

Time-dependent linear-response variational Monte Carlo.

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The **excitation energies** can be calculated by linear response of the ground-state wave function to a time-dependent perturbation (TDDFT; TDHF and other costly wavefunction methods; CIS is the simplest way to approach it).

QMC methods were originally formulated for ground state problems and their extension to excited states is not straightforward.

State-average VMC [Filippi,Zaccheddu,Buda JCTC **5** (2009)]

State-specific VMC [Zimmerman,Toulouse,Zhang,Musgrave,Umrigar JCP (2009)]

→ This work is an LR-VMC extension of VMC to the calculation of **electronic excitation energies** and **oscillator strengths** using **time-dependent linear-response theory**.

We exploit the formal analogy existing between the **linear method for wave-function optimization** and the **generalised eigenvalue equation of linear-response theory**.

Very similar derivations and analogy were obtained by E. Neuscamman, in a EOM-VMC context. [Zhao,Neuscamman JCTC **12** (2016)]

The **wavefunction is parametrized with** $\mathbf{p} = \{\alpha, \kappa, \mathbf{c}, \xi\}$

(Jastrow parameters α , orbital rotation κ , CI \mathbf{c} and basis set ξ coefficients) :

$$|\Psi(\mathbf{p})\rangle = \hat{J}(\alpha) e^{\hat{\kappa}(\kappa)} \sum c_I |C_I\rangle$$

Consider the **first-order expansion** around the current parameters \mathbf{p}^0 ($\Delta\mathbf{p} = \mathbf{p} - \mathbf{p}^0$) of the **intermediate-normalized wavefunction** $|\bar{\Psi}(\mathbf{p})\rangle = \frac{|\Psi(\mathbf{p})\rangle}{\langle\Psi_0|\Psi(\mathbf{p})\rangle}$:

$$|\bar{\Psi}_{\text{lin}}(\mathbf{p})\rangle = |\bar{\Psi}_0\rangle + \sum \Delta p_i |\bar{\Psi}_i\rangle$$

$$\text{where : } |\bar{\Psi}_0\rangle = |\Psi(\mathbf{p}^0)\rangle \quad |\bar{\Psi}_i\rangle = \left. \frac{\partial |\bar{\Psi}(\mathbf{p})\rangle}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^0}$$

The **optimal parameters** \mathbf{p}^* are found by minimizing the energy E_{lin} corresponding to the wavefunction $|\bar{\Psi}_{\text{lin}}(\mathbf{p})\rangle$:

$$E_{\text{lin}} = \min_{\mathbf{p}} \frac{\langle \bar{\Psi}_{\text{lin}}(\mathbf{p}) | \hat{H} | \bar{\Psi}_{\text{lin}}(\mathbf{p}) \rangle}{\langle \bar{\Psi}_{\text{lin}}(\mathbf{p}) | \bar{\Psi}_{\text{lin}}(\mathbf{p}) \rangle} \quad (1)$$

and iteratively updating the parameters $\mathbf{p}^0 + \Delta\mathbf{p} \rightarrow \mathbf{p}^0$.

Application of this variational principle amounts to solving the **generalized eigenvalue equation** estimated as :

$$(1) \quad \Longleftrightarrow \quad \begin{pmatrix} E_0 & \mathbf{g}_R^T \\ \mathbf{g}_L & \mathbf{H} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix} = E_{\text{lin}} \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix}$$

where :

- $g_{L,i} = \langle \overline{\Psi}_i | \hat{H} | \Psi_0 \rangle$ and $g_{R,i} = \langle \Psi_0 | \hat{H} | \overline{\Psi}_i \rangle$ are the left- and right-gradients. They are identical except on a finite MC sample.
 - $H_{ij} = \langle \overline{\Psi}_i | \hat{H} | \overline{\Psi}_j \rangle$ is the Hamiltonian matrix in the basis of the first-order derivatives. This estimator is non-symmetric.
 - $S_{ij} = \langle \overline{\Psi}_i | \overline{\Psi}_j \rangle$ is the overlap matrix in this basis.
 - E_0 is the energy of the current $|\Psi_0\rangle$ and E_{lin} is the energy of $|\overline{\Psi}_{\text{lin}}\rangle$.
 - The sizes of the whole matrices are $(1 + N_{\text{param}}).(1 + N_{\text{param}})$
 - [Toulouse, Umrigar JCP **126** (2007)]
- The linear-method can be seen as a stabilized Newton method.
In quantum chemistry, also known as **Super-CI** or **Augmented Hessian method**.

The excited-state energies are calculated **from the optimized ground state** by **linear-response time-dependent perturbation theory** :

$$\hat{H}(t) = \hat{H} + \gamma \hat{V}(t)$$

Consider the **expansion** around the current parameters \mathbf{p}^0 ($\Delta\mathbf{p}(t) = \mathbf{p}(t) - \mathbf{p}^0$) of the **intermediate-normalized wavefunction** $|\bar{\Psi}(\mathbf{p}(t))\rangle = \frac{|\Psi(\mathbf{p}(t))\rangle}{\langle\Psi_0|\Psi(\mathbf{p}(t))\rangle}$:

$$|\bar{\Psi}(\mathbf{p}(t))\rangle = |\Psi_0\rangle + \sum \Delta p_i(t) |\bar{\Psi}_i\rangle + \frac{1}{2} \sum \Delta p_i(t) \Delta p_j(t) |\bar{\Psi}_{ij}\rangle + \dots$$

$$\text{where : } |\Psi_0\rangle = |\Psi(\mathbf{p}^0)\rangle \quad |\bar{\Psi}_i\rangle = \left. \frac{\partial |\bar{\Psi}(\mathbf{p}(t))\rangle}{\partial p_i(t)} \right|_{\mathbf{p}(t)=\mathbf{p}^0} \quad |\bar{\Psi}_{ij}\rangle = \left. \frac{\partial^2 |\bar{\Psi}(\mathbf{p}(t))\rangle}{\partial p_i(t) \partial p_j(t)} \right|_{\mathbf{p}(t)=\mathbf{p}^0}$$

The **approximate ground state** evolves in time via the parameters $\mathbf{p}(t)$ according to the Dirac-Frenkel variational principle :

$$\min_{\mathbf{p}(t)} \frac{\langle \bar{\Psi}(\mathbf{p}(t)) | \hat{H}(t) - i \frac{\partial}{\partial t} | \bar{\Psi}(\mathbf{p}(t)) \rangle}{\langle \bar{\Psi}(\mathbf{p}(t)) | \bar{\Psi}(\mathbf{p}(t)) \rangle} \quad (2)$$

Application of this variational principle (in first order in γ (linear response), keeping only first-order terms in $\Delta \mathbf{p}(t)$, and in the limit of a vanishing perturbation) yields

$$(2) \quad \Longleftrightarrow \quad \mathbf{A} \Delta \mathbf{p}(t) + \mathbf{B} \Delta \mathbf{p}(t)^* = i\mathbf{S} \frac{\partial \Delta \mathbf{p}(t)}{\partial t}$$

where : - $A_{ij} = \langle \bar{\Psi}_i | \hat{H} - E_0 | \bar{\Psi}_j \rangle = H_{ij} - E_0 S_{ij}$

- $B_{ij} = \langle \bar{\Psi}_{ij} | \hat{H} | \Psi_0 \rangle$ contains (without any surprise) the **second-order derivatives** of the wavefunction with respect to its parameters.

Looking for free-oscillation solutions of ω excitation (de-excitation) energies :

$$\Delta \mathbf{p}(t) = \mathbf{X} e^{-i\omega t} + \mathbf{Y}^* e^{i\omega t}$$

we arrive at the **linear-response equation** in the form of a **non-Hermitian generalized eigenvalue equation** :

$$(2) \quad \Longleftrightarrow \quad \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & -\mathbf{S}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}.$$

- The sizes of the whole matrices are $(2N_{\text{param}}).(2N_{\text{param}})$

- The solutions come in pairs : $(\omega, (\mathbf{X}, \mathbf{Y}))$ and $(-\omega, (\mathbf{Y}^*, \mathbf{X}^*))$

The TDA neglects \mathbf{B} , i.e. : $\mathbf{AX} = \omega\mathbf{SX}$

Note : at the ground-state minimum, **the energy gradient is zero**, the generalised eigenvalue equation of the linear method is equivalent to the TDA equation :

$$\begin{pmatrix} E_0 & \mathbf{0}^T \\ \mathbf{0} & \mathbf{H} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta\mathbf{p} \end{pmatrix} = E_{\text{lin}} \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta\mathbf{p} \end{pmatrix} \quad \Longleftrightarrow \quad \mathbf{H}\Delta\mathbf{p} = E_{\text{lin}}\mathbf{S}\Delta\mathbf{p}$$

[remember : $\mathbf{A} = \mathbf{H} - E_0\mathbf{S}$ and : $\omega = E_{\text{lin}} - E_0$] $\Longleftrightarrow \quad \mathbf{AX} = \omega\mathbf{SX}$

Some remarks

- If the response is calculated on a stable ground state the matrix $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$ is positive-definite : the excitation energies are real (as they should be).
- In practice, the approximate ground state can be unstable (spin-symmetry breaking), or the response can be calculated in a bigger parameter space the minimization was done in \rightarrow **unexploitable imaginary excitation energies**.

$$E_0 = \langle E_L \rangle$$

$$g_{L,i} = \langle \bar{\Psi}_i | \hat{H} | \Psi_0 \rangle = \langle \Psi_i | \hat{H} | \Psi_0 \rangle - \langle \Psi_i | \Psi_0 \rangle \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \left\langle \frac{\Psi_i}{\Psi_0} E_L \right\rangle - \left\langle \frac{\Psi_i}{\Psi_0} \right\rangle \langle E_L \rangle$$

$$g_{R,i} = \langle \Psi_0 | \hat{H} | \bar{\Psi}_i \rangle = \langle \Psi_0 | \hat{H} | \Psi_i \rangle - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \langle \Psi_0 | \Psi_i \rangle = \left\langle \frac{\hat{H} \Psi_i}{\Psi_0} \right\rangle - \left\langle \frac{\Psi_i}{\Psi_0} \right\rangle \langle E_L \rangle$$

$$S_{ij} = \langle \bar{\Psi}_i | \bar{\Psi}_j \rangle = \langle \Psi_i | \Psi_j \rangle - \langle \Psi_i | \Psi_0 \rangle \langle \Psi_0 | \Psi_j \rangle = \left\langle \frac{\Psi_i}{\Psi_0} \frac{\Psi_j}{\Psi_0} \right\rangle - \left\langle \frac{\Psi_i}{\Psi_0} \right\rangle \left\langle \frac{\Psi_j}{\Psi_0} \right\rangle$$

$$H_{ij} = \langle \bar{\Psi}_i | \hat{H} | \bar{\Psi}_j \rangle = \dots$$

$$A_{ij} = H_{ij} - E_0 S_{ij} = \dots$$

$$B_{ij} = \langle \bar{\Psi}_{ij} | \hat{H} | \Psi_0 \rangle = \dots$$

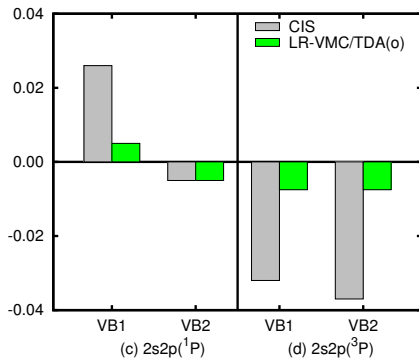
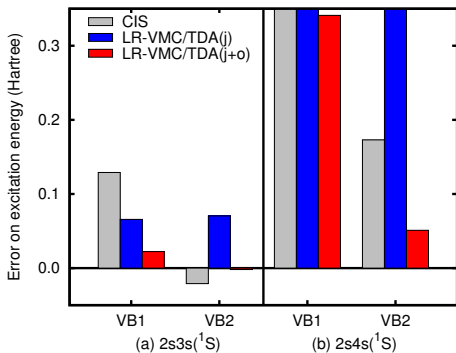
$$E_L(\mathbf{R}) = \frac{\hat{H}(\mathbf{R})\Psi_0(\mathbf{R})}{\Psi_0(\mathbf{R})}$$

$$E_{L,i}(\mathbf{R})$$

$$\frac{\Psi_i(\mathbf{R})}{\Psi_0(\mathbf{R})}$$

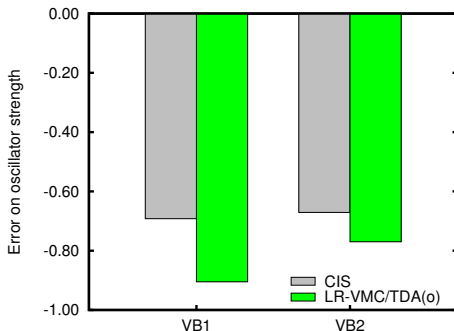
$$\frac{\Psi_{ij}(\mathbf{R})}{\Psi_0(\mathbf{R})}$$

HF orbitals, VB1[5s, 1p] VB2[6s, 2p, 1d], Jastrow (en,ee,een, 24 parameters)



- (a)** Jastrow adds significant physics
Further effect of orbitals
Big effect of the basis with CIS
- (b)** CIS fails dramatically
Jastrow reduces the error by 2 Ha in VB1
Poor description of the 4s orbital

- (c)** Lowest energy excitation
Good results for CIS
LR better than CIS for VB1
- (d)** CIS greatly underestimates
LR are very close
Little basis effect in this case



- LR-VMC/TDA(o) oscillator strengths seem **more sensitive to the basis set** compared to the CIS oscillator strengths.
- The inclusion of the Jastrow factor does not improve the oscillator strength.

LR-VMC generally outperforms CIS for excitation energies and is thus a **promising approach for calculating electronic excited-state properties**.

- In this LR-VMC approach, after **optimizing only one ground-state wave function**, one can easily calculate several excitation energies of different spatial or spin symmetry (v. state-specific or state-average excited-state QMC methods).
- The presence of the **Jastrow factor** in LR-VMC allows one to explicitly treat dynamical correlation (v. similar linear-response quantum chemistry methods).
- A disadvantage is that the excitation energies are **much more sensitive than the ground state energy** to the quality of the optimized ground state wave function (also in other linear-response quantum chemistry methods, but : stochastic).

Coming up :

- systematic study on a set of molecules
- using the full response, beyond TDA (effect of the **B** matrix)
- larger basis sets
- derivatives with respect to the exponents of the Slater functions.
- multideterminantal wavefunction
- ideas to lower some statistical variation