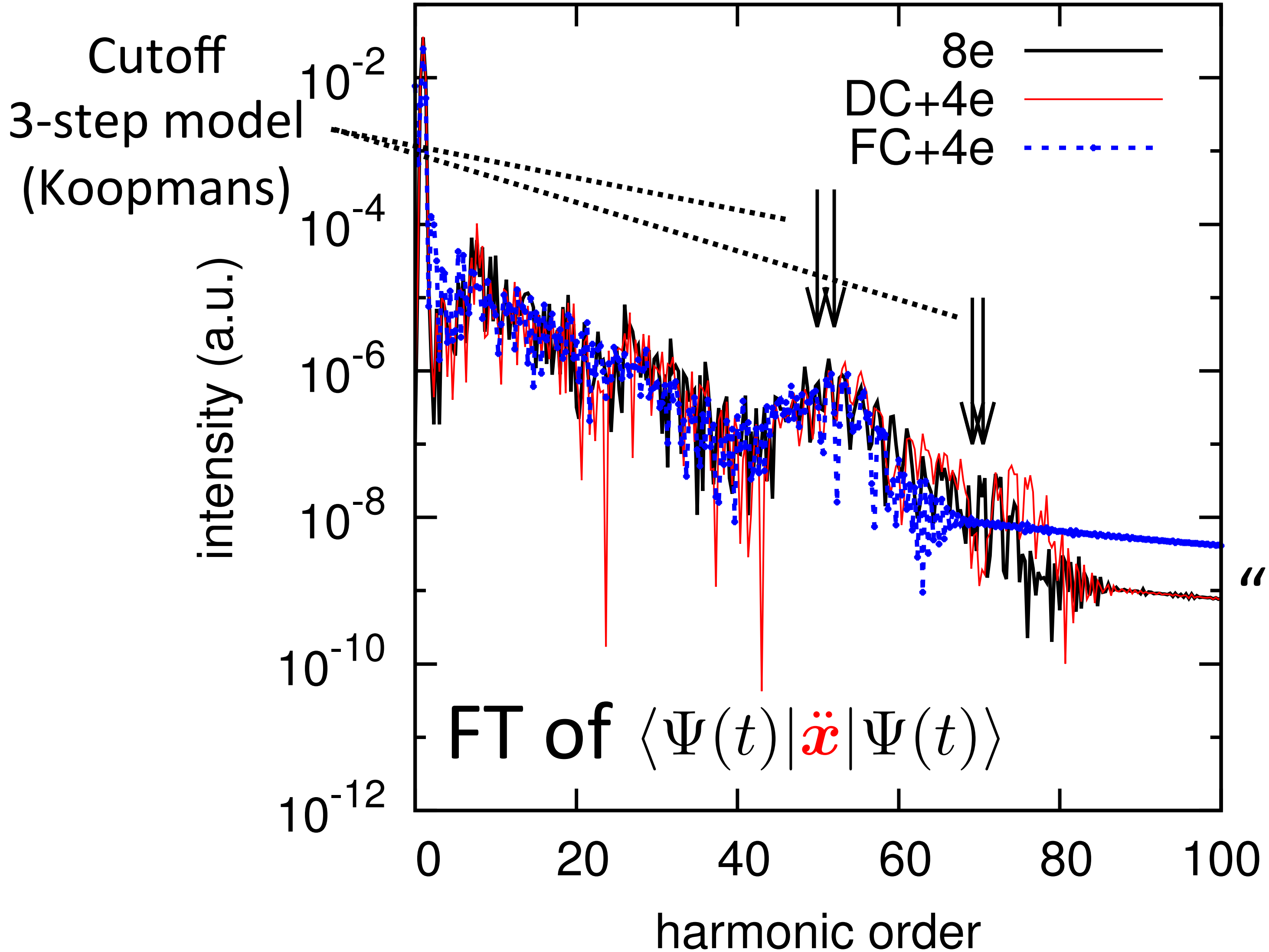


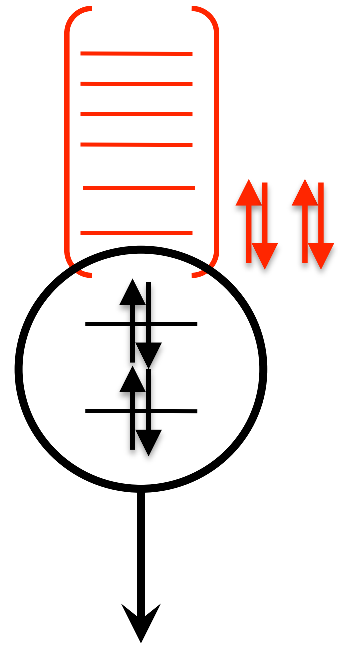


"Dynamical"
or
"Frozen"

Core is important for higher-order response

Applicaions





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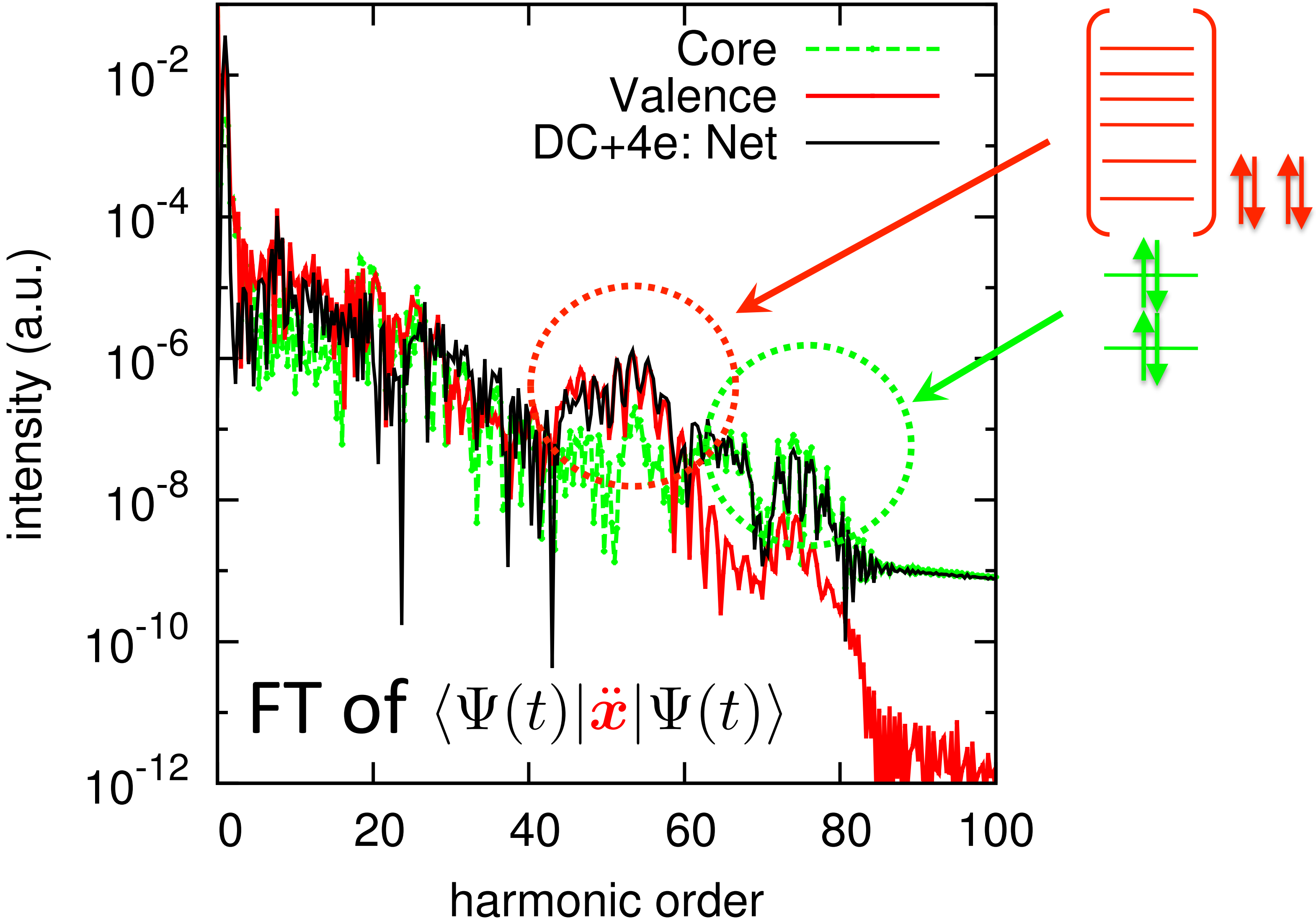


Core and Valence contributions: Deeper physical understanding

Report

Submission due: July 31.
Place to submit: the office of the Nuclear Engineering & Management, 2nd floor of the Bldg. 3. Language: English or Japanese.

(1)

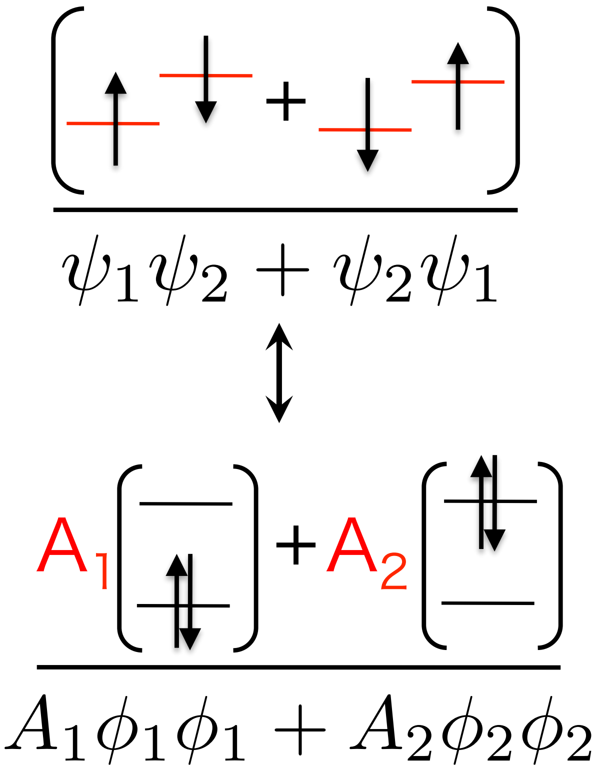
MCTDHF includes single determinant TDHF as a special case.
Derive the TDHF equations of motion (given in p. 7) starting from the MCTDHF equations (p. 15) by ignoring CI equations and inserting HF wave function,

$$|\Psi\rangle = |1_1 1_2 1_3 \cdots 1_N 0000\rangle$$

in the definition of one and two particle reduced density matrices. Here N is the number of electrons. The resultant equations will still look different from those in p. 7. Choose the appropriate Hermitian matrix R in order to obtain exactly the same equations as those in p. 7.

(2)

Derive the transformation (Expressions for A_1, A_2, ϕ_1, ϕ_2 below) from GVB wave function to the MCTDHF wave function for the two-electron singlet system, and explicitly show that MCTDHF orbitals are orthonormal. Assume that GVB orbitals are normalized. See J. Phys. B: At. Mol. Opt. Phys. **47** , 204031 (2014).



$$\Psi_{\rm GVB}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2) + \psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\right]$$

$$= A_1\phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) + A_2\phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)$$

$$A_1 = \frac{1+|S_{12}|}{\sqrt{2(1+|S_{12}|^2)}}\frac{S_{12}^*}{|S_{12}|},$$

$$A_2 = \frac{1-|S_{12}|}{\sqrt{2(1+|S_{12}|^2)}}\frac{S_{12}}{|S_{12}|},$$

$$\phi_1 = \frac{1}{\sqrt{2(1+|S_{12}|)}}\left\{\frac{S_{12}}{|S_{12}|}\psi_1 + \psi_2\right\}$$

$$\phi_2 = \frac{1}{\sqrt{2(1+|S_{12}|)}}\left\{\frac{S_{12}^*}{|S_{12}|}\psi_2 - \psi_1\right\}$$

$$S_{12} = \langle\psi_1|\psi_2\rangle$$