Time-dependent generalized-active-space approaches to the many-electron problem

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Motivation

- New light sources put focus on time-dependent, nonperturbative dynamics - a fundamental problem
- Valence shell dynamics induced by intense femtosecond infrared pulses
- ‘Inner’ shell dynamics induced by XUV attosecond pulses
- Observables are often associated with processes like ionization, break-up, high-order harmonics generation, transient absorption spectroscopy. *Continua*
- Much insight has been obtained by the single-active electron approximation, but a range of processes involve correlation

Motivation

- Direct solution of TDSE limited to very few particles
- Approximate solutions necessary for systems beyond H, He, and H_2
- Numerous approaches in the literature (TDHF, TDCIS, MCTDHF, TDCC, OATDCC, TD-*R* matrix,…TD-CASSCF)
- TD-*R* matrix and TDCIS have found most applications

Approach in Aarhus

- Study quantum chemistry methods
- Extend appropriate quantum chemistry methods to the time-domain
- We have so far identified **two** avenues which appear promising for our purposes

Approach in Aarhus

- Time-dependent restricted-active-space self-consistent-field (TD-RASSCF) method (*Haruhide Miyagi*, Wenliang Li)

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{RAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}(t)\rangle$$

- Time-dependent generalized-active-space configuration-interaction (TD-GASCI) method (*Sebastian Bauch*, *Lasse Kragh Sørensen, Lun Yue*)

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{GAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}\rangle$$

D. Hochstuhl and M. Bonitz, Phys. Rev. A **86**, 053424 (2012)

I. TD-GASCI

- Theory part
  - Idea of GAS/RAS
  - Basis set for photoionization (continuum involved)
- Numerical examples
  - 1D model system: “He” and “Be”
  - 3D systems
- Conclusions

Configuration Interaction

Expand the wave function

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{GAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}\rangle$$

with Slater determinants constructed from single-particle spin-orbitals

$$i\partial_t C_{\mathcal{I}} = \sum_{\mathcal{J}} H_{\mathcal{I}\mathcal{J}}(t) C_{\mathcal{J}}(t)$$

with matrix elements

$$H_{\mathcal{I}\mathcal{J}}(t) = \sum_{ij} h_{ij}(t)\langle\Phi_{\mathcal{I}}|\hat{a}_i^\dagger\hat{a}_j|\Phi_{\mathcal{J}}\rangle + \frac{1}{2}\sum_{ijkl} w_{ijkl}\langle\Phi_{\mathcal{I}}|\hat{a}_i^\dagger\hat{a}_k^\dagger\hat{a}_j\hat{a}_l|\Phi_{\mathcal{J}}\rangle$$

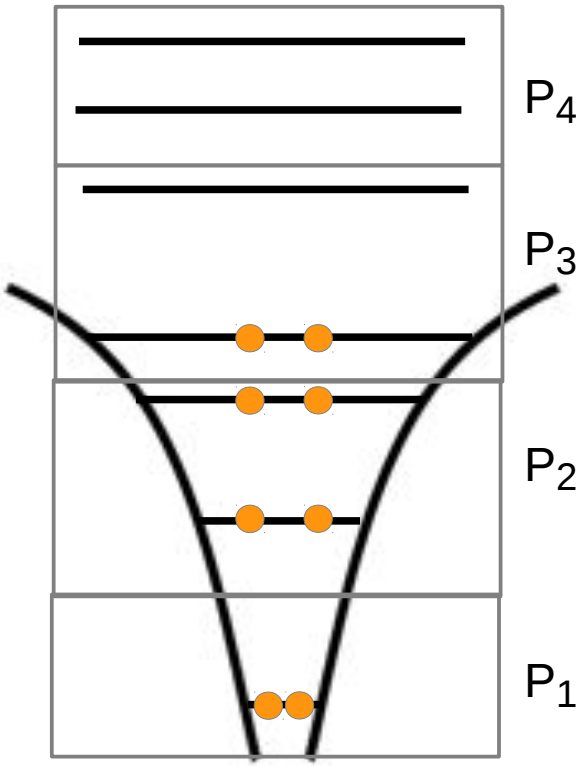
Full-CI basis size:

$$\begin{pmatrix} N_b \\ N_{\mathrm{e}}/2 \end{pmatrix}^2$$

GASCI

- The increase in basis with N_e and N_b is the “curse of dimensionality”
- To decrease the basis size we invoke the GAS/RAS scheme from quantum chemistry

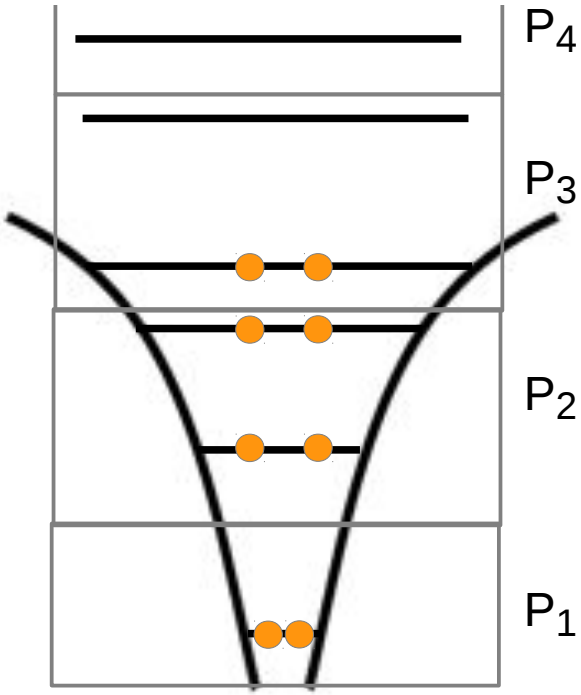
GASCI



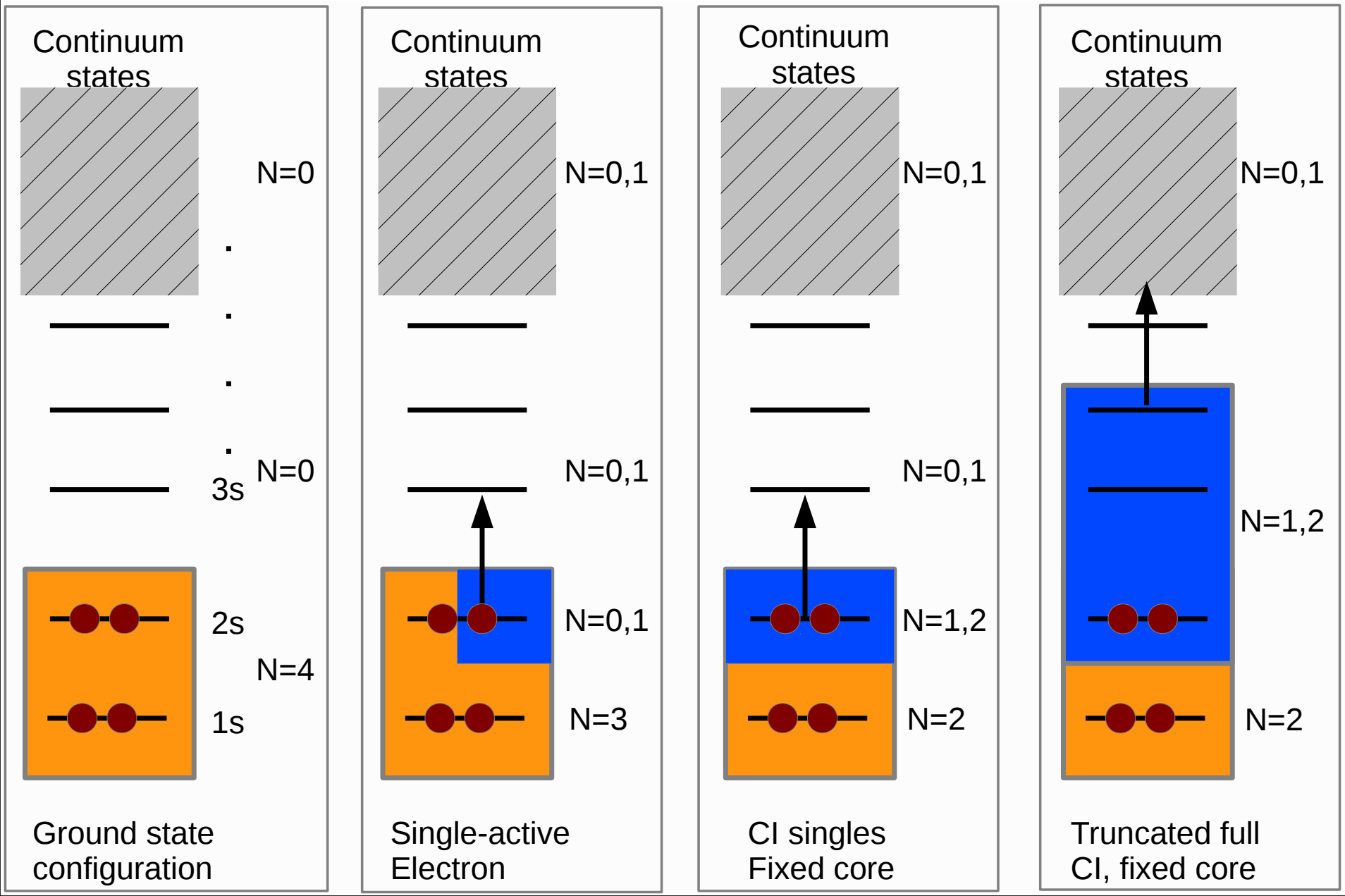
Construction of GAS wave function

- Partition single-particle basis into n_r parts
- Impose restrictions on the particle numbers in the different parts (if, e.g., the core P_1 is frozen $N_1 = 2$, if single excitation out of P_1 is allowed N_1=2,1)
- Construct configurations in subspace P_i

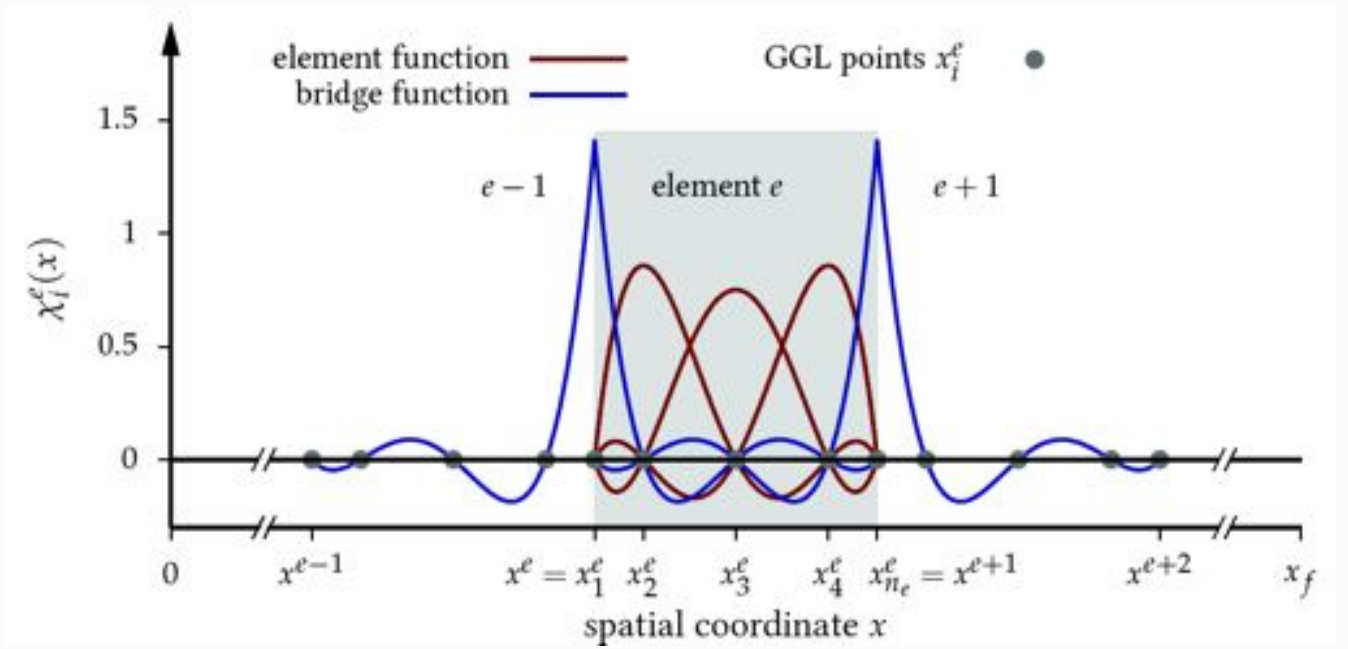
GAS: **Example**: $N_1=2$, $N_2=4$, $N_3=(2,1)$, $N_4=0,1$:



$$|11|1111|1100|00\rangle \quad |11|1111|1001|00\rangle$$
$$|11|1111|0110|00\rangle \quad |11|1111|0011|00\rangle$$
$$|11|1111|0100|10\rangle \quad |11|1111|0001|10\rangle$$
$$|11|1111|1000|01\rangle \quad |11|1111|0010|01\rangle$$


Continuum states
N=0
3s
N=0
2s
1s
N=4
Ground state configuration
Continuum states
N=0,1
N=0,1
N=0,1
N=3
Single-active Electron
Continuum states
N=0,1
N=0,1
N=1,2
N=2
CI singles Fixed core
Continuum states
N=0,1
N=1,2
N=2
Truncated full CI, fixed core

Basic adequate for continuum description: Finite-element DVR basis



Gauss-Lobatto DVR with quadrature points x_i and weights w_i

$$
\begin{aligned}
x_i^e &= \frac{1}{2}\left[\left(x^{e+1}-x^e\right)x_i + \left(x^{e+1}+x^e\right)\right] \\
w_i^e &= \frac{w_i}{2}\left[x^{e+1}-x^e\right] .
\end{aligned}
$$

FE-DVR

Lobatto-shape functions: $$f_i^e(x) = \prod_{q \neq i} \frac{x - x_q^e}{x_i^e - x_q^e}$$

Elements: $$\chi_i^e(x) \equiv \frac{f_i^e(x)}{\sqrt{w_i^e}}, \quad i = 2, \ldots, n_e - 1$$

Brigdes: $$\chi_{n_e}^e(x) \equiv \frac{f_{n_e}^e(x) + f_1^{e+1}(x)}{\sqrt{w_{n_e}^e + w_1^{e+1}}}$$

See, e.g., Rescigno and McCurdy, Phys. Rev. A **62** 032706 (2000)

FE-DVR

- Matrix elements

$$\langle \chi_i | V(x_1) | \chi_j \rangle = V_{ij} \delta_{ij}$$

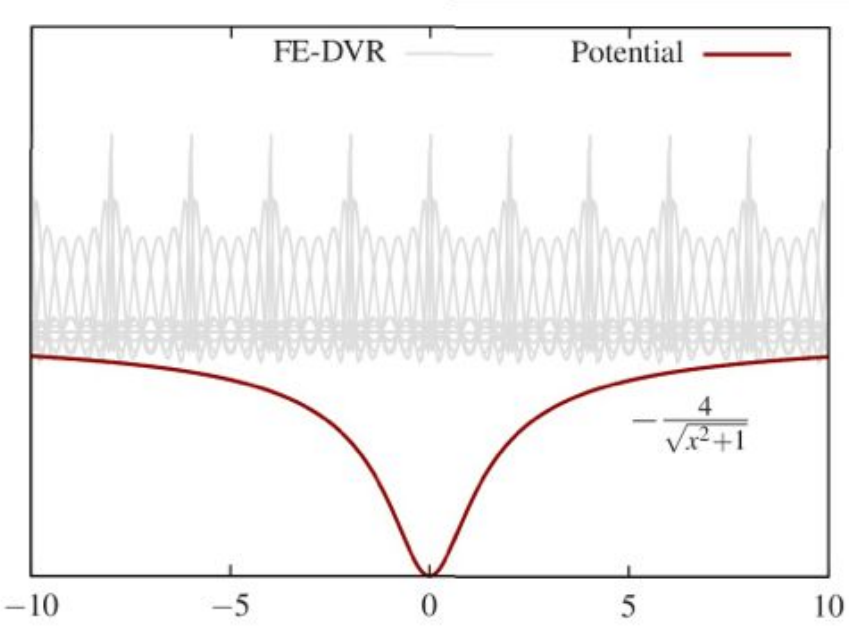
$$\langle \chi_i | T(x_1) | \chi_j \rangle = T_{ij} \delta_{e \pm (1,0), f}$$

$$\langle \chi_i \chi_k | w(x_1, x_2) | \chi_j \chi_l \rangle = w_{ij,kl} \delta_{ij} \delta_{kl}$$

Interaction energy diagonal in (*ij*), (*kl*)

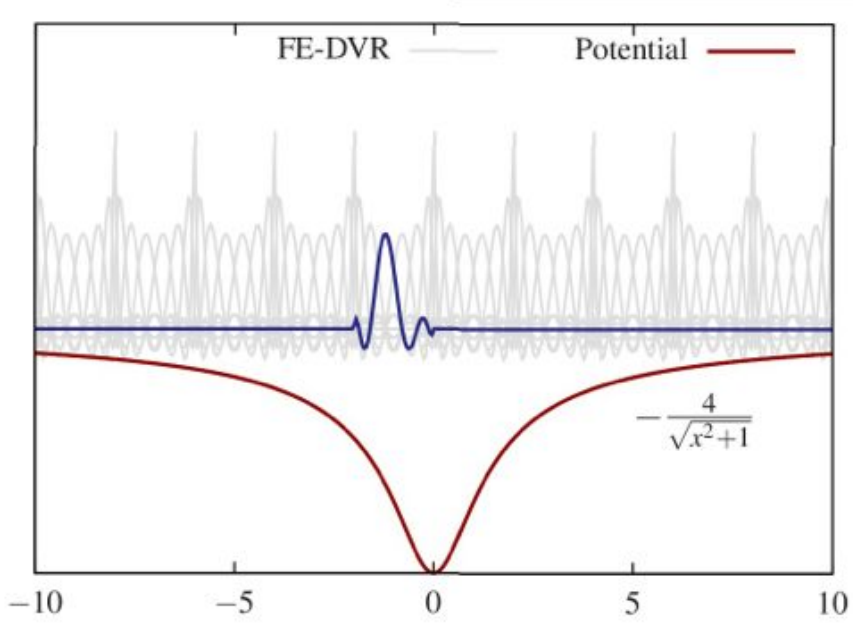
$$\mathcal{O}(N_b^2)$$

Single-particle basis: FE-DVR



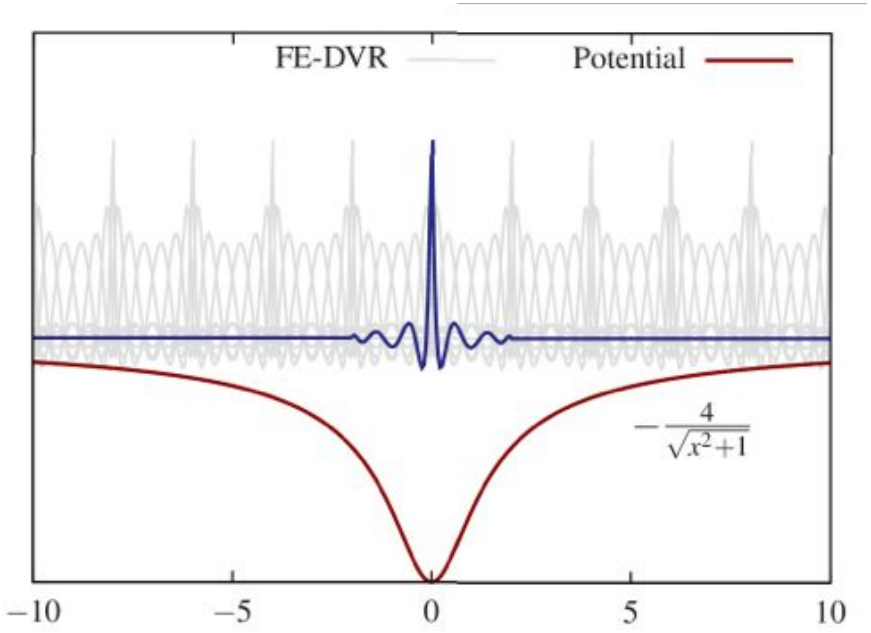
- FE-DVR basis provides efficient storage of 2-electron integrals

Single-particle basis: FE-DVR



- FE-DVR basis provides efficient storage of 2-electron integrals
- **Drawback**: A priori no means to exclude basis functions (-> Full CI)

Single-particle basis: FE-DVR



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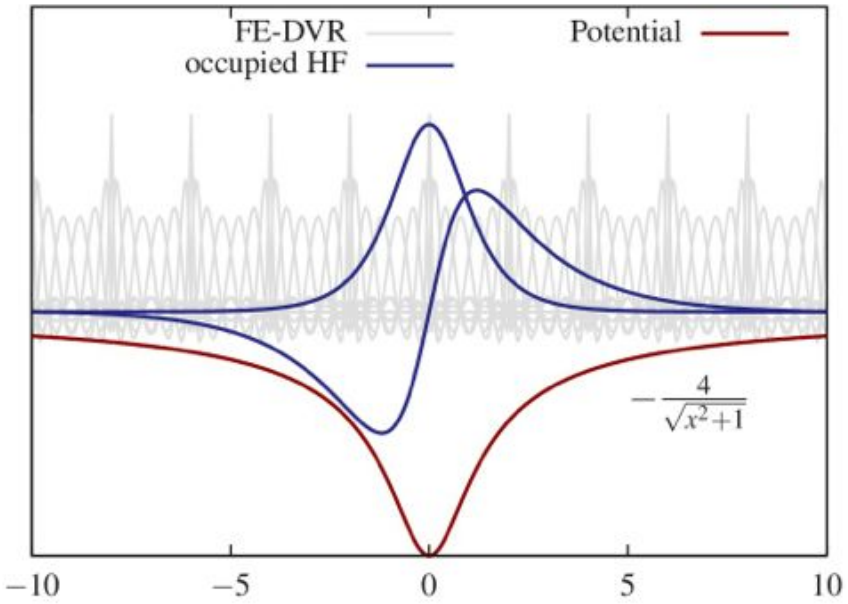
Single-particle basis: HF



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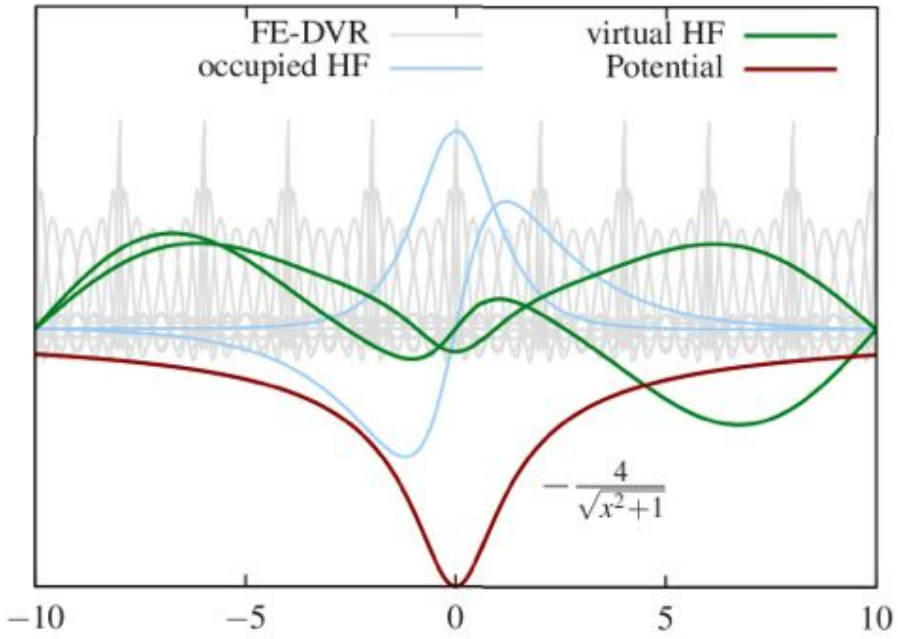
- **Solution**: Include configurations based on HF orbitals

Single-particle basis: HF



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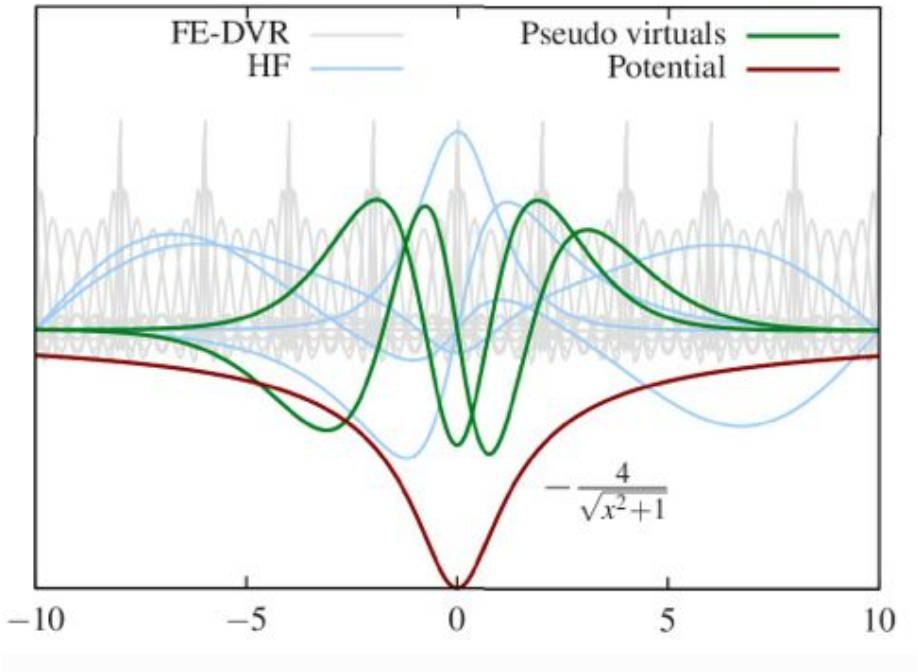
- **Drawback**: Virtual HF orbitals are delocalised (far from true states)

Single-particle basis: HF



- FE-DVR basis provides efficient storage of 2-electron integrals
- **Drawback**: A priori no means to exclude basis functions (-> Full CI)
- **Solution**: Include configurations based on HF orbitals
- **Drawback**: Virtual HF orbitals are delocalised (far from true states)
- **Solution**: Use pseudo orbitals for virtual states

Pseudo orbitals

Use pseudo orbitals for virtual states

$$\hat{H}_0 \varphi_n^0 = E_n \varphi_n^0$$

$$\hat{H}_0 = \sum_i \hat{t}_i + \hat{v}(x_i)$$

$$\left\{ \varphi_0^{\mathrm{hf}}, \ldots, \varphi_{N/2}^{\mathrm{hf}}, \varphi_{N/2+1}^0, \ldots, \varphi_{Nb}^0 \right\}$$

$$\varphi_i^{\mathrm{hf}} \perp \varphi_i^0$$

Note: we also can use ‘natural orbital’..long discussion

Single-particle basis: HF

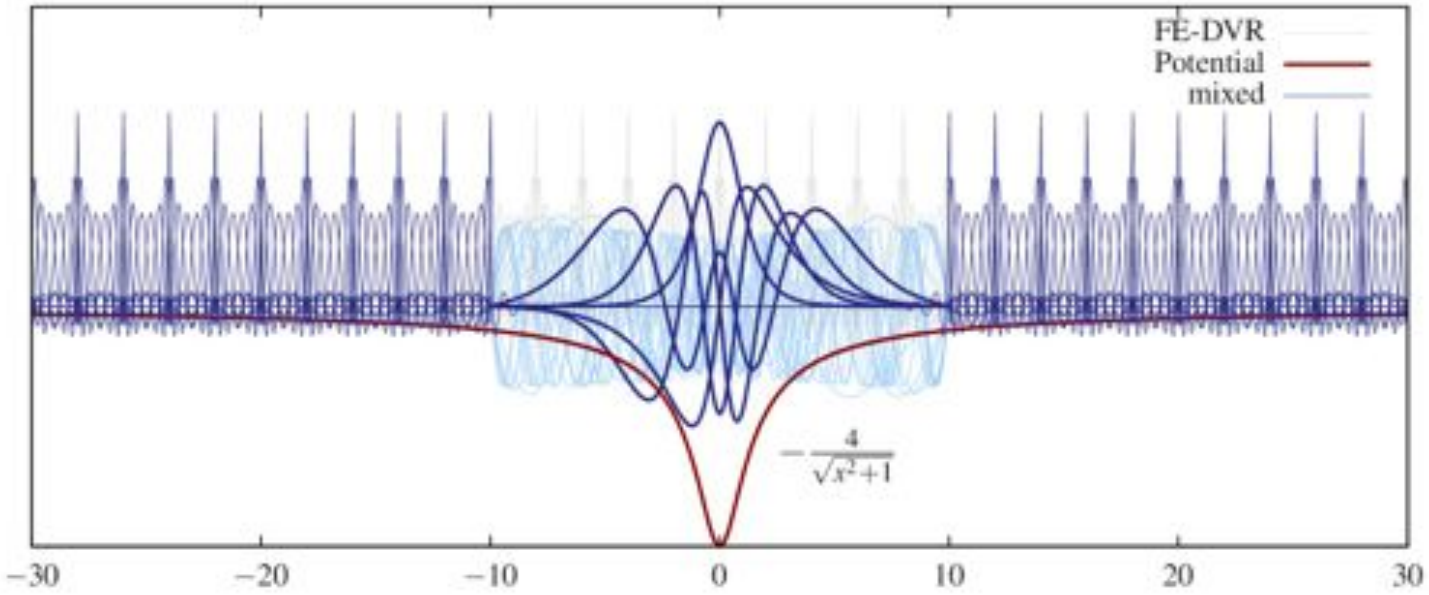
In the HF basis, the CI expansion converges, but there is a serious drawback:

$w^{\mathrm{HF}}_{ij,kl} = w_{ij,kl}$ scales as $\mathcal{O}(N_b^4)$

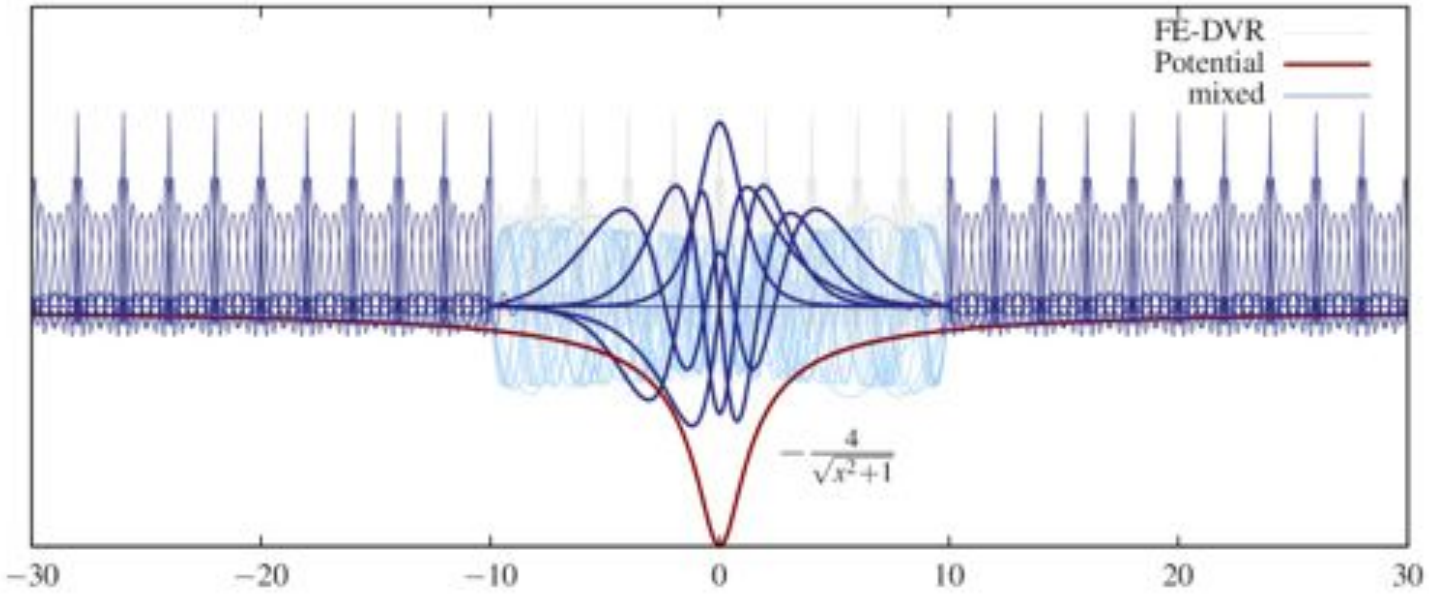
Such an approach would limit the number of basis functions to about 100.
Hence, processes involving a continuum would be difficult to address

Solution: Mixed single-particle basis
HF to describe bound-state excitation
FE-DVR to describe continuum

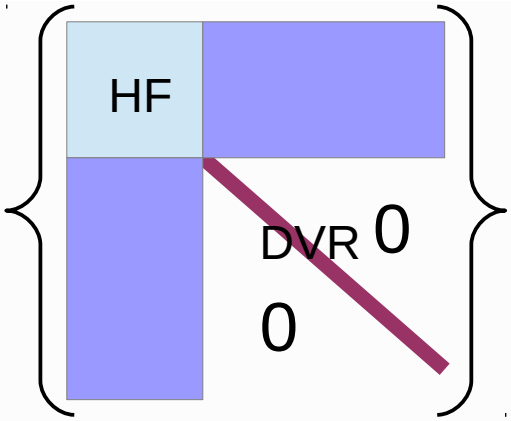
Single-particle basis: mixed basis set approach



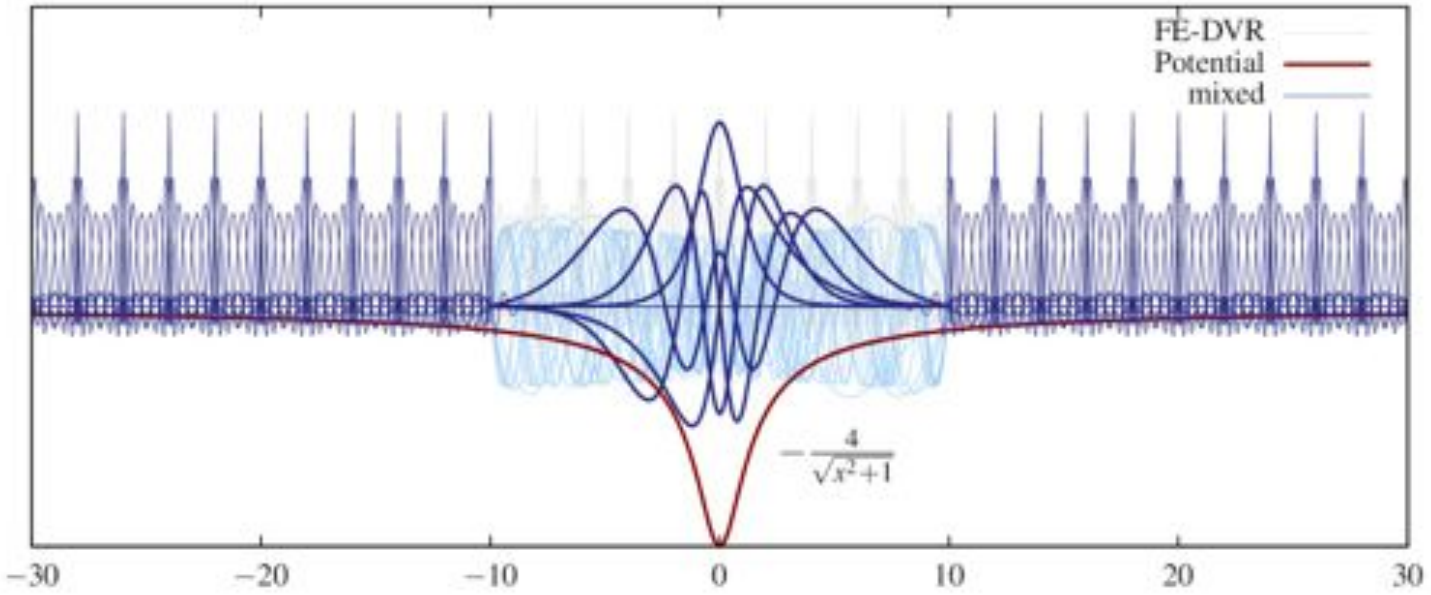
Single-particle basis: mixed basis set approach



$$w_{ij,kl}^{\text{mixed}} =$$



Single-particle basis: mixed basis set approach



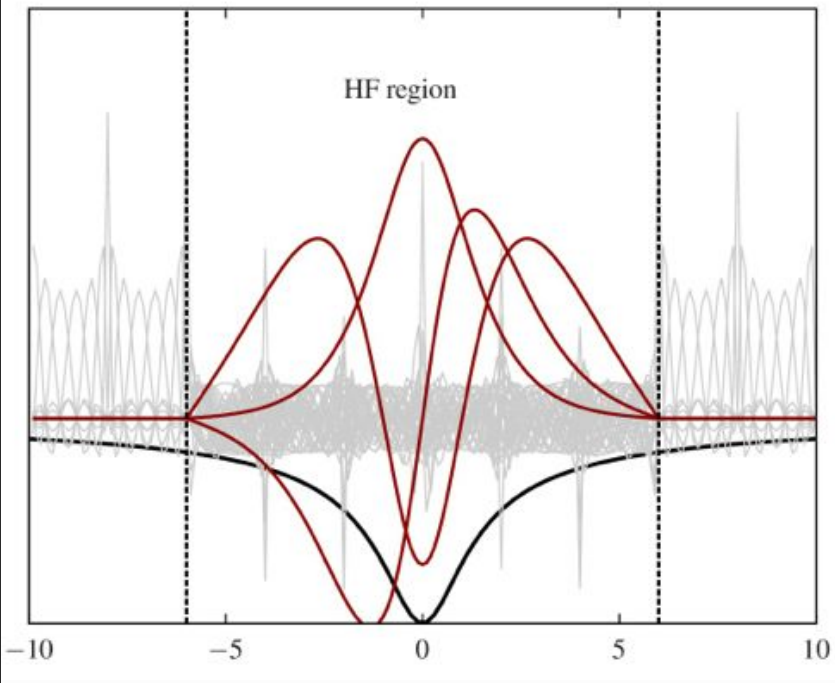
Efficient storage scheme: approximately $\mathcal{O}(N_b^2)$
Allows for the calculation of ionization without approximating the electron-electron interaction (in addition to the GAS scheme)

TD-GASCI overview

1. Set up physical system (potentials, N, box size, …)
2. Set up FE-DVR basis
3. Construct Hartree-Fock orbitals in vicinity of nucleus
4. Construct pseudo-virtuals
5. Transform FE-DVR matrix elements to mixed basis
6. Construct RAS space
7. Compute CI matrix elements (e.g. Slater-Condon rules)
8. Prepare initial state (e.g. diagonalization of RAS-CI matrix, imaginary time prop,...)
9. Perform time propagation (e.g. Arnoldi/Lanczos propagation [1])

[1] M. H. Beck et al., Phys. Rep. **324** (2000).

Example: 1D Helium



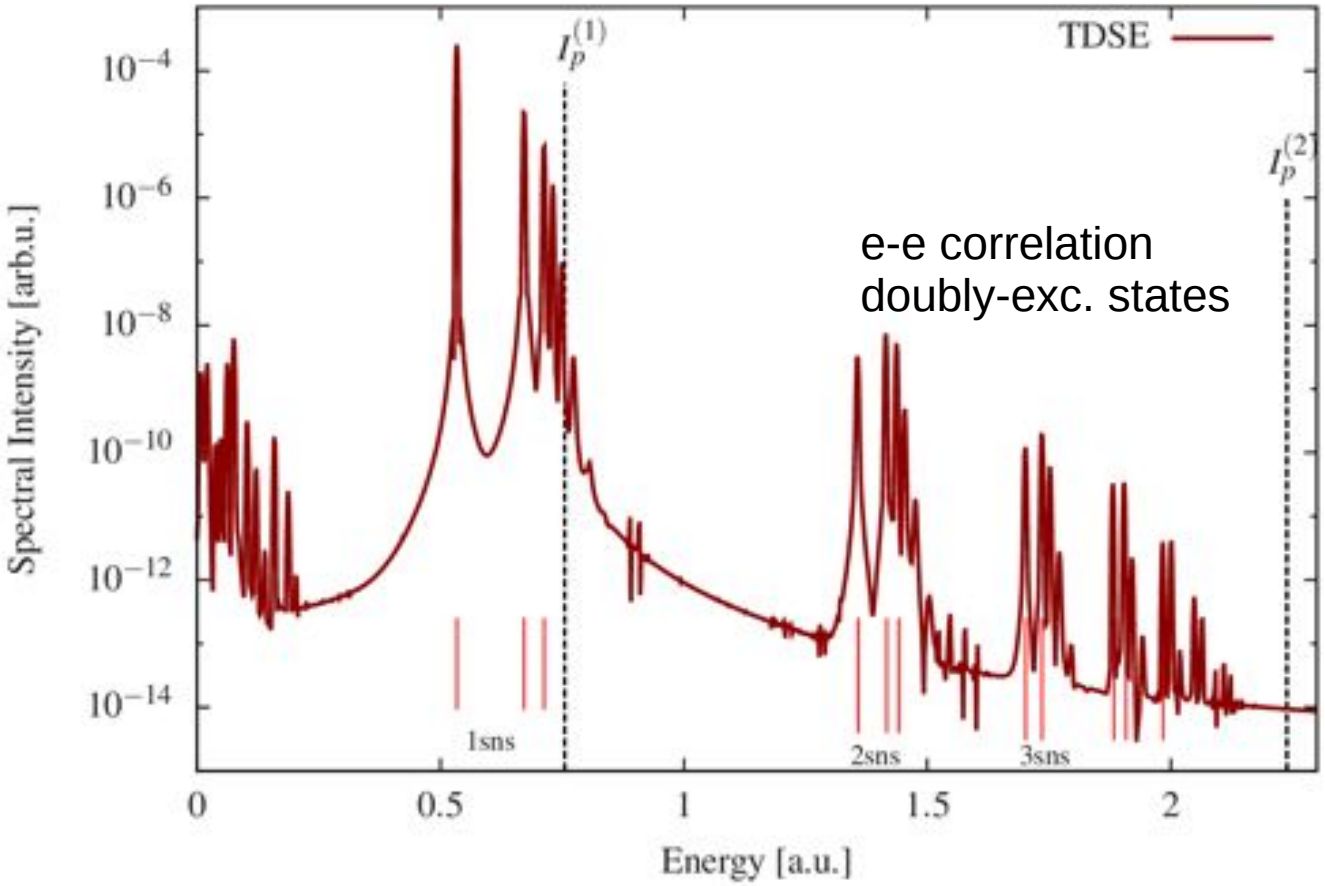
1D Helium model (N=2)

$$V(x) = -\frac{2}{\sqrt{x^2+1}}$$

$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$

Method	E_0	configurations
TDSE	−2.238259	-
HF (full box)	−2.224212	1
HF (small box)	−2.224162	1
SAE (↑)	−2.224187	69
SAE (↓)	−2.224187	69
CI-S	−2.224212	137
CI-RAS1	−2.235258	205
CI-RAS2	−2.236189	272
CI-RAS3	−2.237293	339
CI-RAS4	−2.237566	405
CI-RAS5	−2.237785	471
CI-RAS10	−2.238157	792
CI-SD-HF	−2.238260	855
CI-SD	−2.238260	4761

Convergence of ground state energy with RAS-CI for #Nb=69, #HF=41



e-e correlation
doubly-exc. states

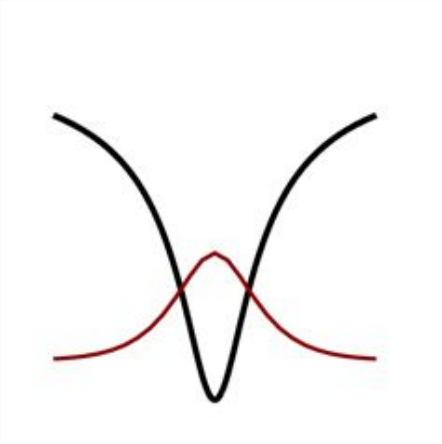
Excite with short half-cycle
(„linear response“)

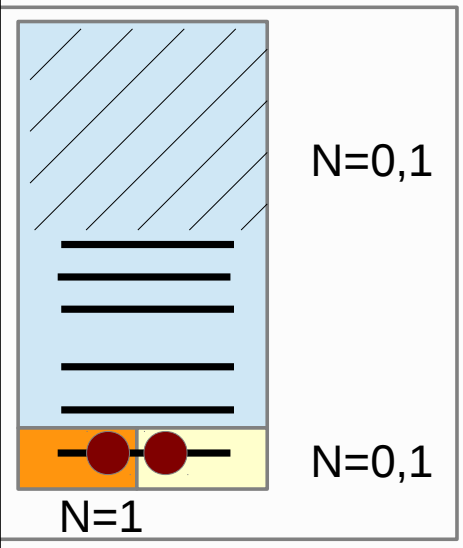
$$E(t) = \exp - \frac{(t - t_0)^2}{(2\sigma^2)}$$

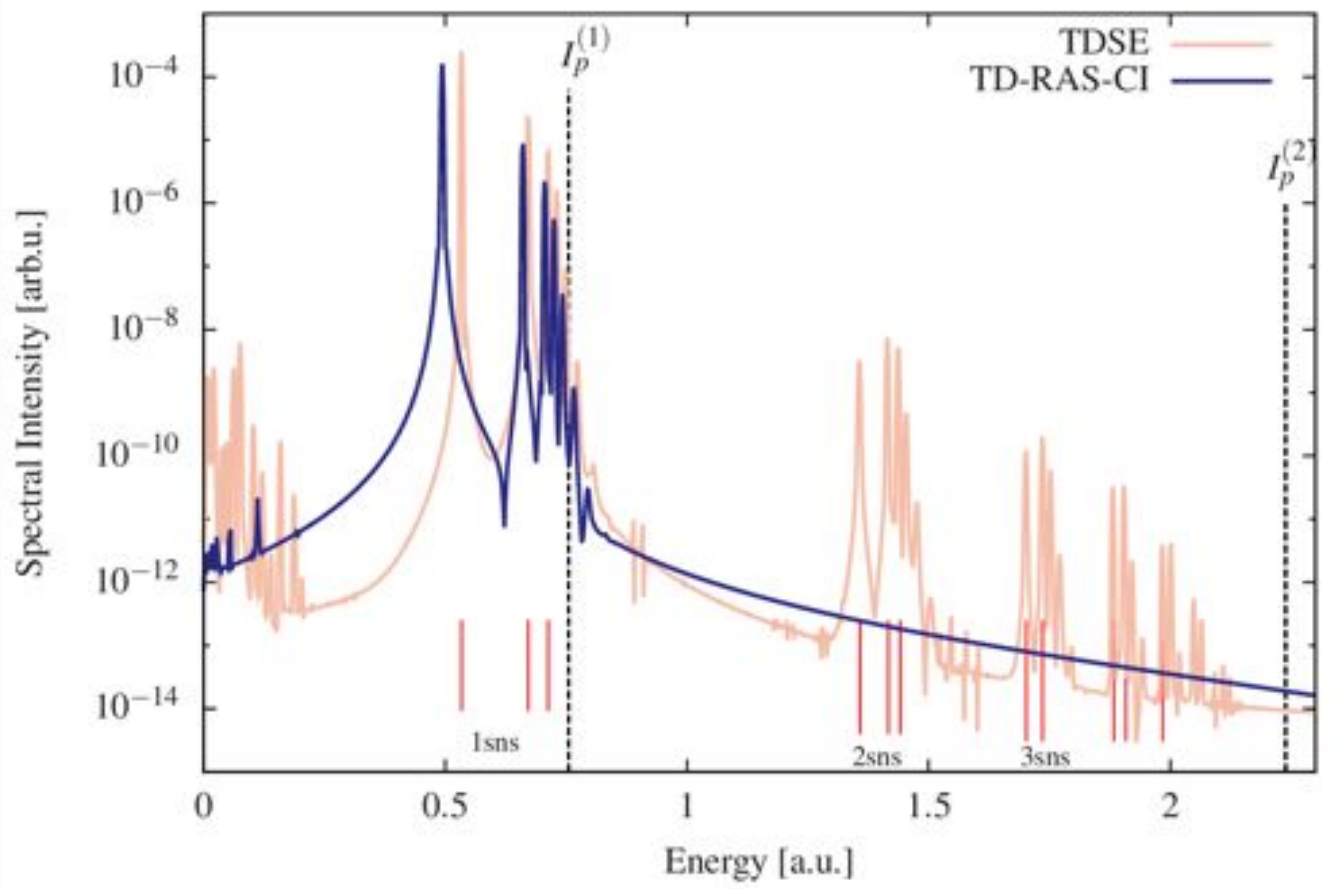
Calculate spectrum:

$$P(\omega) = \left| \int_0^{T_f} \langle x(t) \rangle e^{-i\omega t} \mathrm{d}t \right|^2$$

SAE approx.

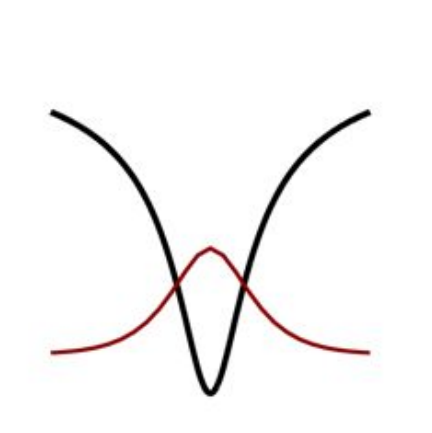


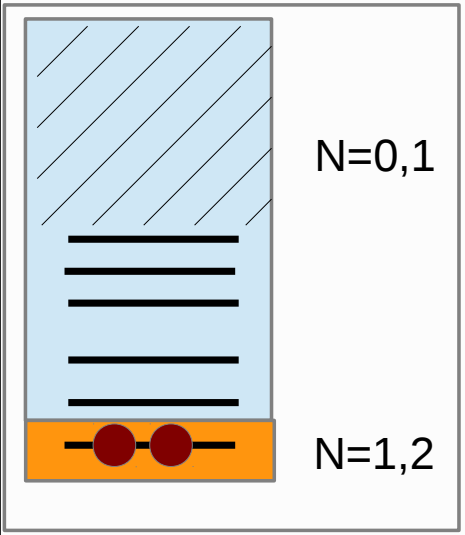


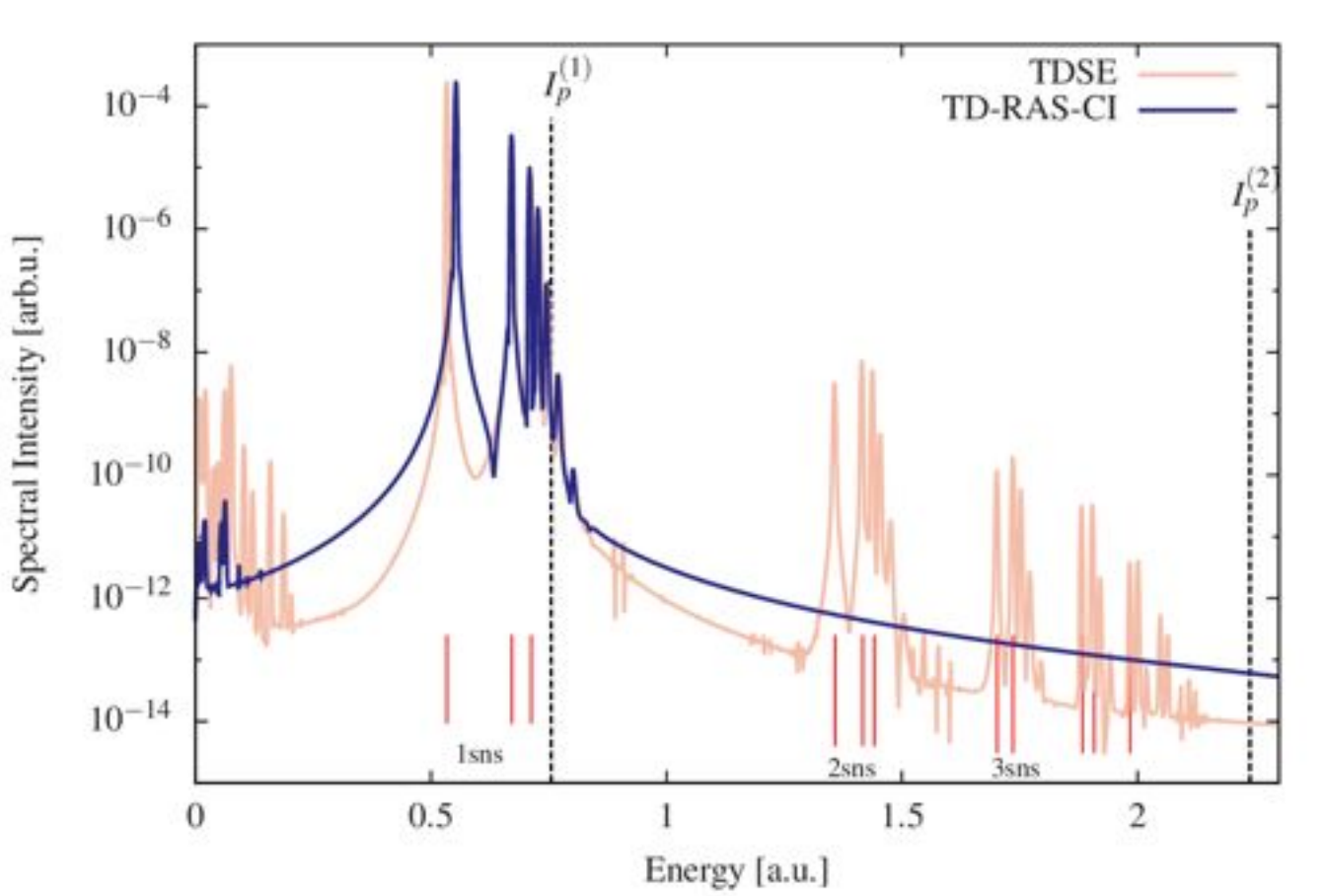


- Single-active electron approximation
- Reproduces single-excitations below first threshold
- Shift towards lower energy
- Autoionizing resonances are absent

CI singles

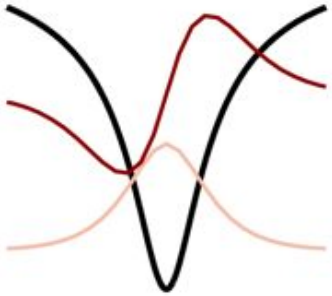


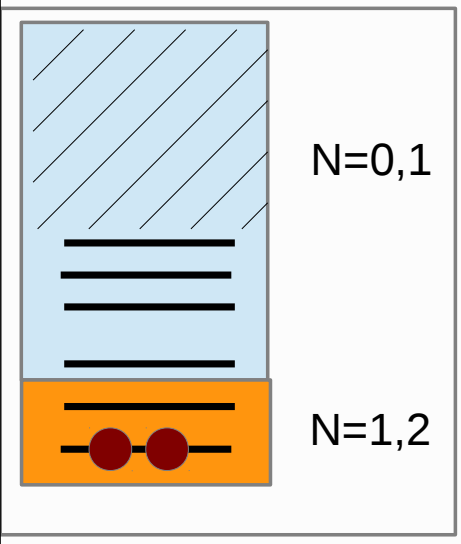


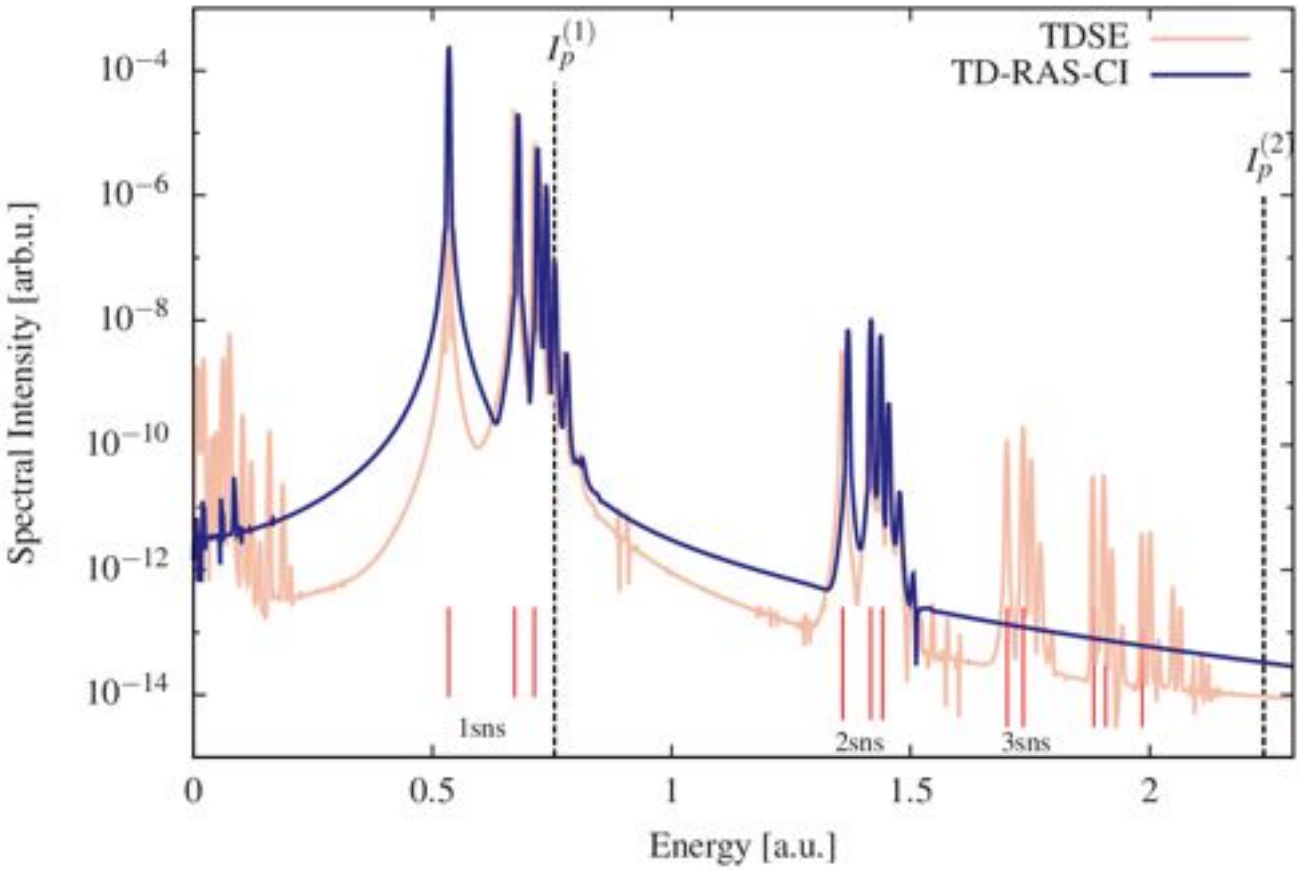


- CI singles approximation
- Structure similar to SAE approximation
- Shift towards higher energy
- Autoionizing resonances are absent

full CI up to n=2

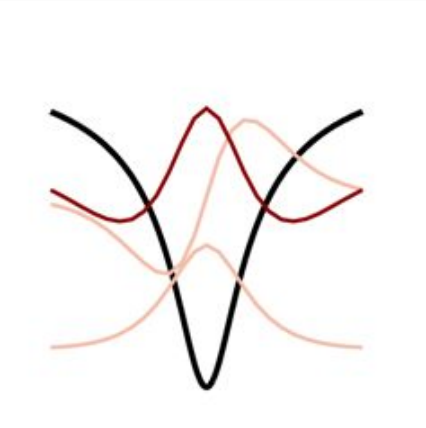


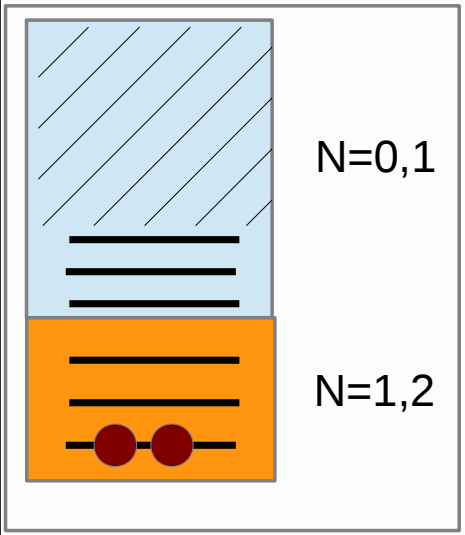


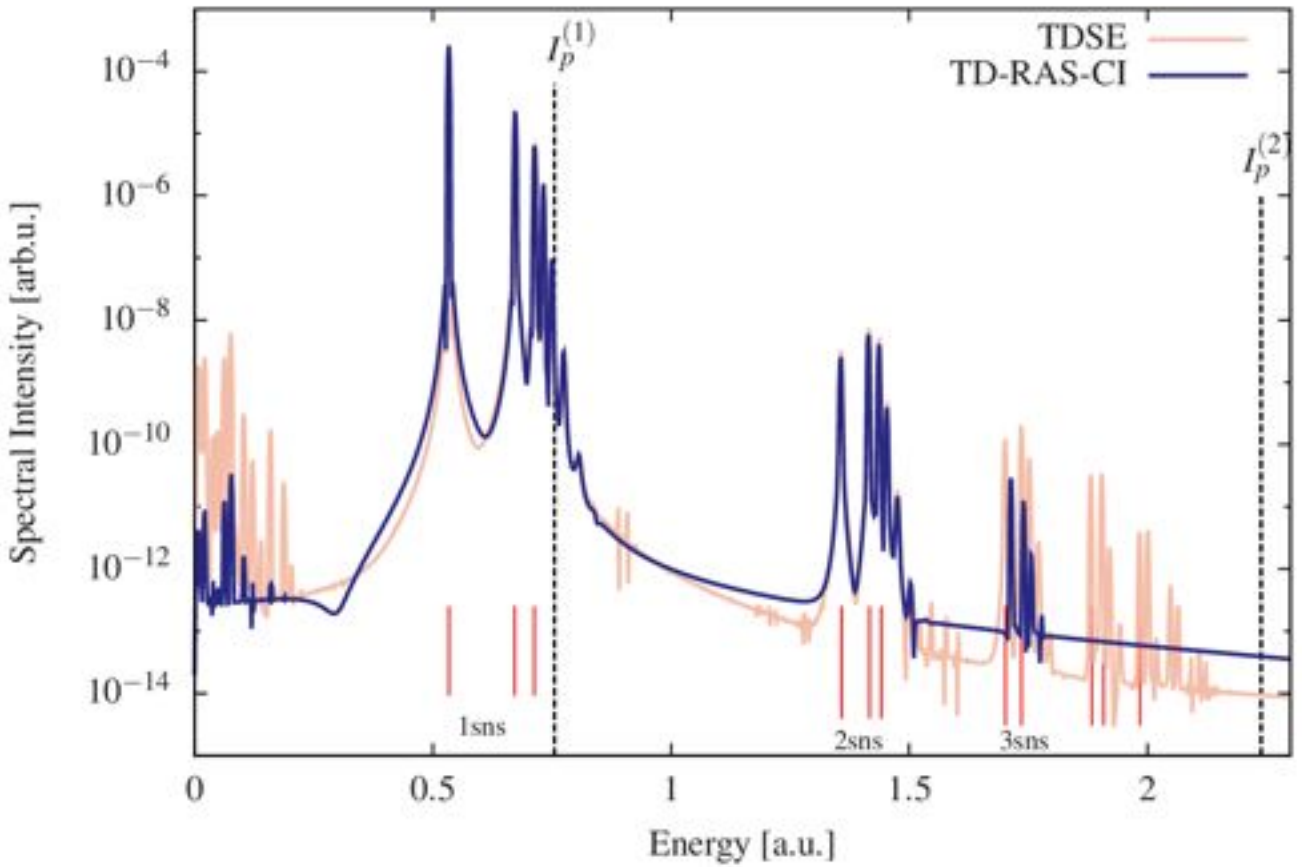


- Include first virtual orbital into full CI space
- Single-excitations shift towards TDSE results
- First series of resonances above first threshold
- Resonances shifted towards higher energy

full CI up to n=3

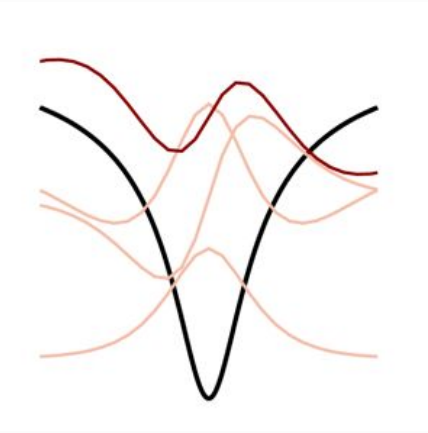


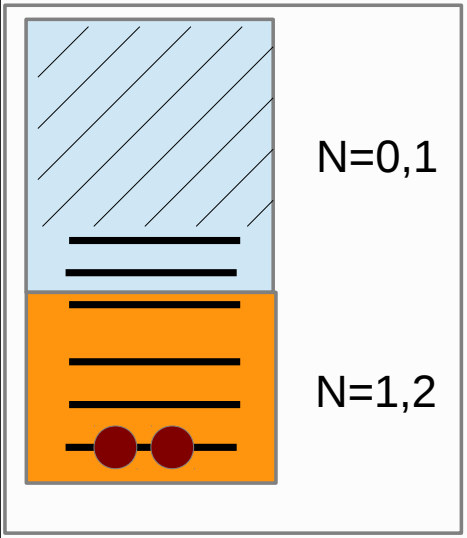


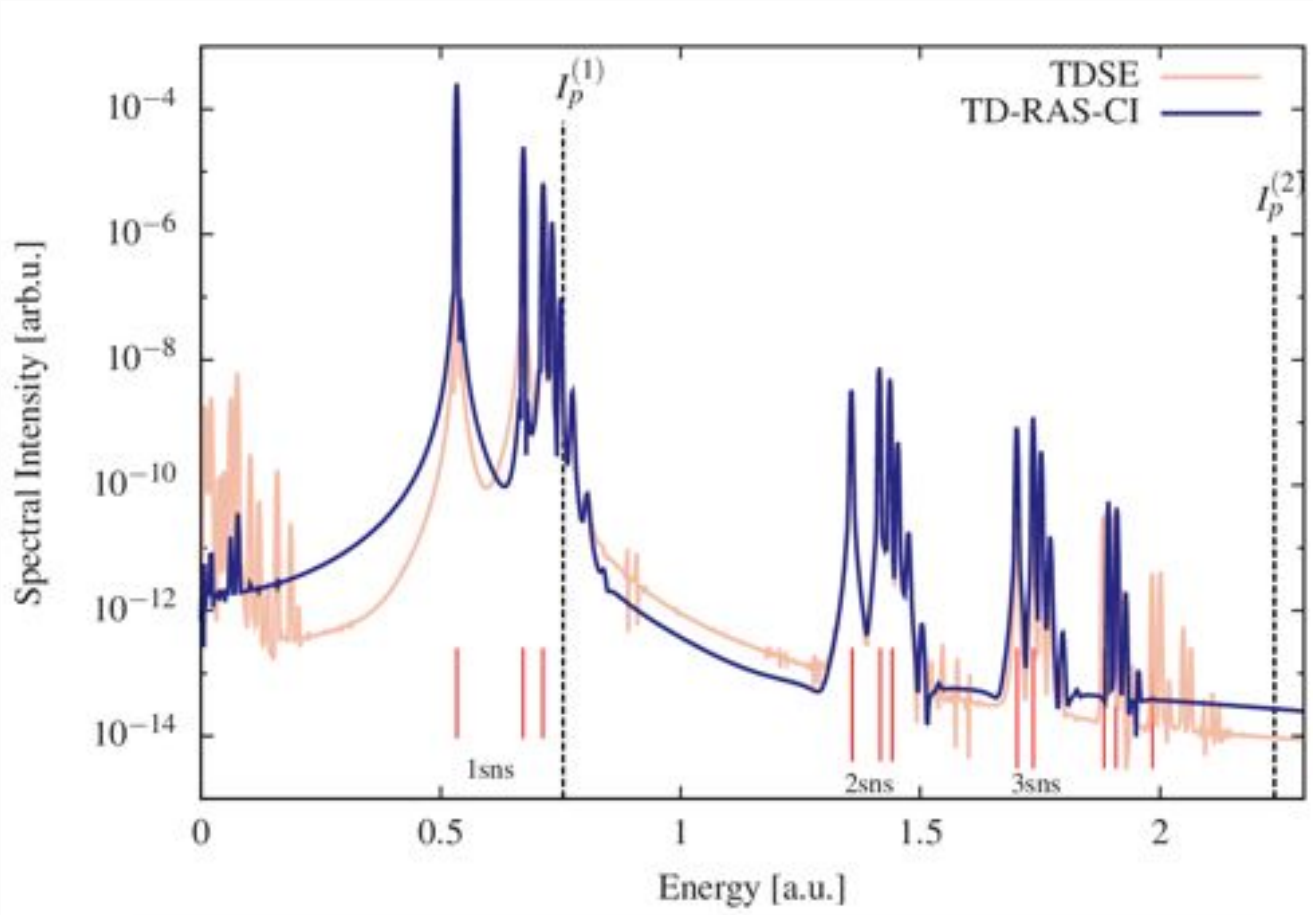


- Include 1st+2nd virtual orbitals into full CI space
- Perfect agreement in first series 2sns with TDSE
- 3sns series appear

full CI up to n=4

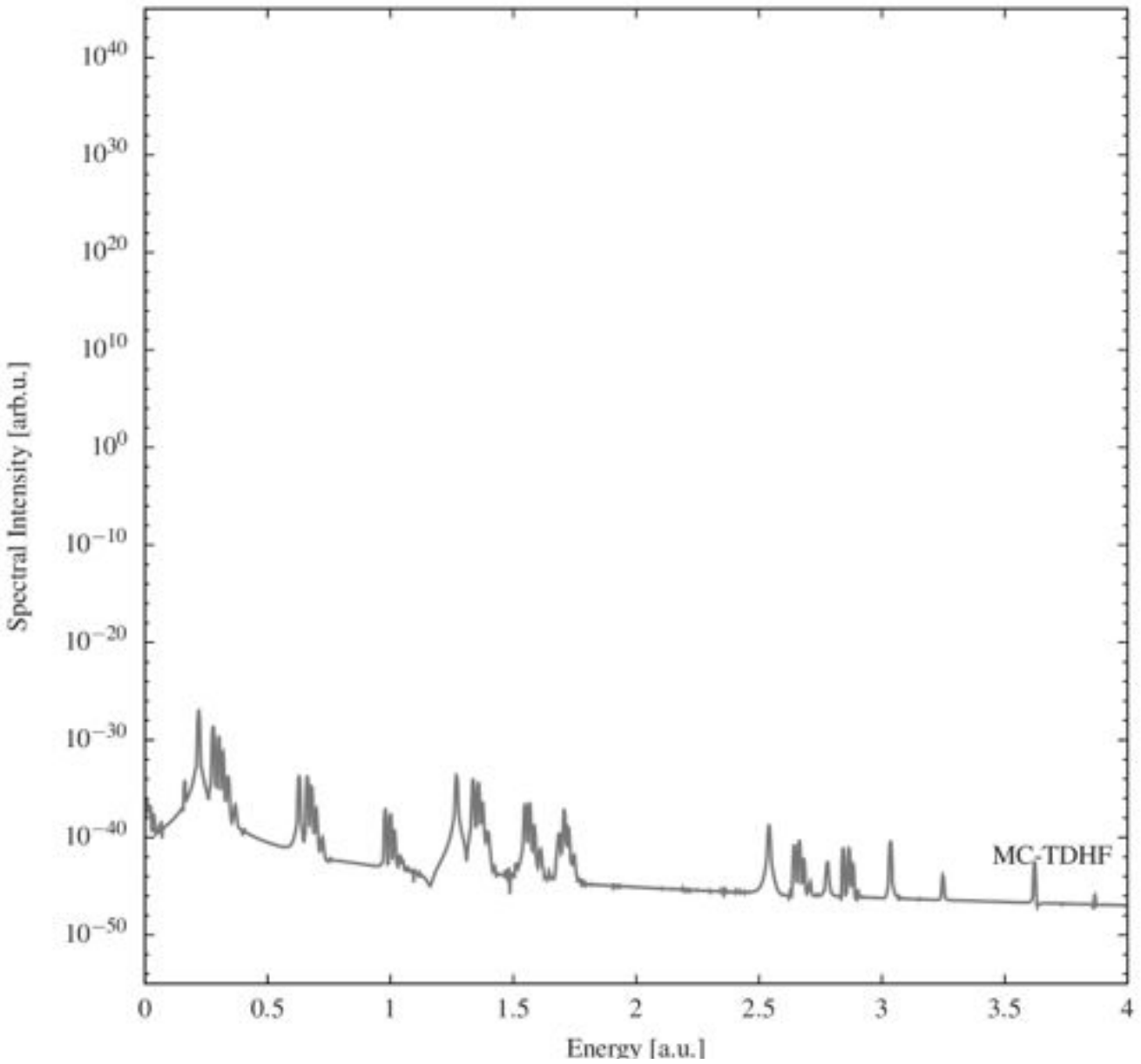






- Include 4 virtual orbitals into full CI space
- Agreement with TDSE for first two series
- Higher series successively appear
- Convergence towards full correlated spectrum

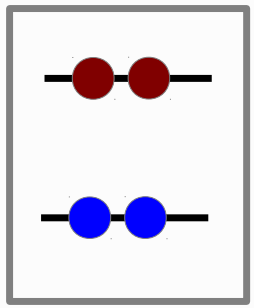
Numerical example: 1D Beryllium



N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

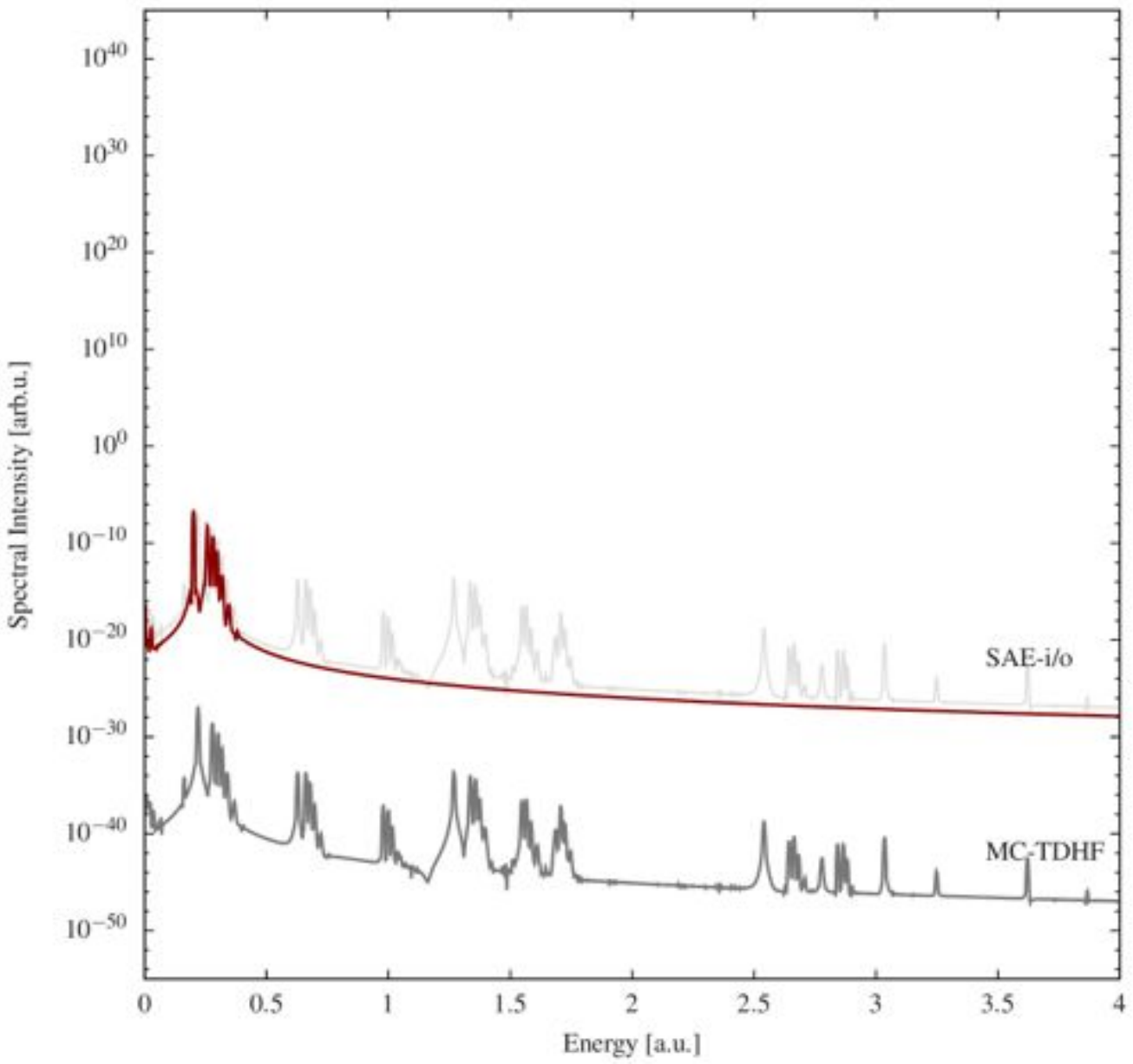
$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$



outer

N=4

inner



$N_{el}=4$

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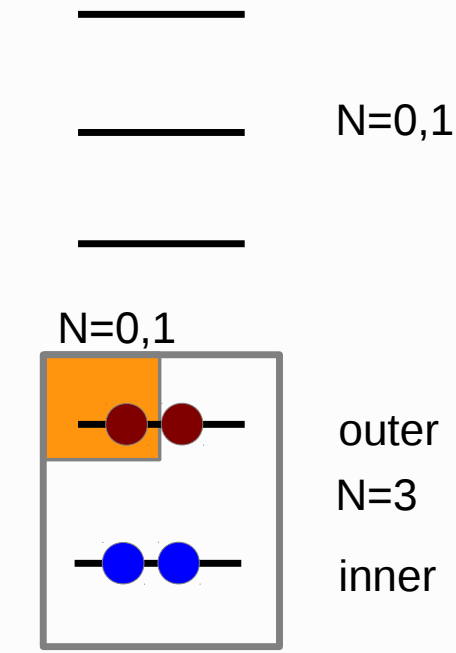
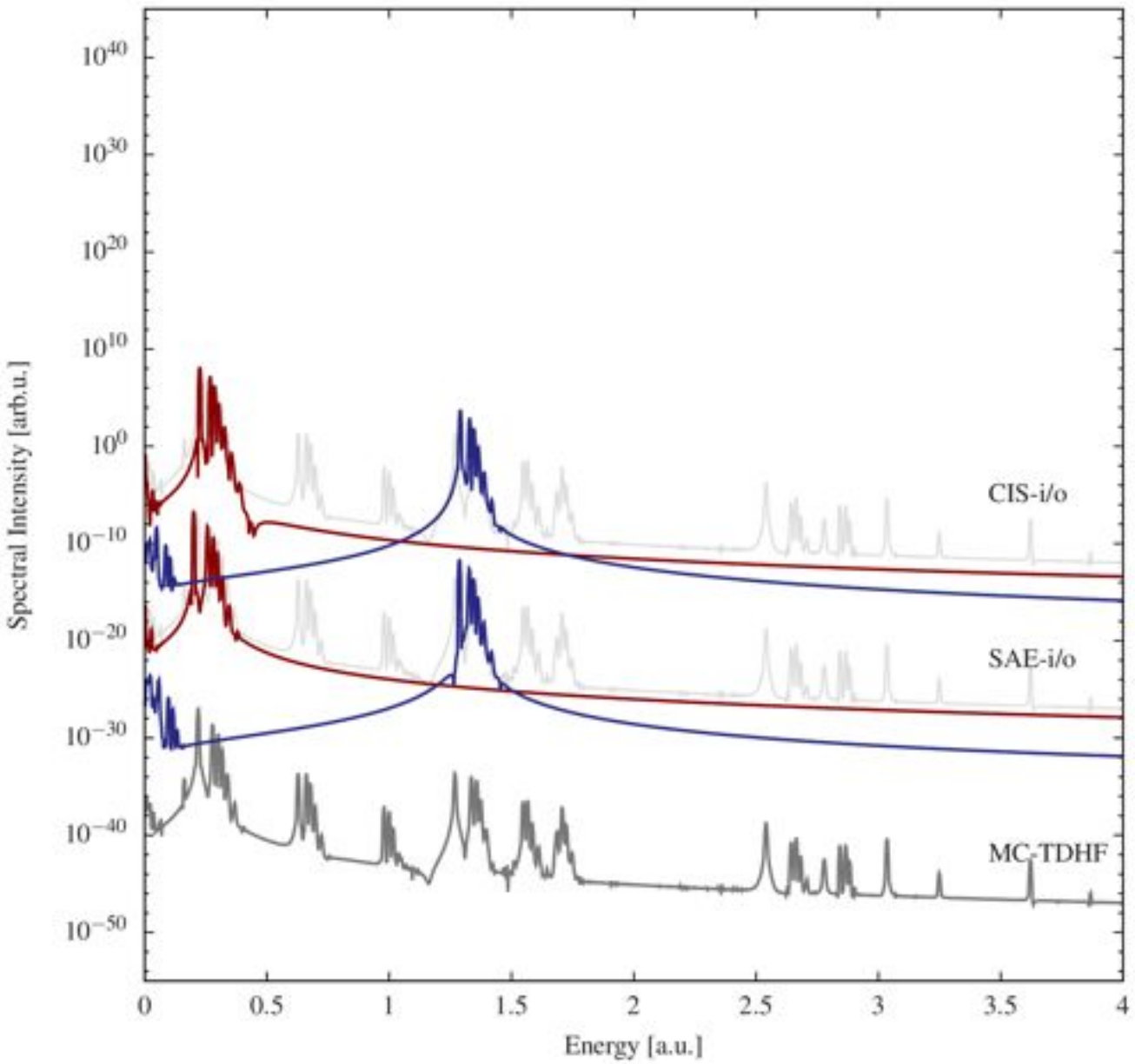
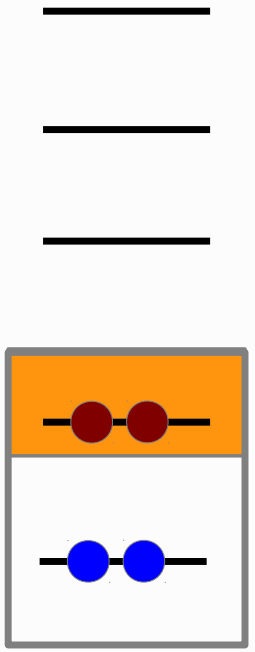




N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

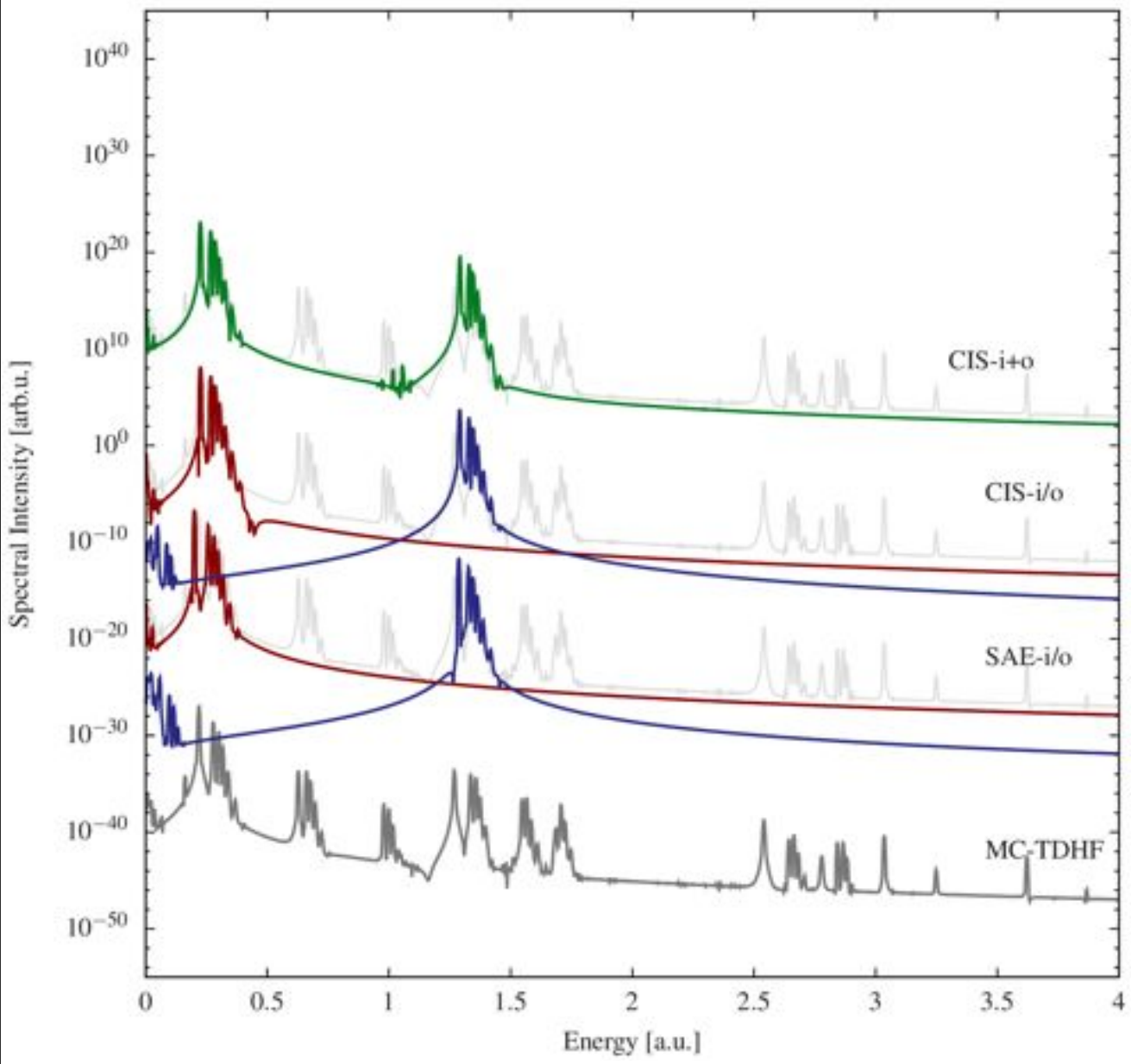
$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$



N=0,1

N=1,2
outer

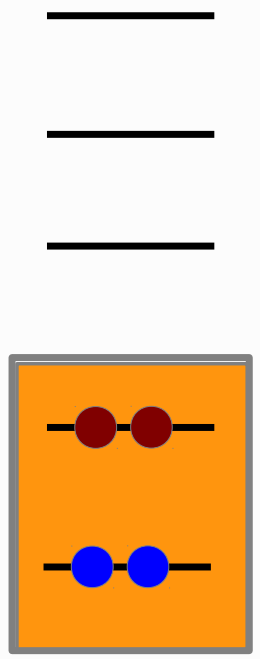
N=2
inner



N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$

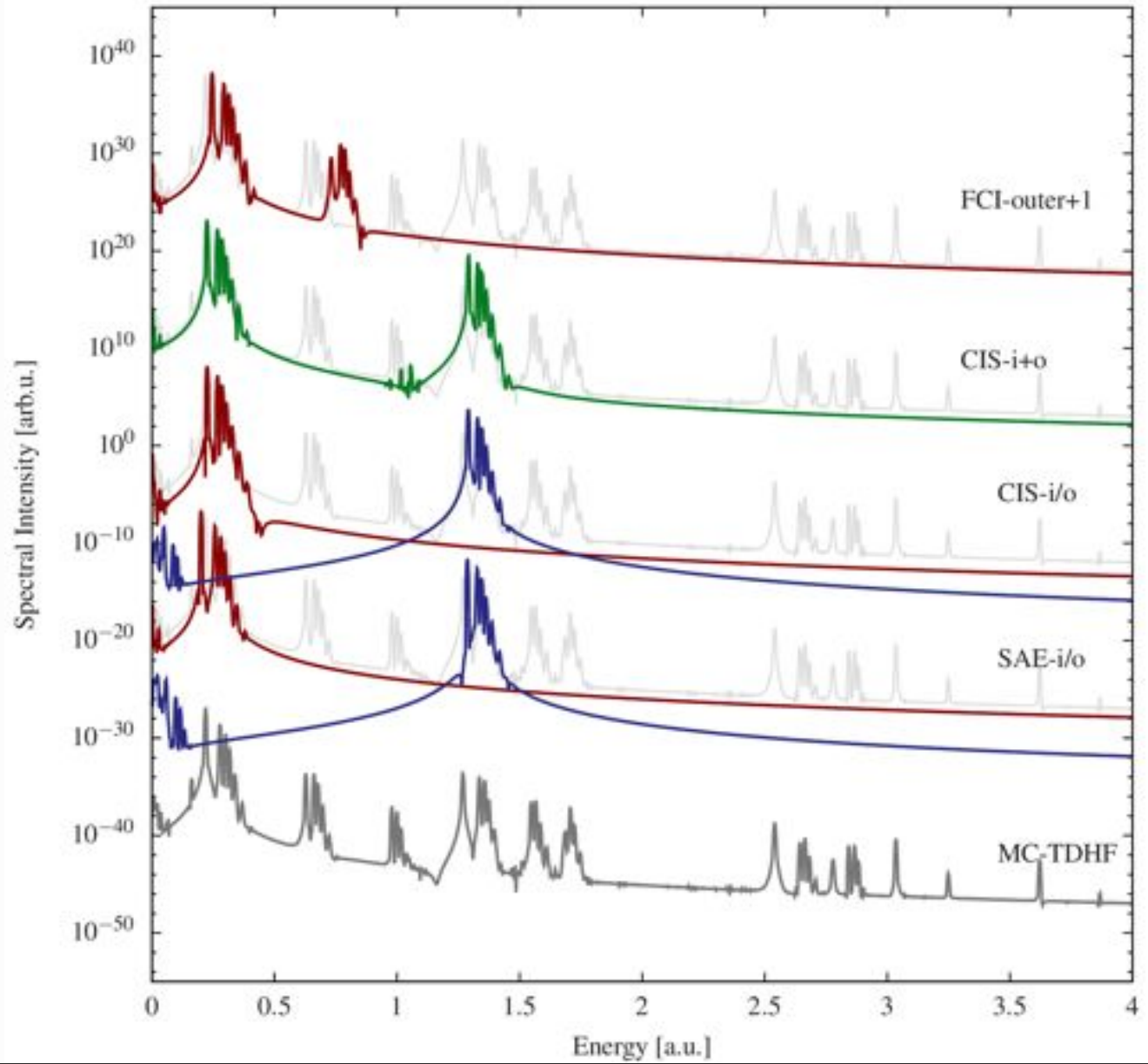


N=0,1

outer

N=3,4

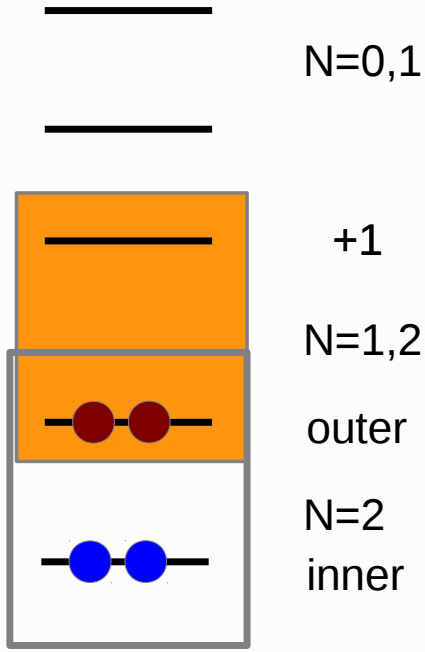
inner

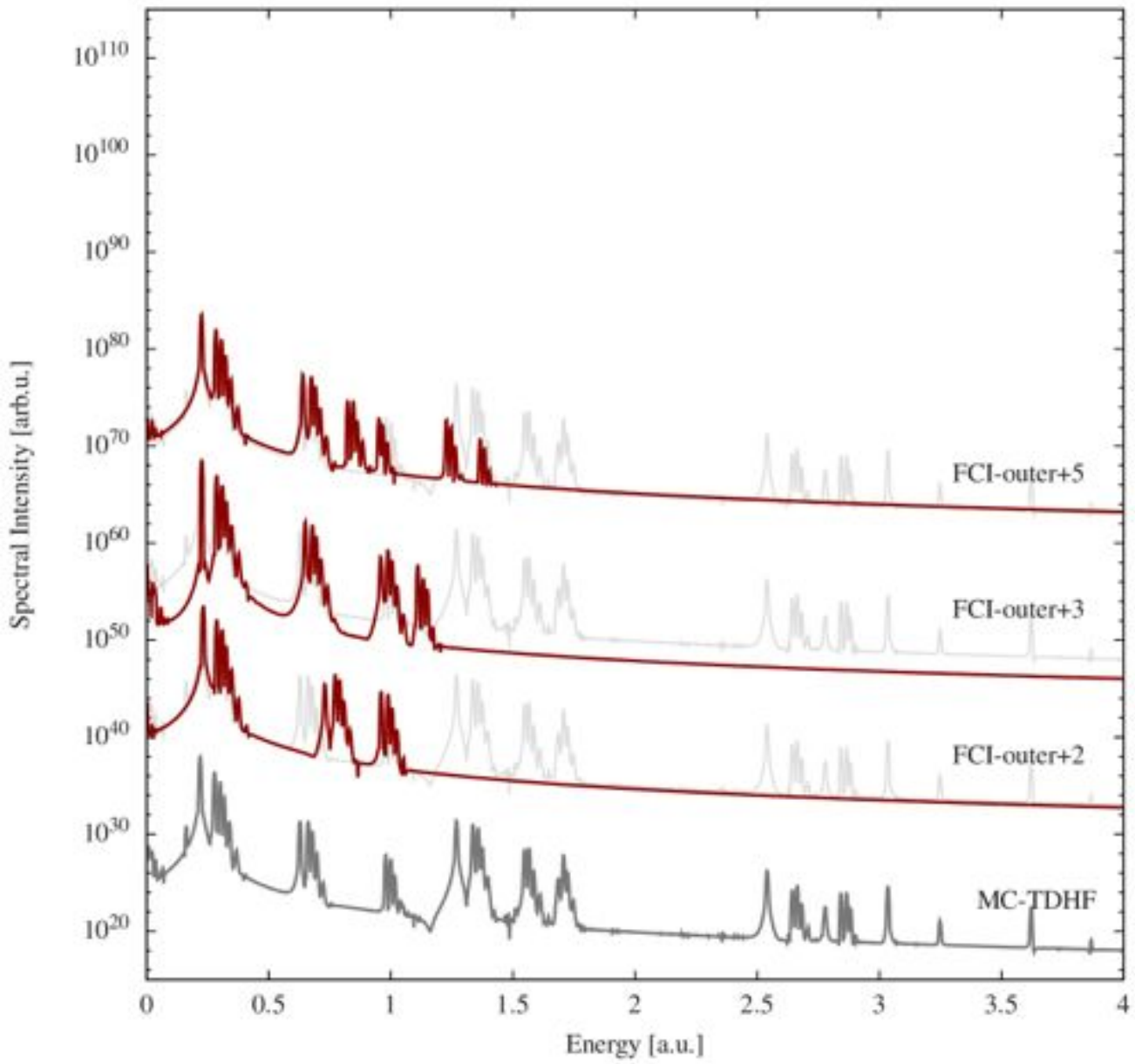


N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$

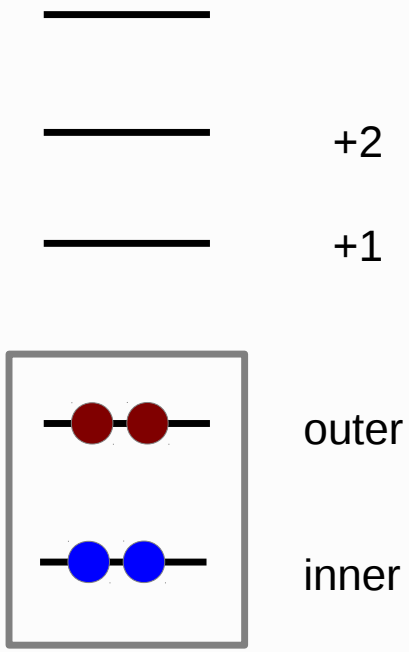


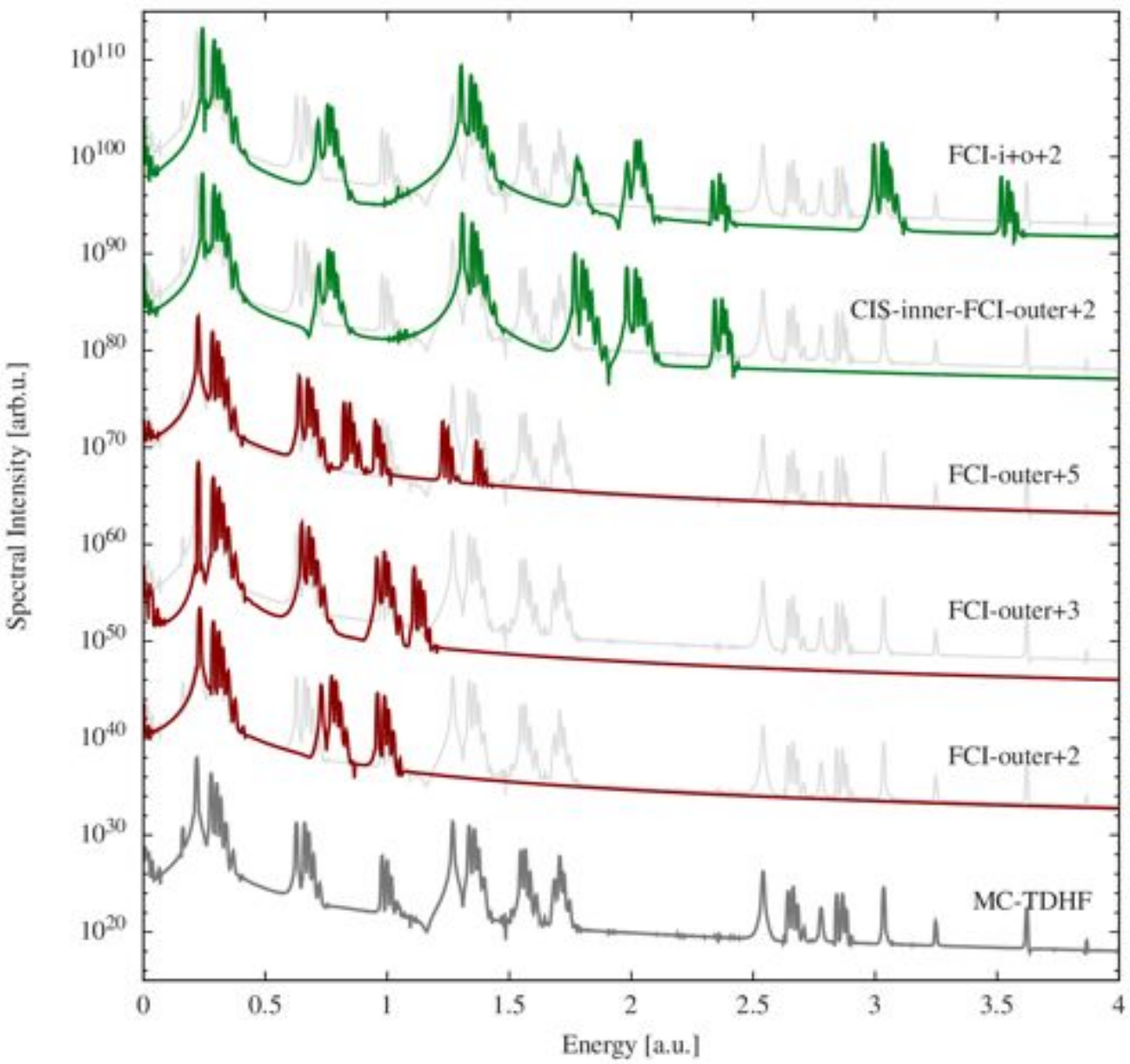


N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$





$N_{el}=4$

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

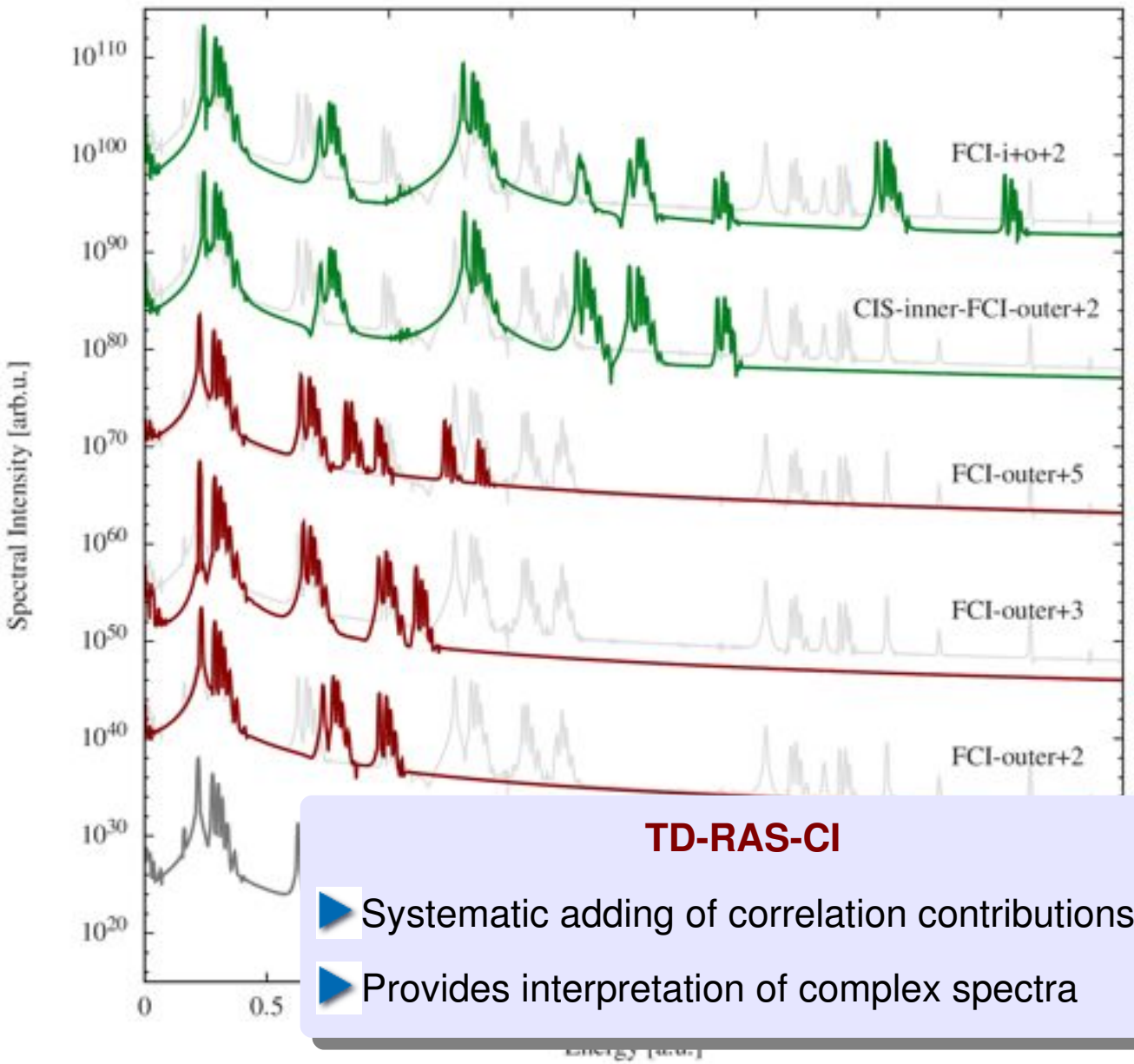
$$w(x_1,x_2) = \frac{1}{\sqrt{(x_1-x_2)^2+1}}$$

+2

+1

outer

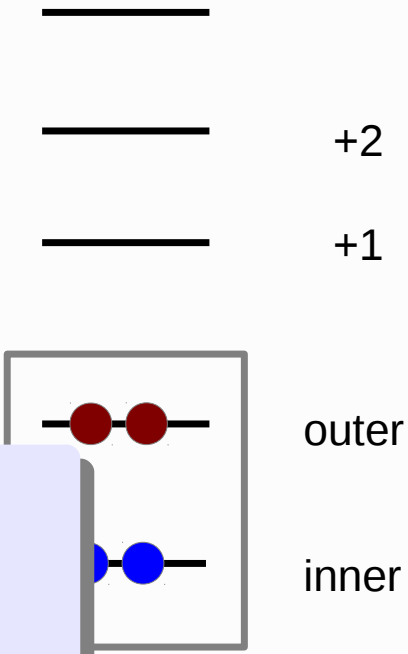
inner



N_{el}=4

$$V(x) = -\frac{4}{\sqrt{x^2+1}}$$

$$w(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}$$



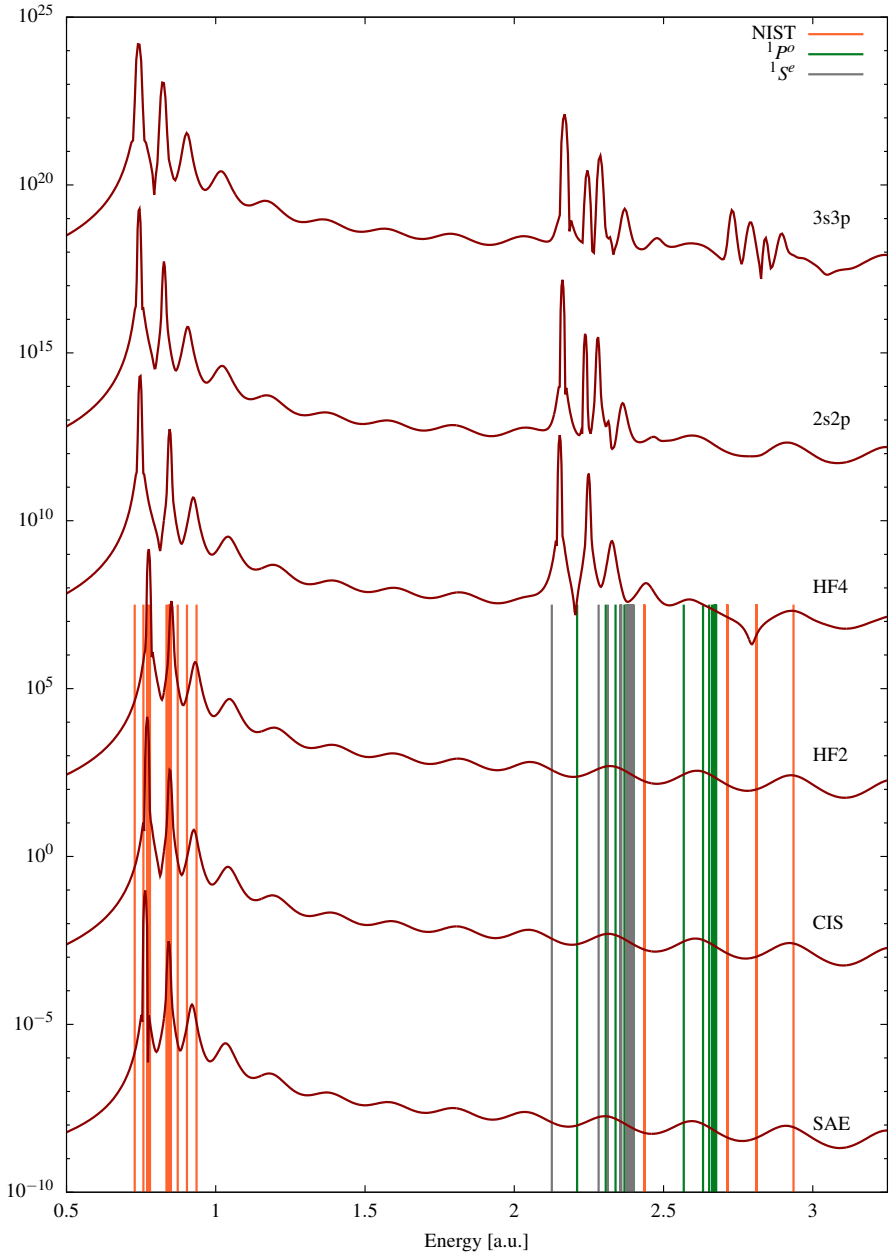
TD-RAS-CI

- Systematic adding of correlation contributions
- Provides interpretation of complex spectra

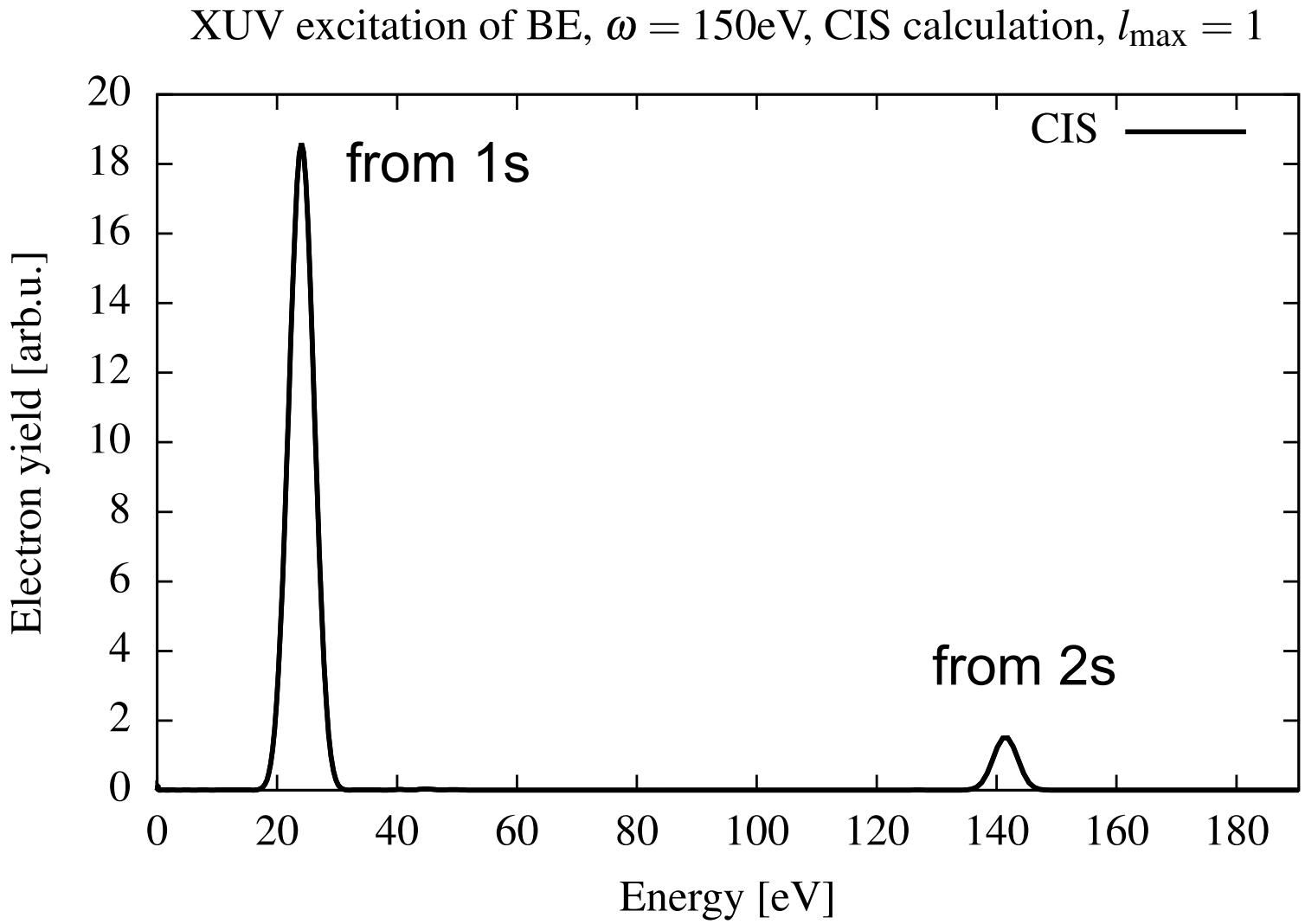
Essentials of TD-RAS-CI approach to photoionization

- ➔ Expand wave function in basis of Slater determinants
- ➔ Determinants are time-*in*dependent
- ➔ Truncate full-CI expansion in different subspaces
  - ➔ Crucial for photoionization: *mixed* basis set
- ➔ Numerical tests on exactly solvable model systems
- ➔ Ongoing research
  - ➔ Tests and benchmarks on 1D systems
  - ➔ Extension to real atoms and small diatomic molecules

3D Helium

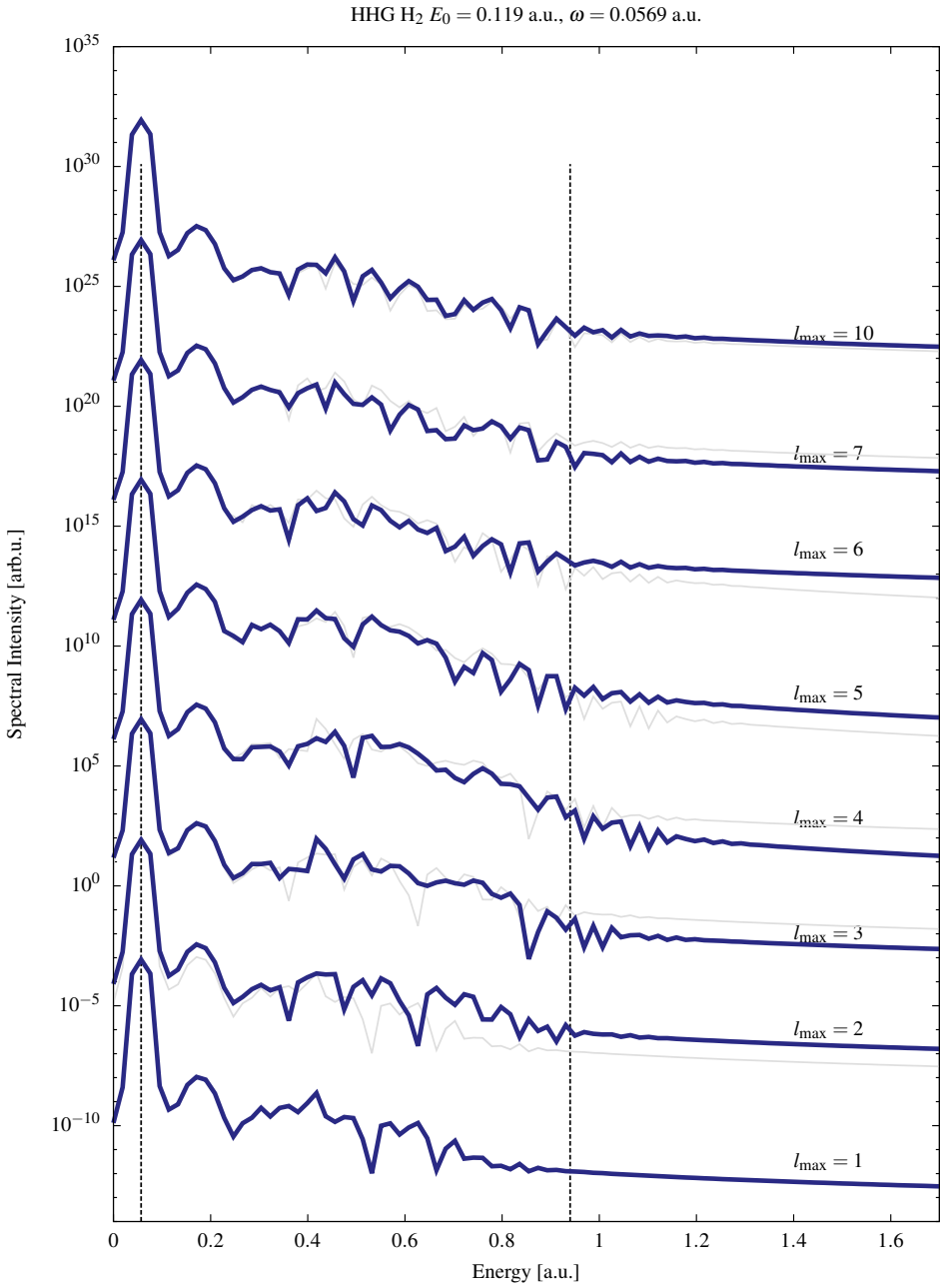

NIST
$^1P^o$
$^1S^e$
3s3p
2s2p
HF4
HF2
CIS
SAE
10^{25}
10^{20}
10^{15}
10^{10}
10^{5}
10^{0}
10^{-5}
10^{-10}
0.5
1
1.5
2
2.5
3
Energy [a.u.]

3D Be


XUV excitation of BE, $\omega = 150$eV, CIS calculation, $l_{max} = 1$
Electron yield [arb.u.]
Energy [eV]
CIS
from 1s
from 2s
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160
180

HHG in H_2

In the figure, the thin grey lines for a given l_{max} is the previous line repeated



Concept of a time-varying basis

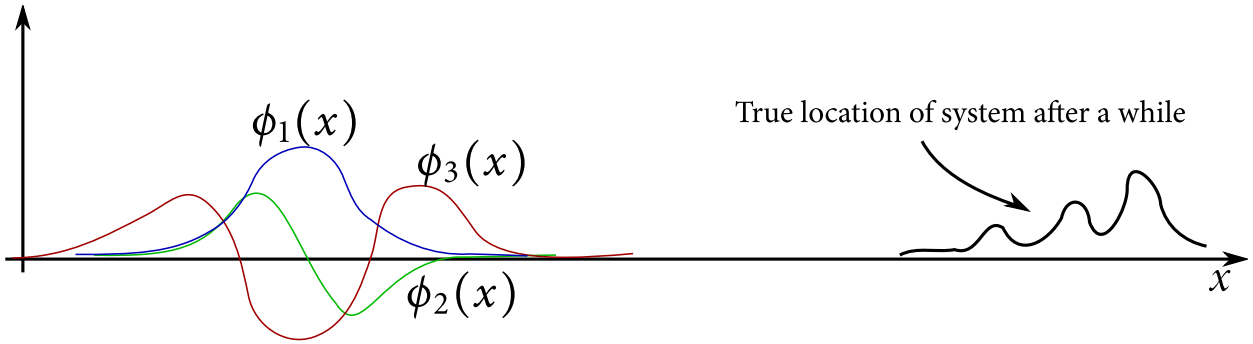


Illustration of fixed orbitals together with true development of the system

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{RAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}(t)\rangle$$

PHYSICAL REVIEW A **87**, 062511 (2013)

Time-dependent restricted-active-space self-consistent-field theory for laser-driven many-electron dynamics

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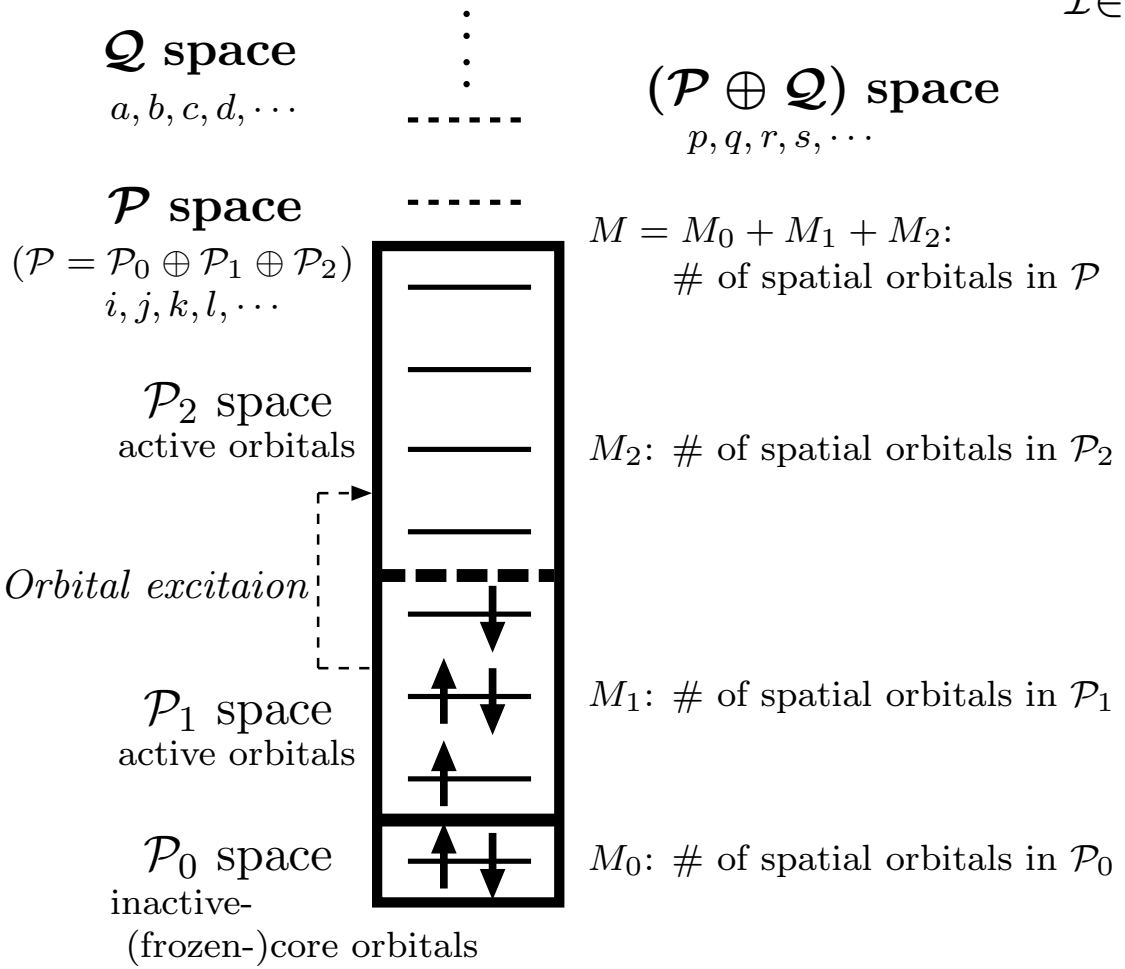
(Received 22 April 2013; published 21 June 2013)

We present the time-dependent restricted-active-space self-consistent-field (TD-RASSCF) theory as a framework for the time-dependent many-electron problem. The theory generalizes the multiconfigurational time-dependent Hartree-Fock (MCTDHF) theory by incorporating the restricted-active-space scheme well known in time-independent quantum chemistry. Optimization of the orbitals as well as the expansion coefficients at each time step makes it possible to construct the wave function accurately while using only a relatively small number of electronic configurations. In numerical calculations of high-order harmonic generation spectra of a one-dimensional model of atomic beryllium interacting with a strong laser pulse, the TD-RASSCF method is reasonably accurate while largely reducing the computational complexity. The TD-RASSCF method has the potential to treat large atoms and molecules beyond the capability of the MCTDHF method.

TD-RASSCF theory

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{RAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}(t)\rangle$$



Special cases: M_2=0: TD-CASSCF. M_0=M_2=0 : MCTDHF

For a wave function written as

$$|\Psi(t)\rangle = \sum_{\mathcal{I}\in\mathcal{V}_{\mathrm{RAS}}} C_{\mathcal{I}}(t)|\Phi_{\mathcal{I}}(t)\rangle,$$

we derive the EOM obeyed by the CI coefficients and orbitals.

Dirac-Frenkel-McLachlan TD variational principle:[9–11]

Define an action functional

$$\mathcal{S}\big[\{C_{\mathcal{I}}\},\{\phi_i\},\{\varepsilon^i_j\}\big] = \int_0^T \left[\langle\Psi|\left(i\frac{\partial}{\partial t} - H\right)|\Psi\rangle + \sum_{ij}\varepsilon^i_j(t)\Big(\langle\phi_i|\phi_j\rangle - \delta^i_j\Big)\right] dt,$$

and seek a stationary point, $\delta\mathcal{S} = 0$.

[9] P. A. M. Dirac, P. Camb. Philos. Soc. **26**, 376 (1930).

[10] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Oxford, 1934).

[11] A. D. McLachlan, Mol. Phys. **8**, 39 (1964).

$$H(t) = \sum_{pq} h_q^p(t) c_p^\dagger c_q + \frac{1}{2} \sum_{pqrs} v_{qs}^{pr}(t) c_p^\dagger c_r^\dagger c_s c_q,$$

Explicit form of the EOM:

$$\begin{cases} i\dot{C}_{\mathcal{I}} = \sum_{ij} \mathrm{sgn}(\tau) C_{\tau(\mathcal{I}_i^j)} (h_j^i - i\eta_j^i) + \frac{1}{2} \sum_{ijkl} \mathrm{sgn}(\tau) C_{\tau(\mathcal{I}_{ik}^{jl})} v_{jl}^{ik}, & \leftarrow C_{\mathcal{I}} \\ i \sum_j Q|\dot{\phi}_j\rangle \rho_i^j = \sum_j Q h(t) |\phi_j\rangle \rho_i^j + \sum_{jkl} Q W_l^k |\phi_j\rangle \rho_{ik}^{jl}, & \leftarrow \mathcal{Q} \\ \sum_{k''l'} (h_{l'}^{k''} - i\eta_{l'}^{k''}) A_{k''i'}^{l'j''} + \sum_{klm} (v_{kl}^{j''m} \rho_{i'm}^{kl} - v_{i'm}^{kl} \rho_{kl}^{j''m}) = i\dot{\rho}_{i'}^{j''}. & \leftarrow \mathcal{P} \end{cases}$$

where

$C_{\mathcal{I}_i^j} = \langle \Phi_{\mathcal{I}} | c_i^\dagger c_j | \Psi \rangle$, $C_{\mathcal{I}_{ik}^{jl}} = \langle \Phi_{\mathcal{I}} | c_i^\dagger c_k^\dagger c_l c_j | \Psi \rangle$,

$h_q^p(t) = \int \phi_p^\dagger(z,t) h(x,t) \phi_q(z,t) dz$,

$v_{qs}^{pr}(t) = \iint \phi_p^\dagger(z_1,t) \phi_r^\dagger(z_2,t) v(x_1,x_2) \phi_q(z_1,t) \phi_s(z_2,t) dz_1 dz_2$,

$Q = 1 - \sum_i |\phi_i\rangle\langle\phi_i|$, $\rho_i^j \equiv \langle \Psi | c_i^\dagger c_j | \Psi \rangle$, $\rho_{ik}^{jl} \equiv \langle \Psi | c_i^\dagger c_k^\dagger c_l c_j | \Psi \rangle$,

$W_l^k(\mathbf{r}) = \int \phi_k^\dagger(z') v(\mathbf{r},\mathbf{r}') \phi_l(z') dz'$, $A_{k''i'}^{l'j''} = \langle \Psi | \left[c_{i'}^\dagger c_{j''}, c_{k''}^\dagger c_{l'} \right] | \Psi \rangle = \delta_{k''}^{j''} \rho_{i'}^{l'} - \delta_{i'}^{l'} \rho_{k''}^{j''}$,

and $\dot{\rho}_{i'}^{j''} = \sum_{\mathcal{I} \in \mathcal{V}_{\mathrm{RAS}}} \left(\dot{C}_{\mathcal{I}}^* \langle \Phi_{\mathcal{I}} | \Psi_{j''}^{i'} \rangle + \langle \Psi_{i'}^{j''} | \Phi_{\mathcal{I}} \rangle \dot{C}_{\mathcal{I}} \right)$.

$$|\dot{\phi}_i\rangle = (P+Q)|\dot{\phi}_i\rangle = \sum_j |\phi_j\rangle \eta_i^j + Q|\dot{\phi}_i\rangle.$$

MCTDHF method

$$\begin{cases} i\dot{C}_{\mathcal{I}} = \sum_{ij} \mathrm{sgn}(\tau) C_{\tau(\mathcal{I}_i^j)} h_j^i + \frac{1}{2} \sum_{ijkl} \mathrm{sgn}(\tau) C_{\tau(\mathcal{I}_{ik}^{jl})} v_{jl}^{ik}, & \leftarrow C_{\mathcal{I}} \\ i \sum_j Q|\dot{\phi}_j\rangle \rho_i^j = \sum_j Qh(t)|\phi_j\rangle \rho_i^j + \sum_{jkl} QW_l^k |\phi_j\rangle \rho_{ik}^{jl}, & \leftarrow \mathcal{Q} \end{cases}$$

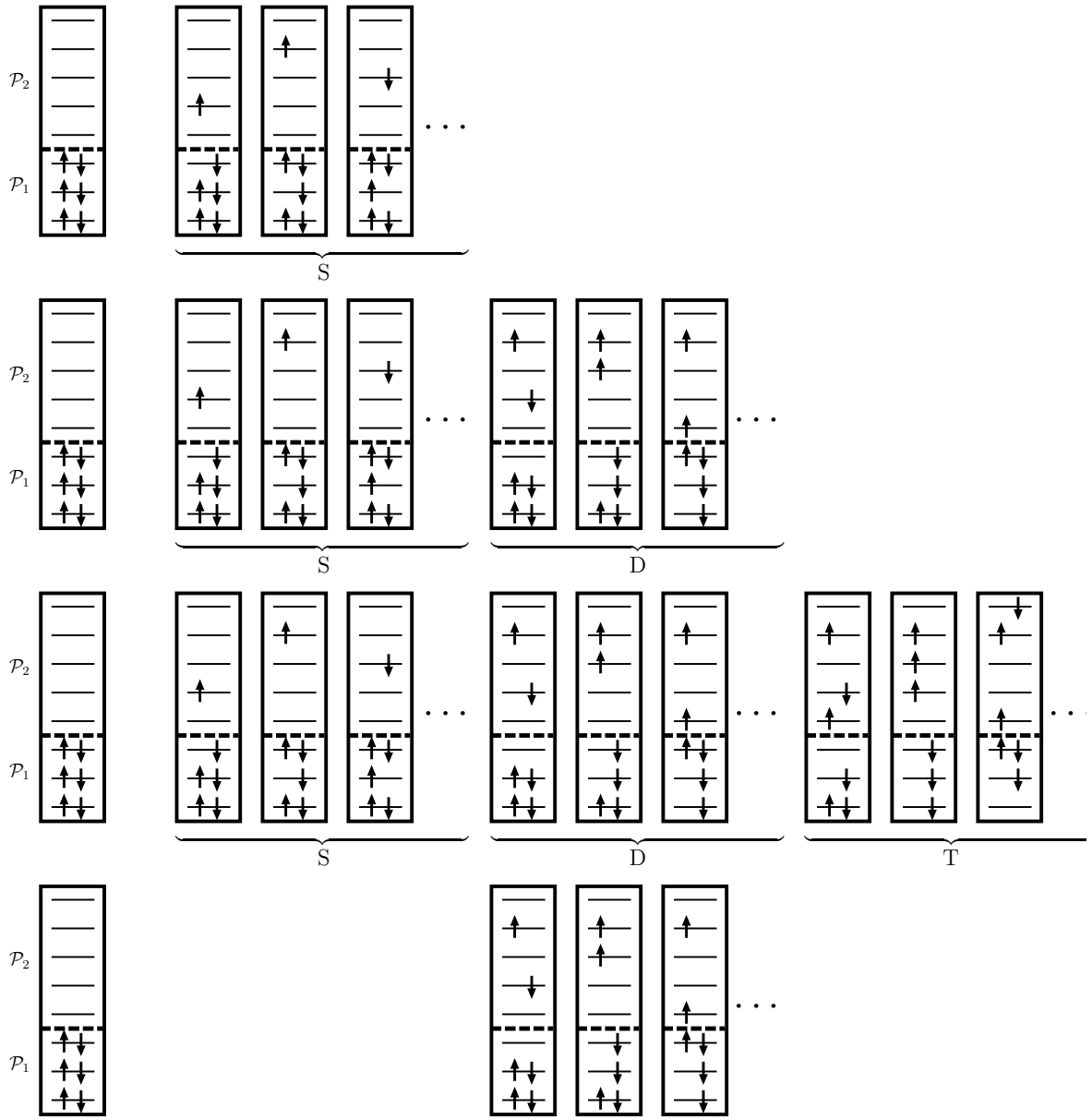
—TD-RASSCF family—

TD-RASSCF-S

TD-RASSCF-SD

TD-RASSCF-SDT

TD-RASSCF-D



Properties of the TD-RASSCF theory

- Gauge-invariance
  - A property for SCF methods (TDHF, MCTDHF,…)
- Special convergence property for TD-RASSCF-S
- The TD-RASSCF scheme reduces the number of configurations a lot while being still accurate

HF: -6.739450

Method	(M_0, M_1, M_2)	M = 3	4	8	12	16	20
TD-RASSCF-S	$(0, 2, M-2)$	-6.771254 (5)	$\underline{-6.773288}$ (9)	$\underline{-6.773288}$ (25)	$\underline{-6.773288}$ (41)	$\underline{-6.773288}$ (57)	$\underline{-6.773288}$ (73)
-D	$(0, 2, M-2)$	$-6.771296^{\flat}$ (5)	-6.779805 (19)	-6.784501 (175)	-6.784533 (491)	-6.784534 (967)	-6.784534 (1603)
-SD	$(0, 2, M-2)$	$-6.771296^{\flat}$ (9)	-6.780026 (27)	-6.784667 (199)	-6.784697 (531)	-6.784698 (1023)	-6.784698 (1675)
-SDT	$(0, 2, M-2)$		-6.780026 (35)	-6.785038 (559)	-6.785074 (2331)	-6.785074 (6119)	-6.785075 (12691)
MCTDHF	$(0, M, 0)$	$-6.771296^{\flat}$ (9)	-6.780026 (36)	-6.785041 (784)	-6.785077 (4356)	-6.785078 (14400)	-6.785078 (36100)

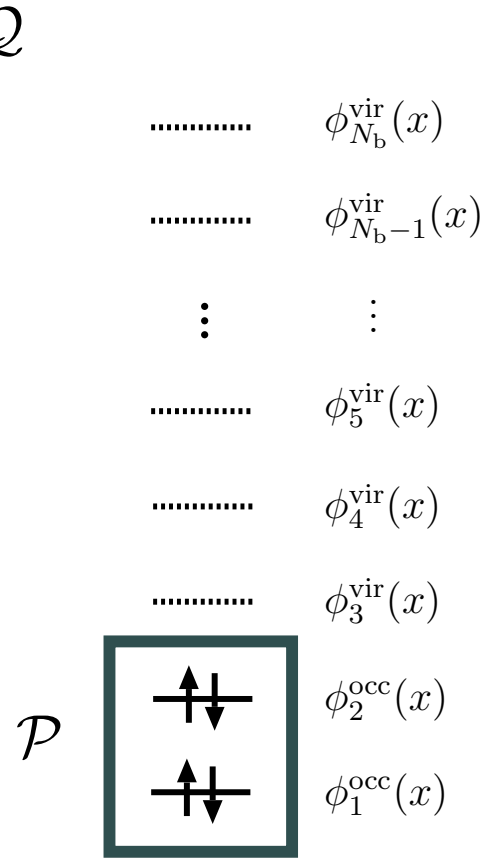
In the SCF based methods (MCTDHF and TD-RASSCF-S):
More orbitals $\Rightarrow$ More accurate but more expensive

Question:
How many orbitals are needed to make the TD-RASSCF-S wave function sufficiently converged and more accurate than the TDCIS wave function?

Answer:
We need only $M = N_{\mathrm{e}}$ orbitals, by which the TD-RASSCF-S wave function is fully converged and more accurate than the TDCIS wave function!

The TDCIS wave function reads

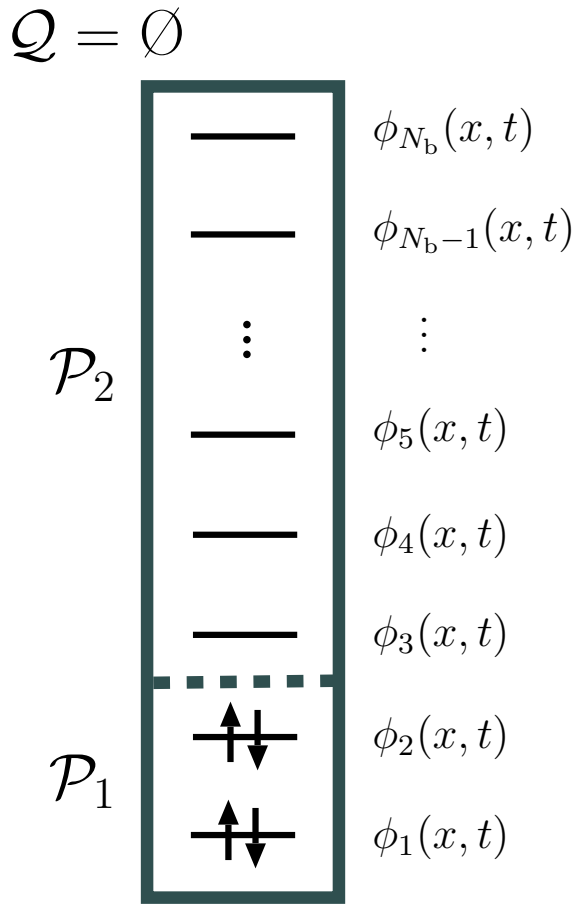
$$|\Psi_{\mathrm{CIS}}(t)\rangle = \alpha_0(t)|\mathrm{HF}\rangle + \sum_{ia} \alpha_i^a(t)|\mathrm{HF}_i^a\rangle.$$



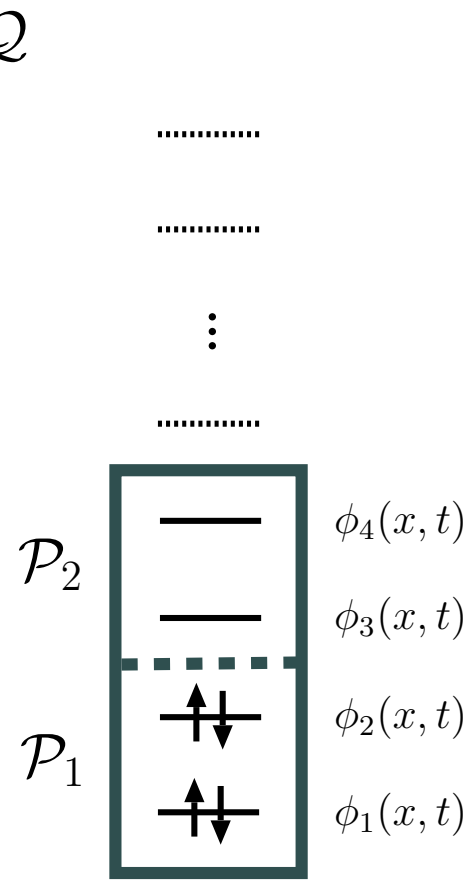
The TD-RASSCF-S wave function reads

$$|\Psi(t)\rangle = C_0(t)|\Phi(t)\rangle + \sum_{i'j''} C_{i'}^{j''}(t)|\Phi_{i'}^{j''}(t)\rangle.$$

When $\mathcal{P}_1 \oplus \mathcal{P}_2$ covers the single-particle Hilbert space, $|\Psi(t)\rangle$ is more accurate than $|\Psi_{\mathrm{CIS}}(t)\rangle$.

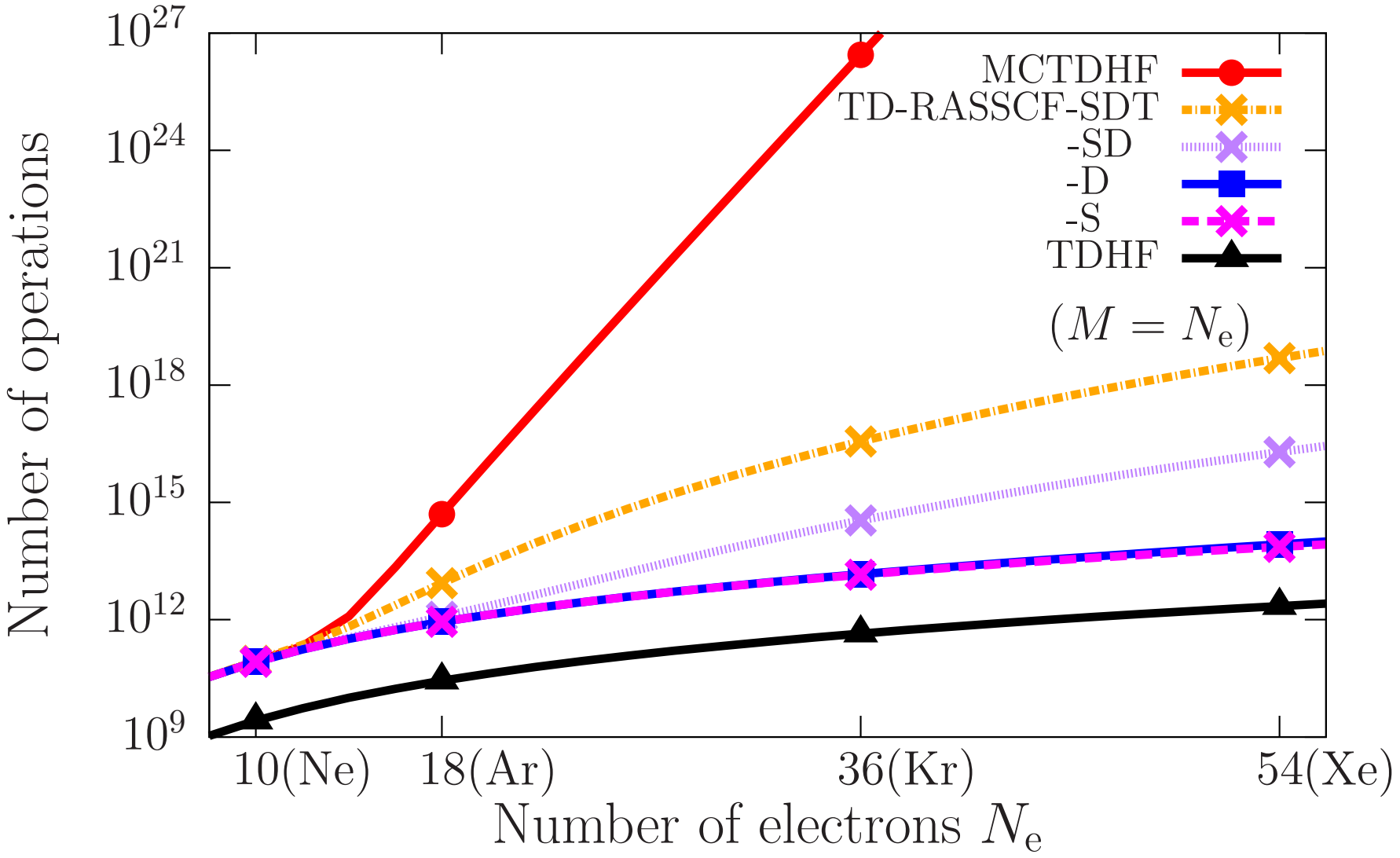


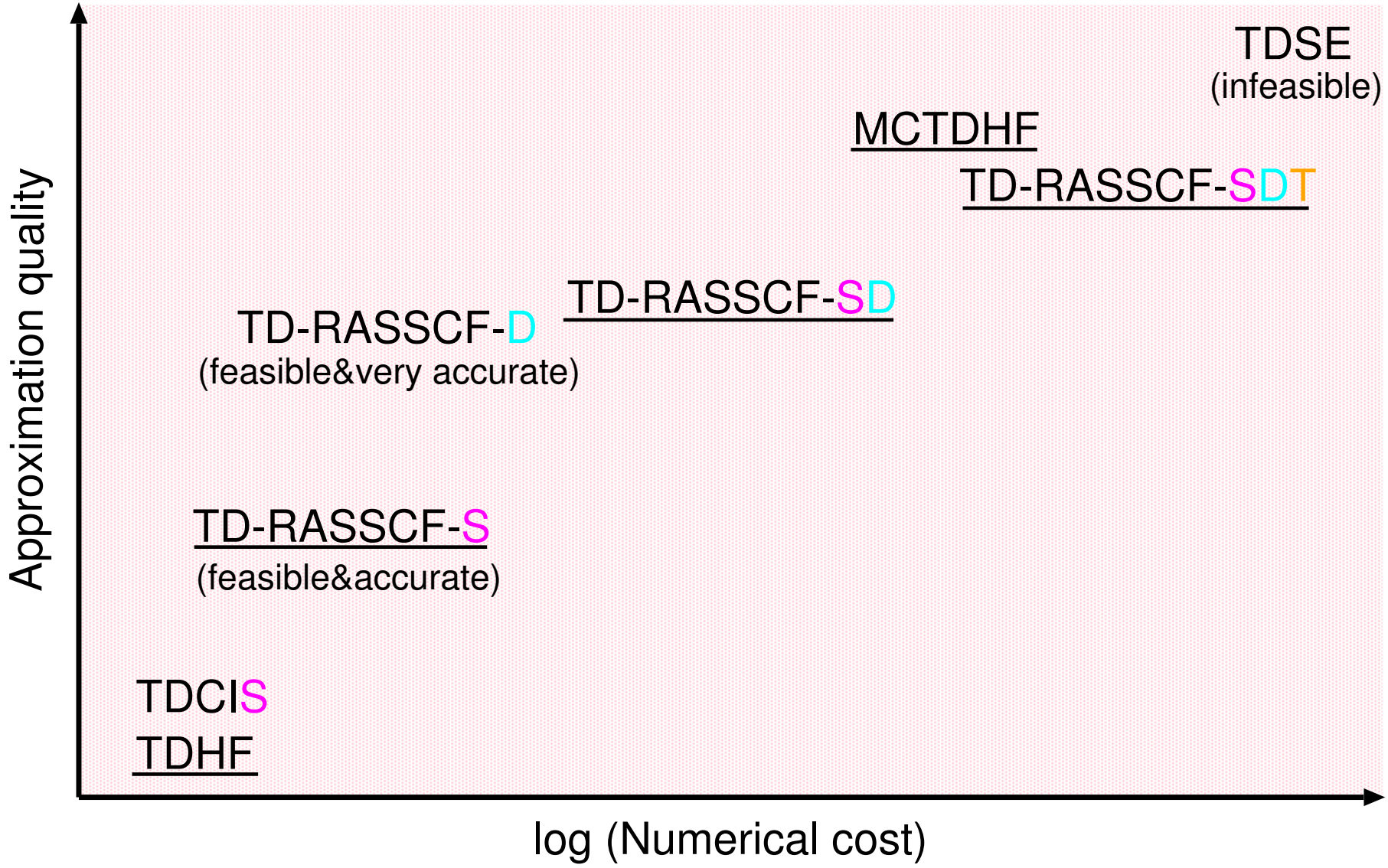
The theorem allows us to use the most economical condition ($M = N_{\mathrm{e}}$), leaving the wave function invariant.

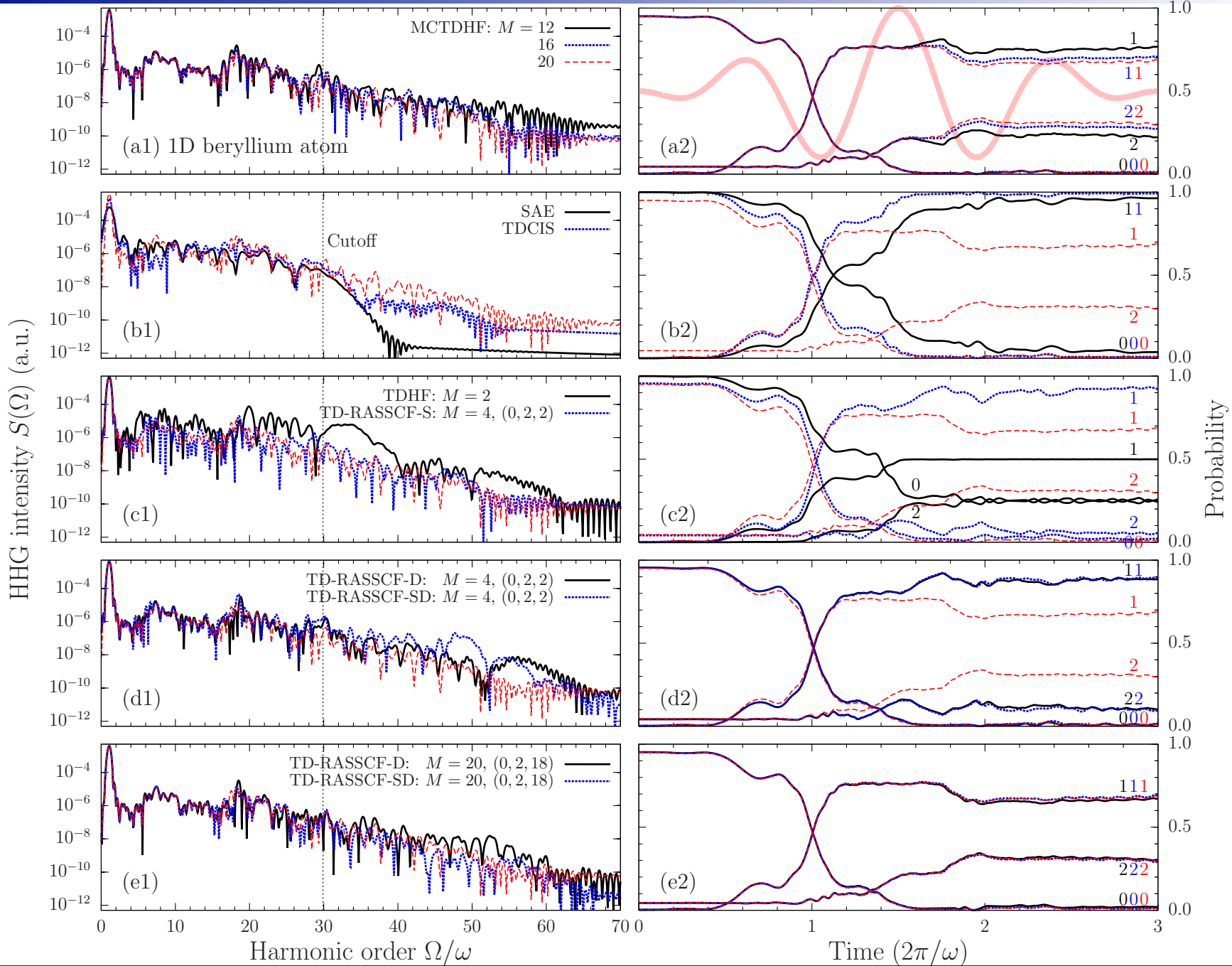


Method	(M_0, M_1, M_2)	14
w/o core $(M_0 = 0)$		
TD-RASSCF-S	$(0, 3, M-3)$	$\underline{-13.30039}$ $\underline{(64)}$
-D	$(0, 3, M-3)$	-13.32732 (1420)
-SD	$(0, 3, M-3)$	-13.32753 (1486)
-SDT	$(0, 3, M-3)$	-13.33136 (12706)
MCTDHF	$(0, M, 0)$	-13.33154 (132496)
w/ core $(M_0 = 1)$		
TD-RASSCF-S	$(1, 2, M-3)$	$\underline{-13.30037}$ $\underline{(45)}$
-D	$(1, 2, M-3)$	-13.32440 (595)
-SD	$(1, 2, M-3)$	-13.32551 (639)
-SDT	$(1, 2, M-3)$	-13.32791 (3059)
TD-CASSCF	$(1, M-1, 0)$	-13.32796 (6084)

HF energy -13.23117


Number of operations
10^{27}
10^{24}
10^{21}
10^{18}
10^{15}
10^{12}
10^{9}
MCTDHF
TD-RASSCF-SDT
-SD
-D
-S
TDHF
$(M = N_e)$
10(Ne)
18(Ar)
36(Kr)
54(Xe)
Number of electrons N_e


TDSE
(infeasible)
MCTDHF
TD-RASSCF-SDT
TD-RASSCF-SD
TD-RASSCF-D
(feasible&very accurate)
TD-RASSCF-S
(feasible&accurate)
TDCIS
TDHF
Approximation quality
log (Numerical cost)


MCTDHF: $M = 12$
16
20
(a1) 1D beryllium atom
(a2)
SAE
TDCIS
Cutoff
(b1)
(b2)
TDHF: $M = 2$
TD-RASSCF-S: $M = 4,\ (0, 2, 2)$
(c1)
(c2)
TD-RASSCF-D: $M = 4,\ (0, 2, 2)$
TD-RASSCF-SD: $M = 4,\ (0, 2, 2)$
(d1)
(d2)
TD-RASSCF-D: $M = 20,\ (0, 2, 18)$
TD-RASSCF-SD: $M = 20,\ (0, 2, 18)$
(e1)
(e2)
HHG intensity $S(\Omega)$ (a.u.)
Harmonic order Ω/ω
Time $(2\pi/\omega)$
Probability

Conclusions

- TD-RASSCF offers a reduction in the number of configurations
- TD-RASSCF is gauge invariant
- TD-RASSCF-S has a special convergence property
- TD-RASSCF-S, (-D), -SD, -SDT become increasingly accurate
- TD-RASSCF-S and TD-RASSCF-D are computationally feasible and promising tools for TD dynamics

Outlook

- Efficient 3D implementations of TD-GAS schemes
- Extraction of observables. Applications
- TD-GAS-CC
- …

- TD-GAS schemes for Bosons and distinguishable particles
- TD-GAS schemes for electronic and nuclear degrees of freedom
- …

Acknowledgments

- Haru, Sebastian, Lasse, Lun, Wenliang
- Danish Research Foundation
- ERC grant (2011-2016)
- Villum Kann Rasmussen CoE (2014-2019)

Thank you for your attention!