Ensemble density functional theory of electrons and nuclei

Fatih Yildirim[a], Benjamin Lasorne[b] and Emmanuel Fromager[a]

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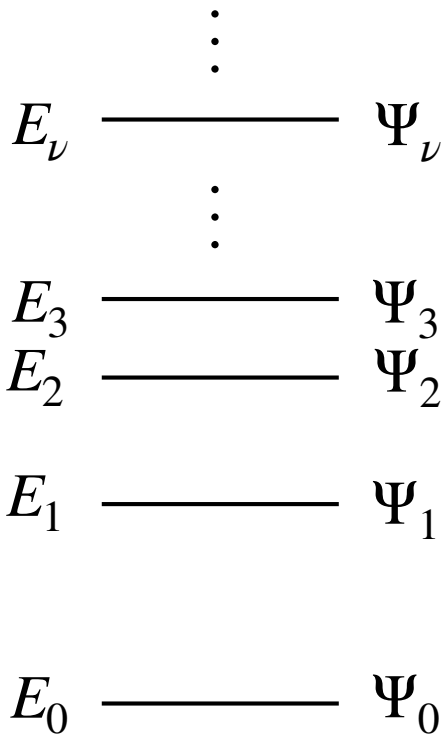
[b]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

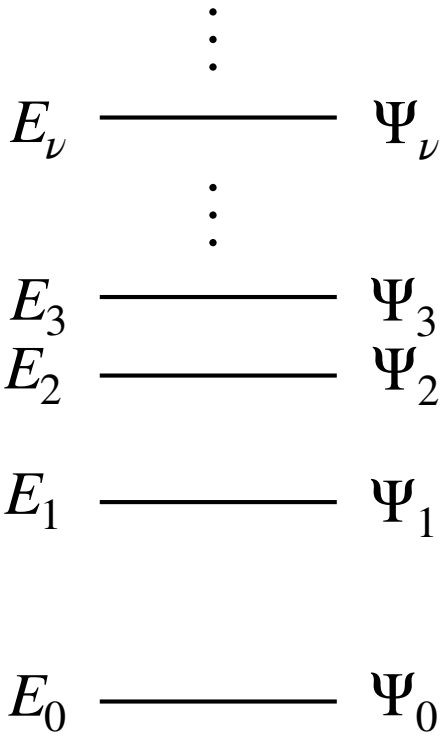
Brief review of (ensemble) ***density-functional***
electronic structure ***theory***

Density functional theory (DFT) of ground and excited states



Density functional theory (DFT) of ground and excited states

$$\hat{H}\Psi_\nu = E_\nu \Psi_\nu$$



Density-functional theory (DFT) of N-electron ground states

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

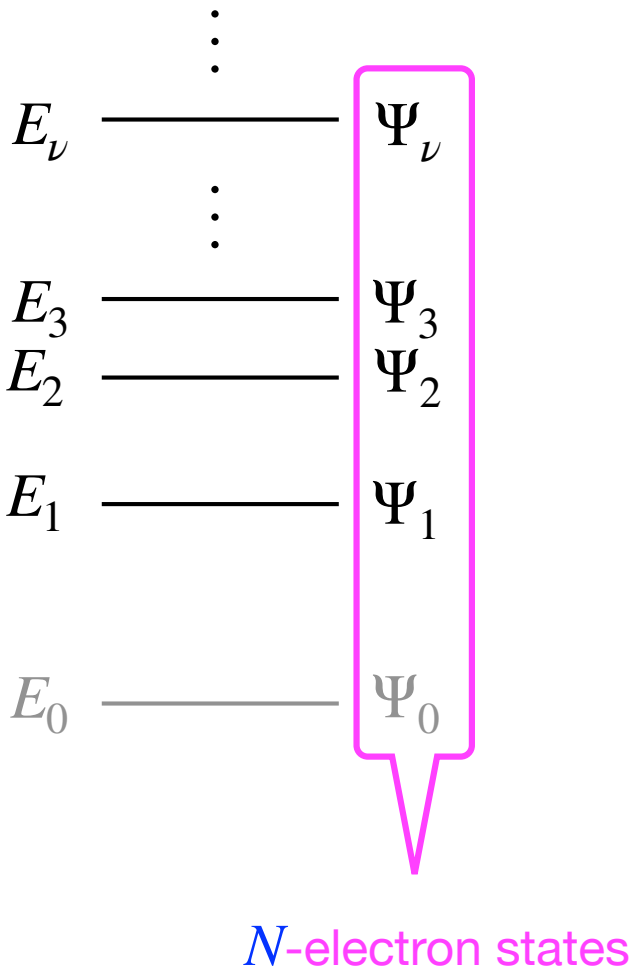
Variational principle

$$n_{\Psi_0}(\mathbf{r}) \equiv n_0^N(\mathbf{r})$$

*Ground-state electronic **density***

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

Theophilou-Gross-Oliveira-Kohn (TGOK) ensembles



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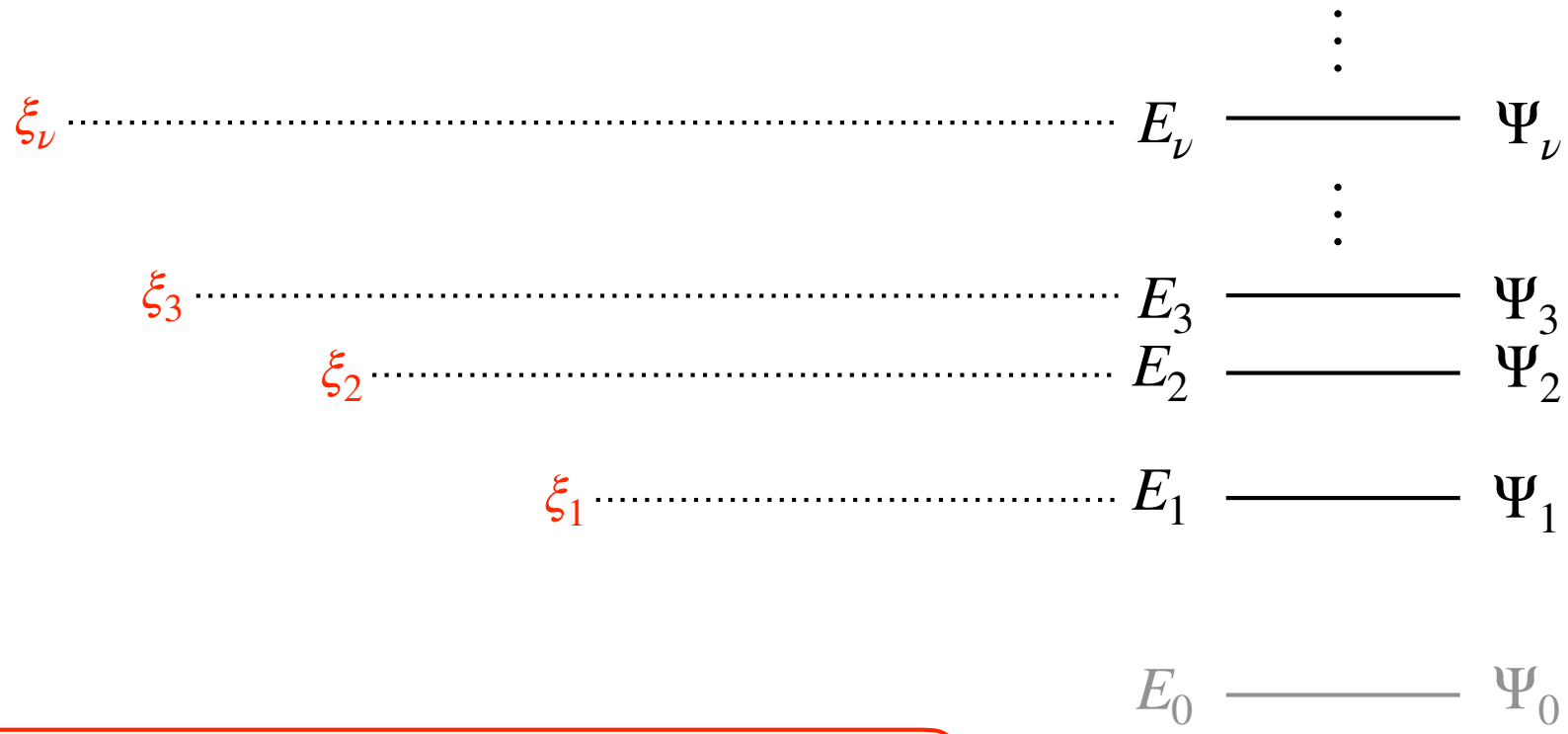

(Almost) independent ***ensemble weights*** $\{\xi_\nu\}$ *are assigned to the excited states*

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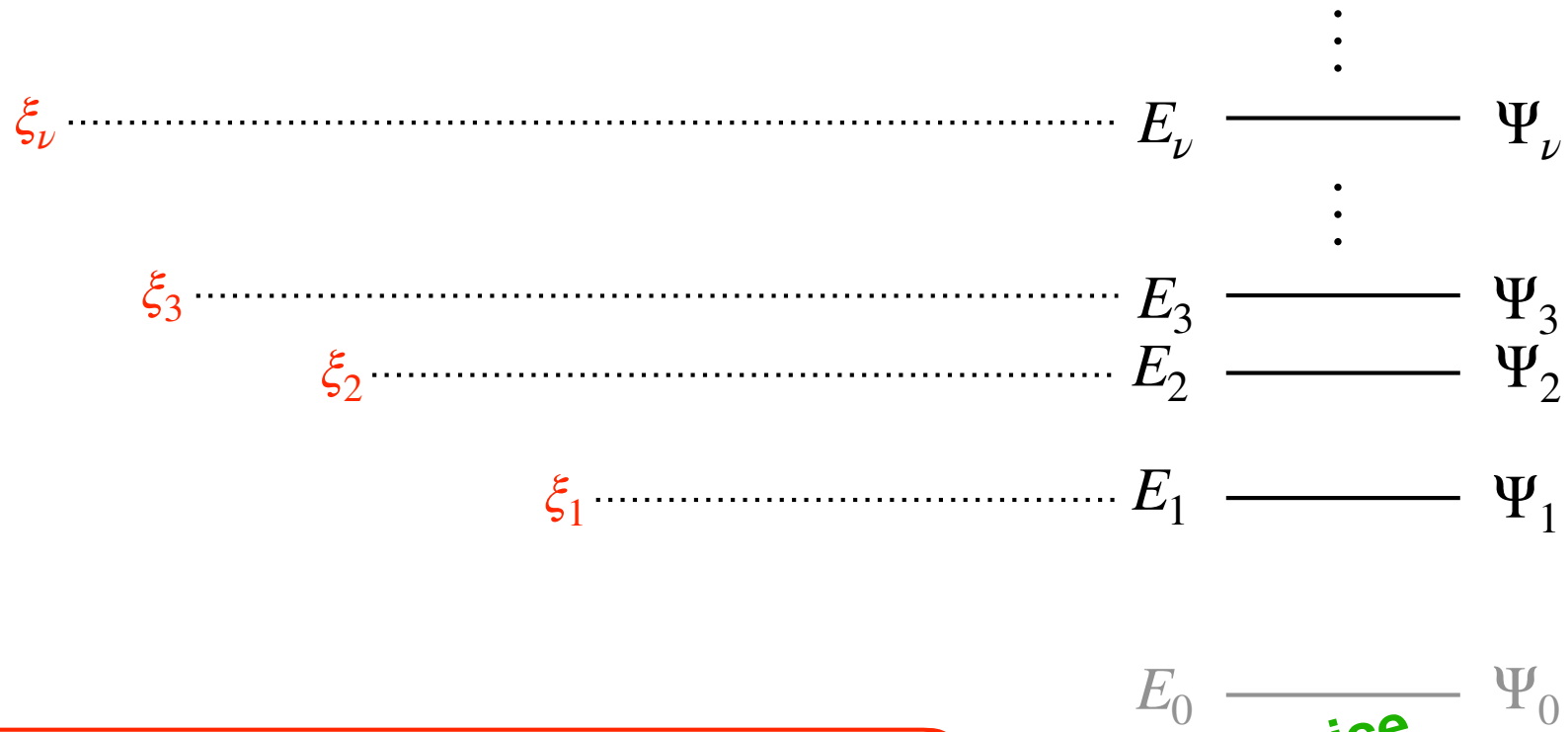

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Arbitrary choice in practice!

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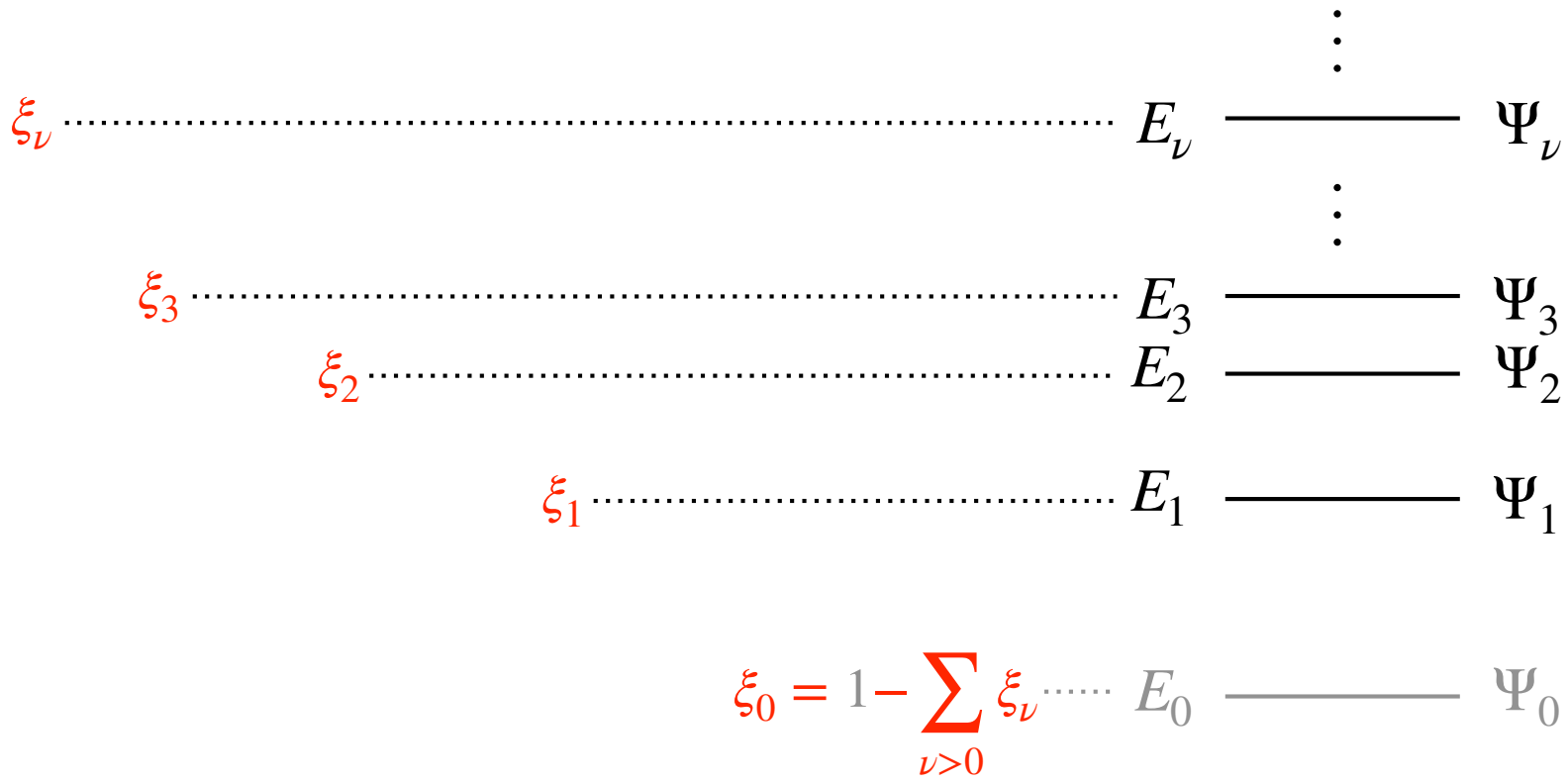

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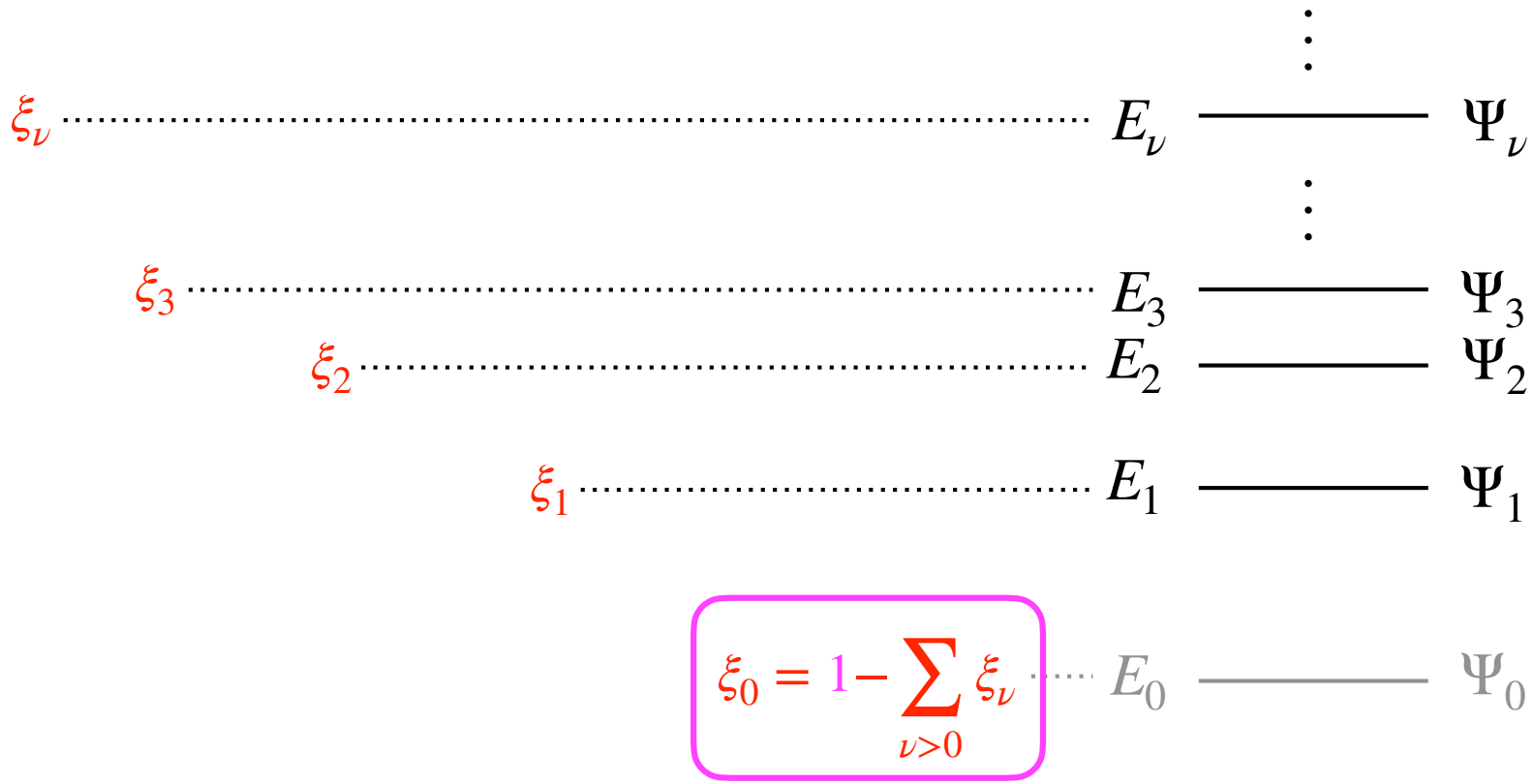

Neutral excitation processes

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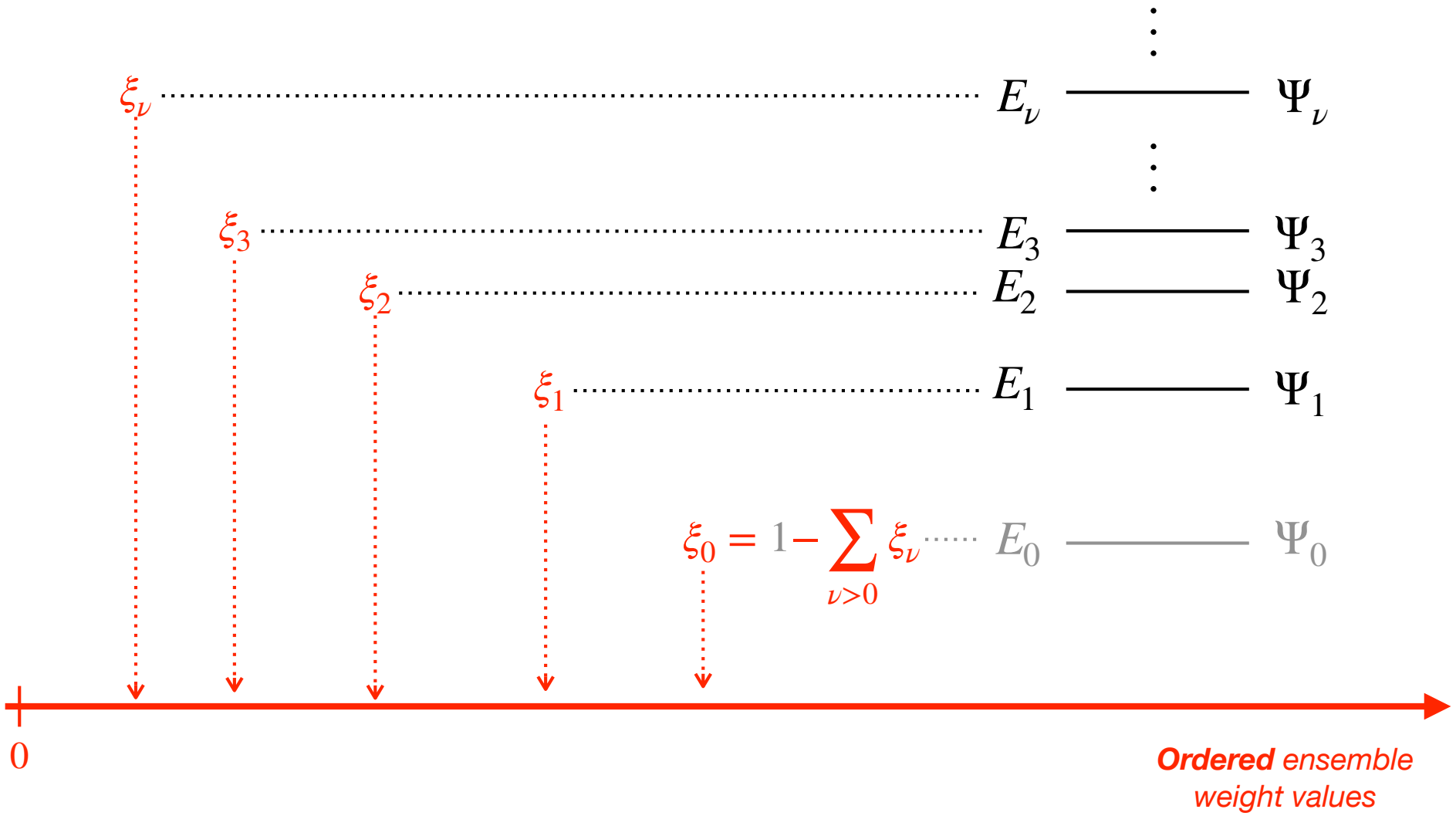

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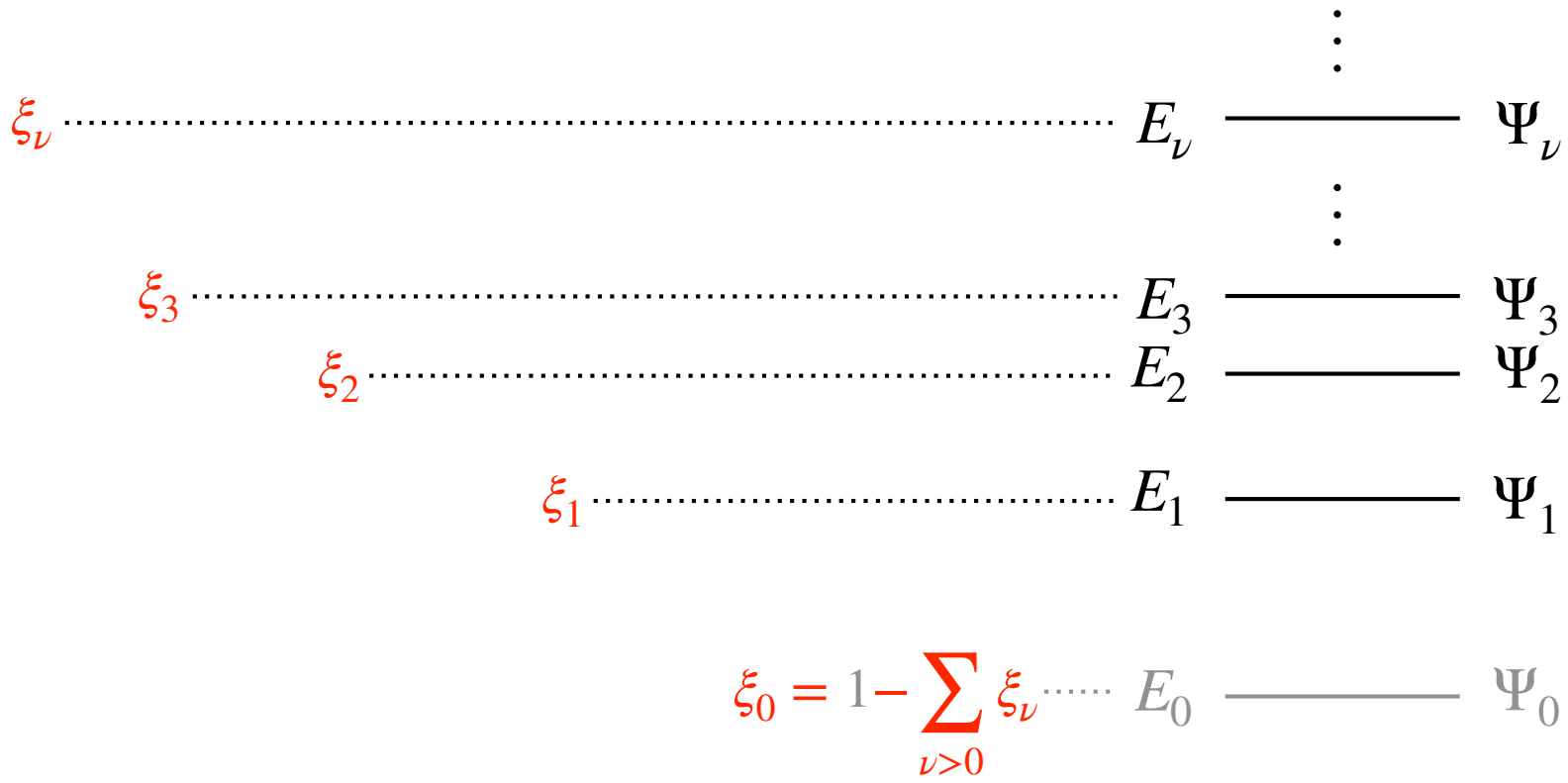
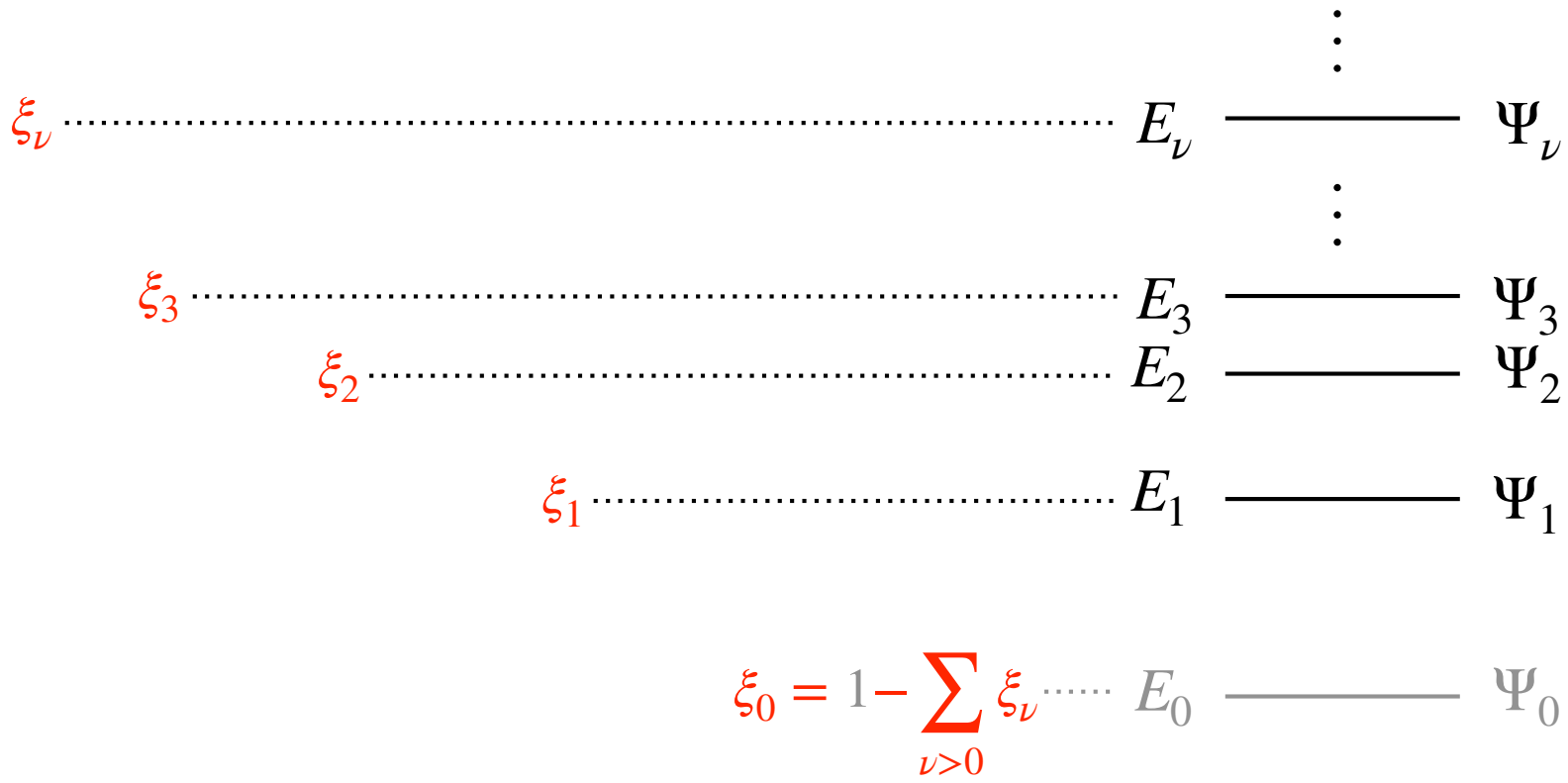
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\sum_{\nu\geq 0} \xi_\nu \langle \tilde{\Psi}_\nu | \hat{H} | \tilde{\Psi}_\nu \rangle \overset{\langle \tilde{\Psi}_\mu | \tilde{\Psi}_\nu \rangle = \delta_{\mu\nu}}{\geq} \sum_{\nu\geq 0} \xi_\nu E_\nu$$

Variational principle for ensembles

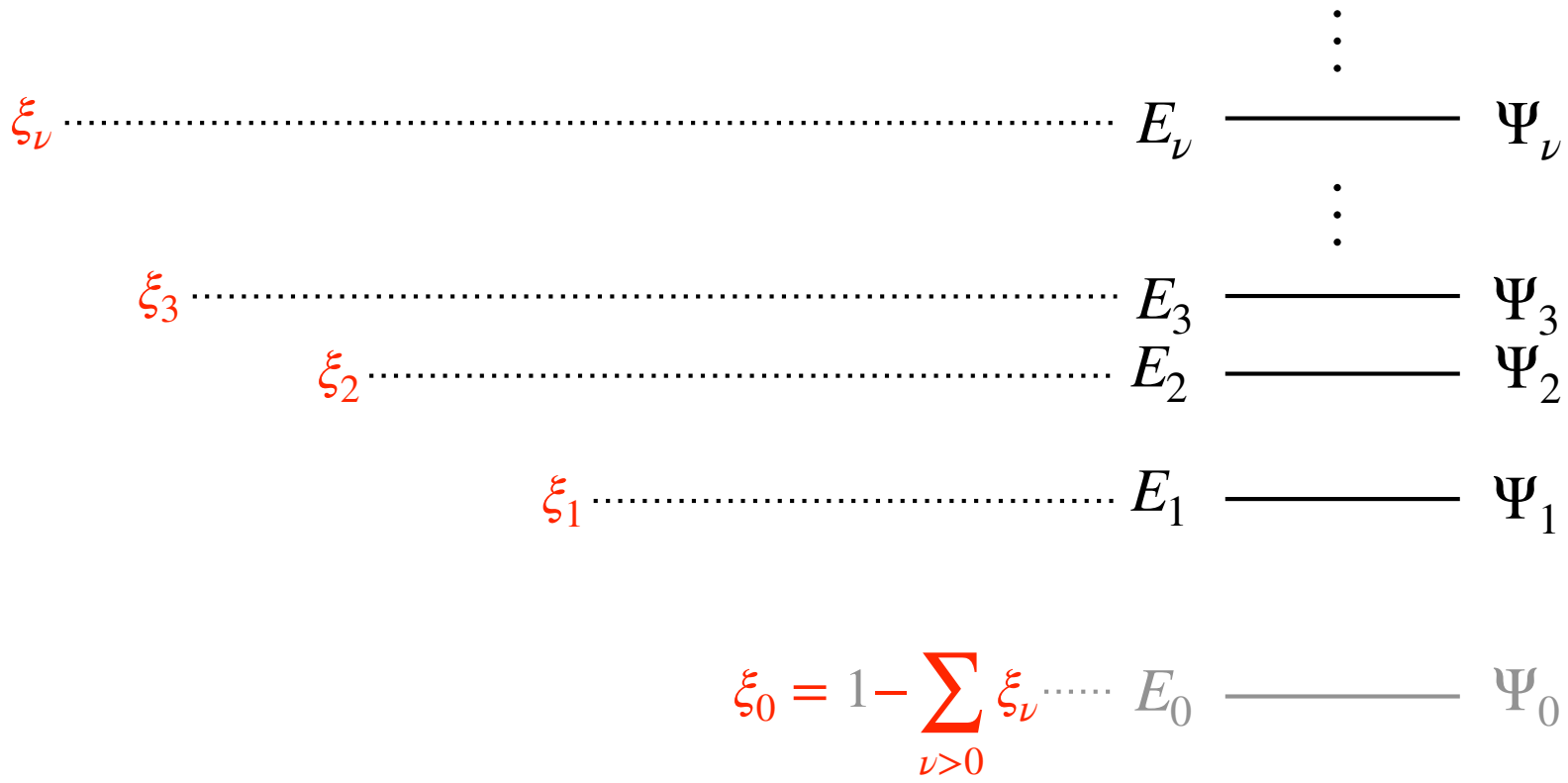
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\sum_{\nu\geq 0} \xi_\nu \langle \tilde{\Psi}_\nu | \hat{H} | \tilde{\Psi}_\nu \rangle \overset{\langle \tilde{\Psi}_\mu | \tilde{\Psi}_\nu \rangle = \delta_{\mu\nu}}{\geq} \sum_{\nu\geq 0} \xi_\nu E_\nu \equiv E^{\{\xi_\nu\}}$$

Ensemble energy

Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\sum_{\nu\geq 0} \xi_\nu \langle \tilde{\Psi}_\nu | \hat{H} | \tilde{\Psi}_\nu \rangle \overset{\langle \tilde{\Psi}_\mu | \tilde{\Psi}_\nu \rangle = \delta_{\mu\nu}}{\geq} \sum_{\nu\geq 0} \xi_\nu E_\nu \equiv E^{\{\xi_\nu\}}[n] \leftarrow n(\mathbf{r}) \equiv \sum_{\nu\geq 0} \xi_\nu n_{\Psi_\nu}(\mathbf{r})$$

Ensemble energy *Ensemble density*

How different is an **ensemble Kohn—Sham DFT** calculation from a regular (ground-state) one?

How different is an **ensemble Kohn—Sham DFT** calculation from a regular (ground-state) one?

$$n(\mathbf{r}) \equiv \sum_i \left(\sum_{\nu \geq 0} n_{i,\nu} \xi_\nu \right) \left| \varphi_i^{\{\xi_\nu\}}(\mathbf{r}) \right|^2$$

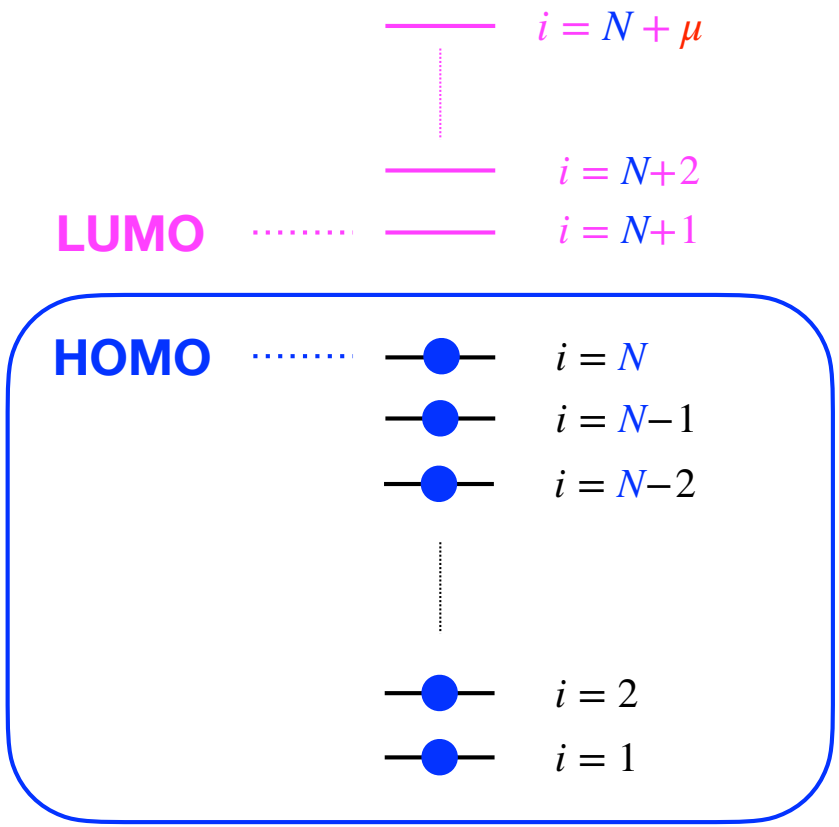
Fractionally *occupied KS orbitals*

How different is an **ensemble Kohn—Sham DFT** calculation from a regular (ground-state) one?

$$E_{\mathrm{Hxc}}[n] \longrightarrow E_{\mathrm{Hxc}}^{\{\xi_\nu\}}[n]$$

Ensemble-weight dependence

Ensemble weight dependence of the xc functional



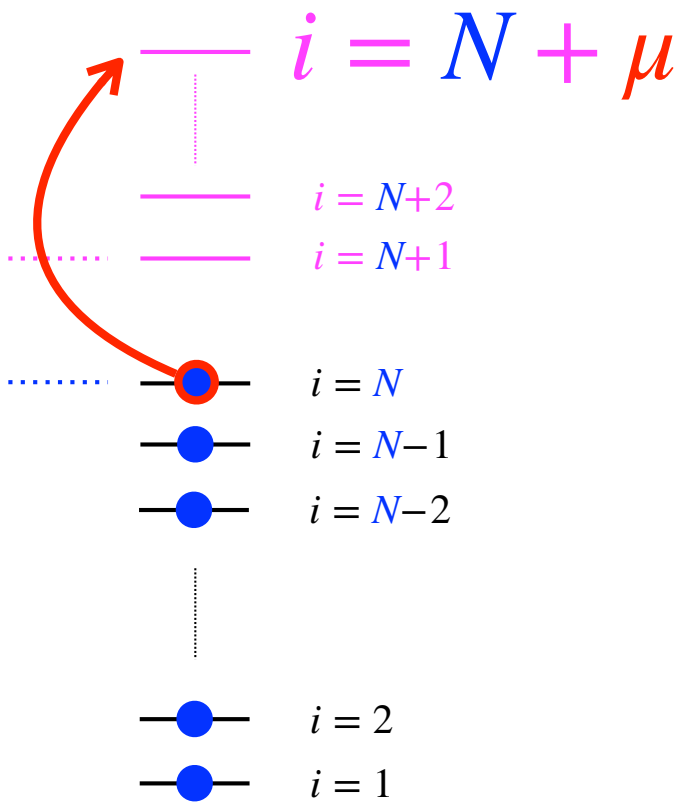
$$\{\xi_\nu\}_{0<\nu\leq\mu} = 0$$

*Regular **ground-state** Kohn—Sham configuration*

*E. Fromager, Phys. Rev. Lett. **124**, 243001 (2020).*
*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*
C. Marut, F. Cernatic, B. Senjean, P.-F. Loos, and E. Fromager, to be submitted (2023).

Ensemble weight dependence of the xc functional

$$\{\xi_\nu\}_{0<\nu\leq\mu} \to 0^+$$



*Infinitesimal **excitation process** in the fictitious Kohn—Sham world*

*E. Fromager, Phys. Rev. Lett. **124**, 243001 (2020).*
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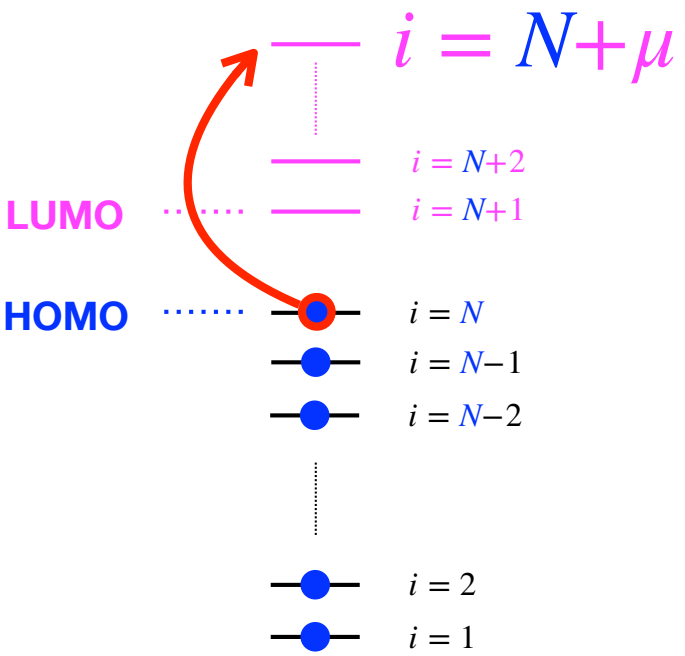

$$E_\mu - E_0 = \varepsilon_{N+\mu}^{\{\xi_\nu\}\to 0^+} - \varepsilon_N^{\{\xi_\nu\}=0}$$

Exact excitation energy!

E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
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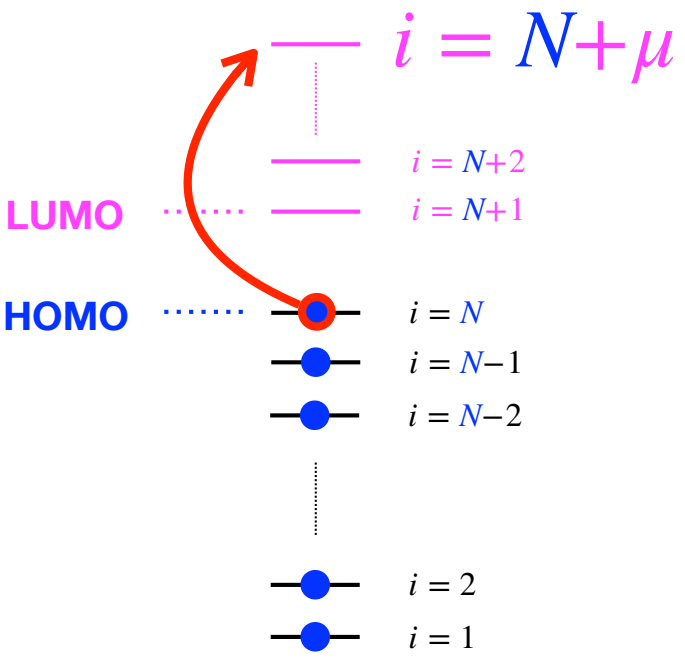

$$E_\mu - E_0 = \varepsilon_{N+\mu}^{\{\xi_\nu\}\to 0^+} - \varepsilon_N^{\{\xi_\nu\}=0}$$

$$v_{\mathrm{Hxc}}^{\{\xi_\nu\}}(\mathbf{r}) = \frac{\delta E_{\mathrm{Hxc}}^{\{\xi_\nu\}}[n]}{\delta n(\mathbf{r})}$$

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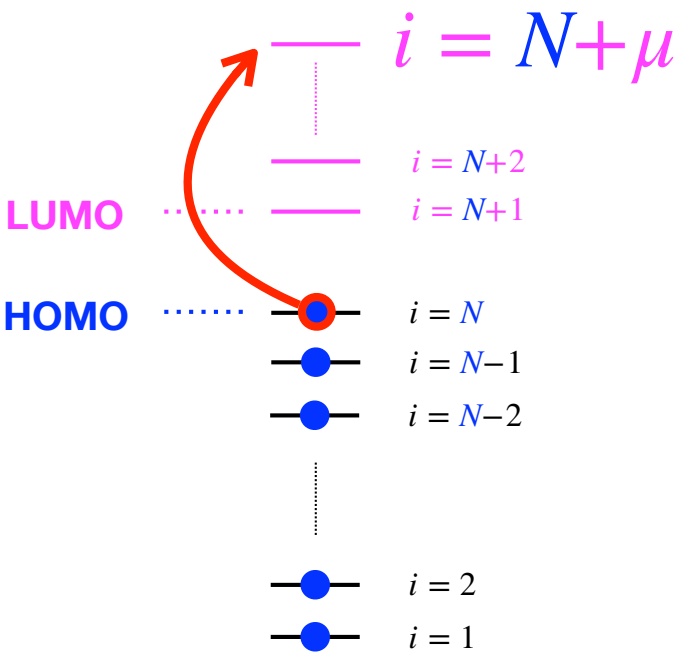

$$E_\mu - E_0 = \varepsilon_{N+\mu}^{\{\xi_\nu\}\to 0^+} - \varepsilon_N^{\{\xi_\nu\}=0}$$

$$v_{\text{Hxc}}^{\{\xi_\nu\}}(\mathbf{r}) = \frac{\delta E_{\text{Hxc}}^{\{\xi_\nu\}}[n]}{\delta n(\mathbf{r})}$$

$$\int \frac{d\mathbf{r}}{N} \left(v_{\text{Hxc}}^{\{\xi_\nu\}\to 0^+}(\mathbf{r}) - v_{\text{Hxc}}^{\{\xi_\nu\}=0}(\mathbf{r}) \right) n(\mathbf{r}) \underset{n=n_0^N}{=} ???$$

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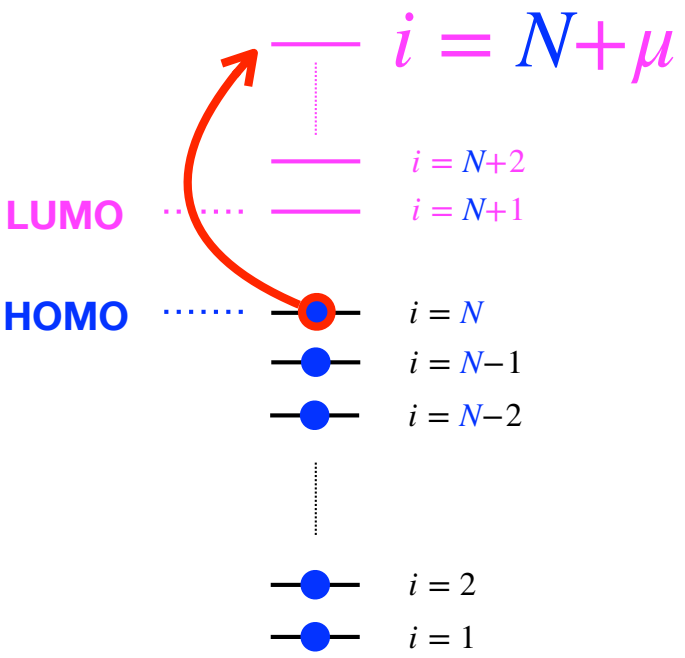

$$E_\mu - E_0 = \varepsilon_{N+\mu}^{\{\xi_\nu\}\to 0^+} - \varepsilon_N^{\{\xi_\nu\}=0}$$

$$v_{\text{Hxc}}^{\{\xi_\nu\}}(\mathbf{r}) = \frac{\delta E_{\text{Hxc}}^{\{\xi_\nu\}}[n]}{\delta n(\mathbf{r})}$$

$$\int \frac{d\mathbf{r}}{N} \left(v_{\text{Hxc}}^{\{\xi_\nu\}\to 0^+}(\mathbf{r}) - v_{\text{Hxc}}^{\{\xi_\nu\}=0}(\mathbf{r}) \right) n(\mathbf{r}) = \left. \frac{\partial E_{\text{Hxc}}^{\{\xi_\nu\}}[n]}{\partial \xi_\mu} \right|_{n=n_0^N} \Bigg|_{\{\xi_\nu\}=0}$$

"Derivative discontinuity"

E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*
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*Towards an **in-principle-exact** ensemble density-functional theory of **electrons and nuclei***

Exact Factorization-Based Density Functional Theory of Electrons and Nuclei

Ryan Requist* and E. K. U. Gross
Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany
(Received 13 July 2016; revised manuscript received 1 September 2016; published 4 November 2016)

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Article
Cite This: *J. Chem. Theory Comput.* 2018, 14, 4499–4512
pubs.acs.org/JCTC

Direct Nonadiabatic Dynamics by Mixed Quantum-Classical Formalism Connected with Ensemble Density Functional Theory Method: Application to *trans*-Penta-2,4-dieniminium Cation

Michael Filatov,* Seung Kyu Min,* and Kwang S. Kim

Department of Chemistry, School of Natural Sciences, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea

Born—Huang expansion of the molecular wave function

Bond distance (for example)

Electronic coordinates

$$\psi^{mol.}(R,r) = \sum_{\nu \geq 0} \chi_\nu(R)\Psi_\nu^{elec.}(R,r)$$

*Trial **molecular** wave function*

***Nuclear** wave functions*

*Ground- and excited-state **electronic** wave functions*

Born—Huang expansion of the molecular wave function

$$\psi^{mol.}(R,r) = \sum_{\nu \geq 0} \chi_\nu(R) \Psi_\nu^{elec.}(R,r)$$

Trial ***molecular*** *wave function*

Nuclear *wave functions*

Ground- and excited-state ***electronic*** *wave functions*

⇕

"Ensemble"

Molecular variational principle

diatomics

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M}\int dR\, \underline{\chi}^{\dagger}(R)\frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left|\underline{\chi}(R)\right|^2 \right.$$

$$-\frac{1}{M}\sum_{j=1}^{2}\frac{1}{j}\int dR\, \underline{\chi}^{\dagger}(R)\ \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R)\ \frac{\partial^{2-j}\underline{\chi}(R)}{\partial R^{2-j}}$$

$$\left. + \int dR\, |\underline{\chi}(R)|^2 \sum_{\nu\geq 0} \xi_\nu(R) E_\nu^{elec.}(R) \right\}$$

$$\psi^{mol.}(R,r) = \underline{\chi}^{\mathrm{T}}(R)\underline{\Psi}^{elec.}(R,r)$$

*The electronic energy within the molecule is an **ensemble energy***

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Molecular variational principle

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M} \int dR\, \underline{\chi}^{\dagger}(R) \frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left| \underline{\chi}(R) \right|^2 \right.$$

$$- \frac{1}{M} \sum_{j=1}^{2} \frac{1}{j} \int dR\, \underline{\chi}^{\dagger}(R)\ \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R)\ \frac{\partial^{2-j} \underline{\chi}(R)}{\partial R^{2-j}}$$

$$\left. + \int dR\, |\underline{\chi}(R)|^2 \sum_{\nu \geq 0} \xi_\nu(R) E^{elec.}_\nu(R) \right\}$$

To-be-determined ***ensemble weights:***

$$\xi_\nu(R) \equiv \frac{|\chi_\nu(R)|^2}{|\underline{\chi}(R)|^2}$$

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Molecular variational principle

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M} \int dR\, \underline{\chi}^{\dagger}(R) \frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left| \underline{\chi}(R) \right|^2 \right.$$

$$\left. -\frac{1}{M} \sum_{j=1}^{2} \frac{1}{j} \int dR\, \underline{\chi}^{\dagger}(R) \boxed{\underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R)} \frac{\partial^{2-j} \underline{\chi}(R)}{\partial R^{2-j}} \right.$$

$$\left. + \ \ldots \right.$$

$$\left\{ \int dr\, \Psi^{elec.}_{\nu}(R,r) \frac{\partial^j \Psi^{elec.}_{\mu}(R,r)}{\partial R^j} \right\} \equiv \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R)$$

Non-adiabatic couplings (NACs)

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Molecular variational principle

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M} \int dR\, \underline{\chi}^{\dagger}(R) \frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left| \underline{\chi}(R) \right|^2 \right.$$

$$\left. -\frac{1}{M} \sum_{j=1}^{2} \frac{1}{j} \int dR\, \underline{\chi}^{\dagger}(R) \boxed{\underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R)} \frac{\partial^{2-j} \underline{\chi}(R)}{\partial R^{2-j}} \right.$$

$$\left. + \ \ldots \right.$$

$$\left\{ \int dr\, \Psi^{elec.}_{\nu}(R,r) \frac{\partial^j \Psi^{elec.}_{\mu}(R,r)}{\partial R^j} \right\} \equiv \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R) = ???$$

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Molecular variational principle

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M} \int dR\, \underline{\chi}^{\dagger}(R) \frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left| \underline{\chi}(R) \right|^2 \right.$$
$$\left. - \frac{1}{M} \sum_{j=1}^{2} \frac{1}{j} \int dR\, \underline{\chi}^{\dagger}(R) \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R) \frac{\partial^{2-j} \underline{\chi}(R)}{\partial R^{2-j}} \right.$$
$$\left. + \ \ldots \right.$$

$$\left\{ \int dr\, \Psi^{elec.}_{\nu}(R,r) \frac{\partial^j \Psi^{elec.}_{\mu}(R,r)}{\partial R^j} \right\} \equiv \underline{\underline{\Lambda}}^{(j)}_{\underline{\Psi}^{elec.}}(R) = ??? \neq \underline{\underline{\Lambda}}^{(j)}_{\underline{\Phi}^{\mathrm{KS}}}(R)$$

True non-adiabatic couplings (NACs)

Kohn—Sham NACs

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

From the interacting to the non-interacting KS representation

$$\psi^{mol.}(R,r) = \underline{\chi}^{\mathrm{T}}(R)\underline{\Psi}^{elec.}(R,r)$$

***Adiabatic** (interacting)*
representation

$$\left(\hat{T}_e + \hat{W}_{ee} + \hat{V}_{Ne}(R)\right)\Psi_\nu^{elec.}(R,r) = E_\nu^{elec.}(R)\,\Psi_\nu^{elec.}(R,r)$$

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

From the interacting to the non-interacting KS representation

$$\psi^{mol.}(R,r) = \underline{\chi}^{\mathrm{T}}(R)\underline{\Psi}^{elec.}(R,r)$$

***Adiabatic** (interacting)*
representation

$$= \underline{\chi}^{\mathrm{T}}(R)\underline{\underline{\mathcal{U}}}(R)\underline{\underline{\mathcal{U}}}^{\dagger}(R)\underline{\Psi}^{elec.}(R,r)$$

Unitary
transformation

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

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$$= \left(\underline{\underline{\mathcal{U}}}^{\mathrm{T}}(R)\underline{\chi}(R)\right)^{\mathrm{T}} \underline{\Phi}^{\mathrm{KS}}(R,r)$$

Ensemble Kohn—Sham representation

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Exact theory using Kohn—Sham non-adiabatic couplings

$$E = \min_{\underline{\chi}} \left\{ -\frac{1}{2M} \int dR\, \underline{\chi}^{\dagger}(R) \frac{\partial^2 \underline{\chi}(R)}{\partial R^2} + \int dR\, V_{NN}(R) \left| \underline{\chi}(R) \right|^2 \right.$$

$$-\frac{1}{M} \sum_{j=1}^{2} \frac{1}{j} \int dR\, \underline{\chi}^{\dagger}(R) \underline{\underline{\Lambda}}^{(j)}_{\underline{\underline{\Phi}}^{\mathrm{KS}}}(R) \frac{\partial^{2-j} \underline{\chi}(R)}{\partial R^{2-j}}$$

$$\left. + \int dR\, |\underline{\chi}(R)|^2 \sum_{\nu \geq 0} \tilde{\xi}_{\nu}(R) E^{elec.}_{\nu}(R) \right\}$$

KS NACs
(no approximation made!)

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

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Electronic ensemble energy with modified weights

$$\tilde{\xi}_{\nu}(R) = \frac{\left|\sum_{\mu\geq 0} \mathcal{U}^{*}_{\nu\mu}(R)\,\chi_{\mu}(R)\right|^2}{\left|\underline{\chi}(R)\right|^2}$$

Now

$$\xi_{\nu}(R) \equiv \frac{|\chi_{\nu}(R)|^2}{|\underline{\chi}(R)|^2}$$

Before

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

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Unitary transformation

$$\underline{\Psi}^{elec.}(R,r) = \underline{\underline{\mathcal{U}}}(R)\ \underline{\Phi}^{\mathrm{KS}}(R,r)$$

$$\tilde{\xi}_{\nu}(R) = \frac{\left|\sum_{\mu\geq 0} \mathcal{U}^{*}_{\nu\mu}(R)\,\chi_{\mu}(R)\right|^2}{\left|\underline{\chi}(R)\right|^2}$$

Now

$$\xi_{\nu}(R) \equiv \frac{|\chi_{\nu}(R)|^2}{|\underline{\chi}(R)|^2}$$

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Ensemble energy
to be described **with a KS system**

Unitary transformation

$$\underline{\Psi}^{elec.}(R,r) = \underline{\underline{\mathcal{U}}}(R)\, \underline{\Phi}^{\mathrm{KS}}(R,r)$$

Ensemble weights →

$$\tilde{\xi}_{\nu}(R) = \frac{\left|\sum_{\mu\geq 0} \mathcal{U}^{*}_{\nu\mu}(R)\, \chi_{\mu}(R)\right|^2}{\left|\underline{\chi}(R)\right|^2}$$

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$$\underline{\Psi}^{elec.}(R, r) = \underline{\underline{\mathcal{U}}}(R) \, \underline{\Phi}^{\mathrm{KS}}(R, r)$$

Ensemble weights →

$$\tilde{\xi}_{\nu}(R) = \frac{\left| \sum_{\mu \geq 0} \mathcal{U}^{*}_{\nu\mu}(R) \chi_{\mu}(R) \right|^2}{\left| \underline{\chi}(R) \right|^2} = ???$$

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$$\sum_\nu \tilde{\xi}_\nu(R)\, n_{\Psi_\nu^{elec.}}(R,\mathbf{r}) = n^{\underline{\tilde{\xi}}(R)}(R,\mathbf{r}) = \sum_\nu \tilde{\xi}_\nu(R)\, n_{\Phi_\nu^{\mathrm{KS}}}(R,\mathbf{r})$$

Ensemble density constraint

Unitary transformation

$$\underline{\Psi}^{elec.}(R,r) = \underline{\underline{\mathcal{U}}}(R)\ \underline{\Phi}^{\mathrm{KS}}(R,r)$$

Ensemble weights →

$$\tilde{\xi}_\nu(R) = \frac{\left|\sum_{\mu\geq 0} \mathcal{U}^*_{\nu\mu}(R)\,\chi_\mu(R)\right|^2}{\left|\underline{\chi}(R)\right|^2} = ???$$

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Unitary transformation

$$\underline{\Psi}^{elec.}(R,r) = \underline{\underline{\mathcal{U}}}(R)\, \underline{\Phi}^{\mathrm{KS}}(R,r)$$

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← **Functionals of the ensemble density!**

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Exact theory using Kohn—Sham non-adiabatic couplings

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Unitary transformation

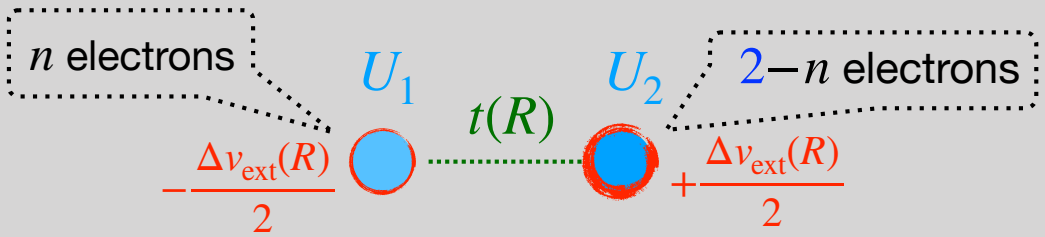
$$\underline{\Psi}^{elec.}(R, r) = \underline{\underline{\mathcal{U}}}(R)\; \underline{\Phi}^{\mathrm{KS}}(R, r)$$

***Self-consistent evaluation** of the ensemble weights $\underline{\tilde{\xi}}(R)$*

$$\underline{\tilde{\xi}}(R) = \underline{\tilde{\xi}} \left[\underline{\underline{\mathcal{U}}} \left[n^{\underline{\tilde{\xi}}(R)} \right], \underline{\chi}(R) \right]$$

F. Cernatic, B. Lasorne, and E. Fromager, "Perspective" paper in J. Chem. Phys, in preparation (2023).

Implementation of the theory (work in progress)

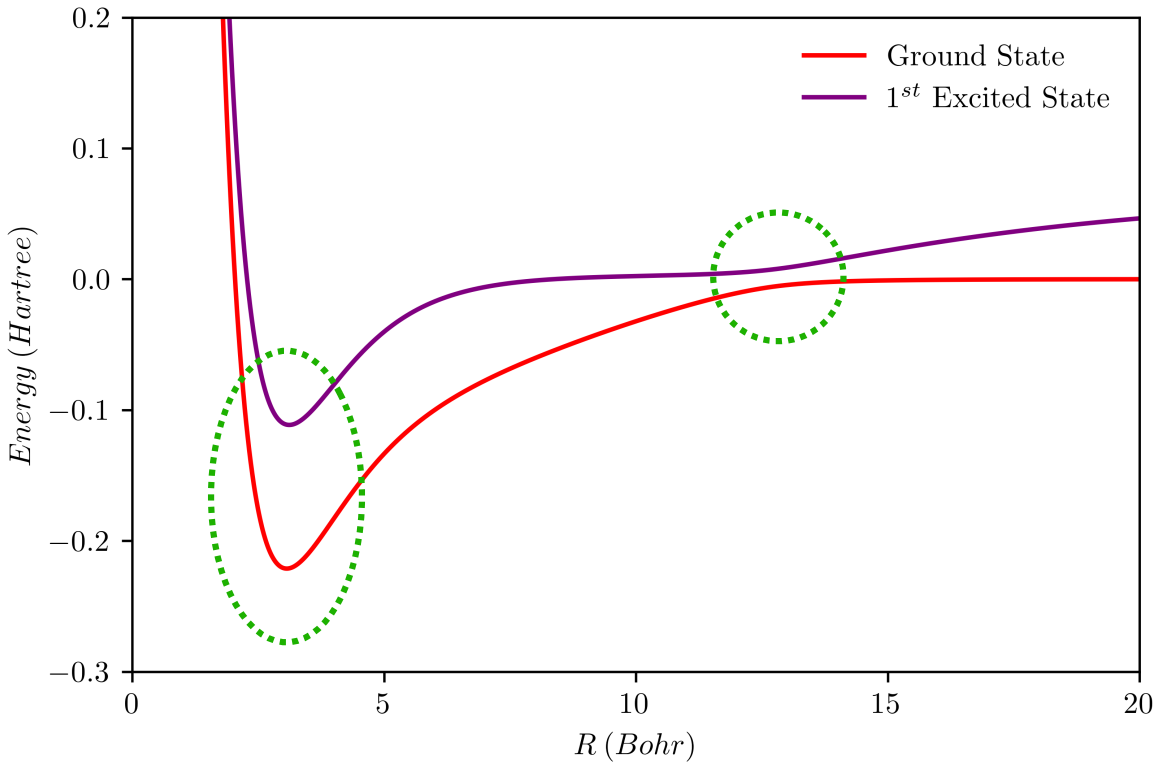


Geometry-dependent
two-electron **Hubbard dimer model**

THE JOURNAL OF CHEMICAL PHYSICS **148**, 084110 (2018)

Density functional theory of electron transfer beyond the Born-Oppenheimer approximation: Case study of LiF

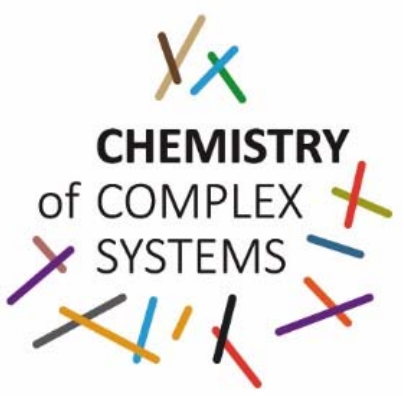
Chen Li,[1,a)] Ryan Requist,[1] and E. K. U. Gross[1,2]



F. Yildirim, B. Lasorne, and E. Fromager, in preparation (2023).

Funding

“Lab of Excellence” project:
LabEx CSC (ANR-10-LABX-0026-CSC)



« Initiative d’Excellence » (IdEx) grant
University of Strasbourg

CoLab ANR project

Unified N-centered ensemble DFT

of charged and neutral excited states

$$n(\mathbf{r}) \equiv \left(1 - \sum_{\nu>0}^{\text{excited states}} \frac{N_\nu}{N} \xi_\nu \right) n_0^N(\mathbf{r}) + \sum_{\nu>0}^{\text{excited states}} \xi_\nu n_\nu(\mathbf{r})$$

*Ensemble enlarged to **charged** excitations*

*B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190
*F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) **380**, 4 (2022).*
C. Marut, F. Cernatic, B. Senjean, P.-F. Loos, and E. Fromager, to be submitted (2023).

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$$\int d\mathbf{r}\, n(\mathbf{r}) = N$$

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$$E^{\{\xi_\nu\}}[n] \equiv \left(1 - \sum_{\nu>0}^{\text{excited states}} \frac{N_\nu}{N} \xi_\nu \right) E_0^N + \sum_{\nu>0}^{\text{excited states}} \xi_\nu E_\nu$$

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$$E_\mu^N - E_0^N = \left(E_\mu^N - E_0^{N-1}\right) + \left(E_0^{N-1} - E_0^N\right)$$

$$E_0^{N-1} - E_0^N = -\varepsilon_N^{\xi_\mu=0} + \frac{\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu=0}(\mathbf{r}) n_0^N(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0^N]\right)}{N} + \frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0^N]}{\partial \xi_-}\bigg|_{\{\xi_\nu\}=0}$$

$\xi_\mu = 0$

Koopmans theorems *if* $= 0$ *(arbitrary choice)*

$\xi_\mu \to 0^+$

$$E_\mu^N - E_0^{N-1} \underset{\mu>0}{=} \varepsilon_{N+\mu}^{\xi_\mu\to 0^+} - \frac{\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu\to 0^+}(\mathbf{r}) n_0^N(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0^N]\right)}{N} - \frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0^N]}{\partial \xi_-}\bigg|_{\{\xi_\nu\}=0} + \frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0^N]}{\partial \xi_\mu}\bigg|_{\{\xi_\nu\}=0}$$

$$E_\mu^N - E_0^N \underset{\mu>0}{=} \varepsilon_{N+\mu}^{\xi_\mu\to 0^+} - \varepsilon_N^{\xi_\mu=0}$$

Exact neutral **excitation energy**

M. Levy, Phys. Rev. A ***52****, R4313 (1995).*
T. Gould, Z. Hashimi, L. Kronik, and S. G. Dale, J. Phys. Chem. Lett. ***13****, 2452 (2022).*
C. Marut, F. Cernatic, B. Senjean, P.-F. Loos, and E. Fromager, to be submitted (2023).

$$E_0^{N-1} - E_0^N = -\varepsilon_N^{\xi_\mu=0} + \frac{\left(\int d\mathbf{r}\, v_{\mathrm{Hxc}}^{\xi_\mu=0}(\mathbf{r}) n_0^N(\mathbf{r}) - E_{\mathrm{Hxc}}[n_0^N]\right)}{N} + \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0^N]}{\partial \xi_-}\right|_{\{\xi_\nu\}=0}$$

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$$\int \frac{d\mathbf{r}}{N} \left(v_{\mathrm{xc}}^{\xi_\mu\to 0^+}(\mathbf{r}) - v_{\mathrm{xc}}^{\xi_\mu=0}(\mathbf{r})\right) n_0^N(\mathbf{r}) = \left.\frac{\partial E_{\mathrm{xc}}^{\{\xi_\nu\}}[n_0^N]}{\partial \xi_\mu}\right|_{\{\xi_\nu\}=0}$$

Derivative **discontinuity!**

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T. Gould, Z. Hashimi, L. Kronik, and S. G. Dale, J. Phys. Chem. Lett. ***13****, 2452 (2022).*
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Extraction of individual energies from the ensemble energy

$$E^{\{\xi_\nu\}} = \left(1 - \sum_{\nu>0} \xi_\nu\right) E_0 + \sum_{\nu>0} \xi_\nu E_\nu$$

Auxiliary quantity *(not an observable) …*

E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
K. Deur and E. Fromager, J. Chem. Phys. ***150****, 094106 (2019).*

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We cannot "read" the individual energies!

E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
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$$E_\mu = E_0 + E_\mu - E_0$$

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$$E_\mu = E_0 + E_\mu - E_0 = E_0 + \sum_{\nu>0} \delta_{\nu\mu} \frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\nu}$$

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… that ***varies linearly*** *with the ensemble* ***weights!***

$$E_\mu = E_0 + E_\mu - E_0 = E_0 + \sum_{\nu>0} \delta_{\nu\mu} \frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\nu} = E^{\{\xi_\nu\}} + \sum_{\nu>0} \left(-\xi_\nu + \delta_{\nu\mu}\right) \frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\nu}$$

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$$E_\mu = E^{\{\xi_\nu\}} + \sum_{\nu>0} \left(\delta_{\nu\mu} - \xi_\nu\right) \frac{\partial E^{\{\xi_\nu\}}}{\partial \xi_\nu}$$

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$$E_\mu = \left[1 + \sum_{\nu>0} \left(\delta_{\nu\mu} - \xi_\nu\right) \frac{\partial}{\partial \xi_\nu}\right] E^{\{\xi_\nu\}}$$

Ensemble Kohn-Sham decomposition

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Deduced from the (ensemble) Kohn-Sham orbital energies

Ensemble Kohn-Sham decomposition

E. Fromager, Phys. Rev. Lett. ***124****, 243001 (2020).*
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Ordered-weight ***ensemble density functional theory***

$$E^{\{\xi_\nu(R)\}} = \sum_{\nu \geq 0} \xi_\nu(R)\, E_\nu^{elec.}(R)$$

What if the weights are ***not*** *in decreasing order?*

Ordered-weight ensemble density functional theory

$$E^{\{\xi_\nu(R)\}} = \sum_{\nu \geq 0} \xi_\nu(R)\, E_\nu^{elec.}(R)$$

$$E^{[\xi_\nu(R)]} = \sum_{\nu \geq 0} [\xi_\nu(R)]\, E_\nu^{elec.}(R)$$

Ordered-weight
Ensemble energy

Ordered-weight ensemble density functional theory

$$E^{\{\xi_\nu(R)\}} = \sum_{\nu\geq 0} \xi_\nu(R)\, E_\nu^{elec.}(R)$$

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Ordered-weight
Ensemble energy

$$n^{[\xi_\nu(R)]}(\mathbf{r}) = \sum_{\nu\geq 0} [\xi_\nu(R)]\, n_{\Psi_\nu^{elec.}(R)}(\mathbf{r})$$

Ordered-weight
Ensemble density

Ordered-weight ensemble density functional theory

$$E^{\{\xi_\nu(R)\}} = \sum_{\nu \geq 0} \xi_\nu(R)\, E_\nu^{elec.}(R)$$

$$E^{[\xi_\nu(R)]} = \sum_{\nu \geq 0} [\xi_\nu(R)]\, E_\nu^{elec.}(R)$$

$$n^{[\xi_\nu(R)]}(\mathbf{r}) = \sum_{\nu \geq 0} [\xi_\nu(R)]\, n_{\Psi_\nu^{elec.}(R)}(\mathbf{r})$$

$$E_\nu^{elec.}(R) \equiv E_\nu^{elec.}\left[n^{[\xi_\nu(R)]}\right]$$

Ordered-weight ensemble density functional theory

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$$E^{[\xi_\nu(R)]} = \sum_{\nu\geq 0} \left[\xi_\nu(R)\right] E_\nu^{elec.}(R)$$

$$n^{[\xi_\nu(R)]}(\mathbf{r}) = \sum_{\nu\geq 0} \left[\xi_\nu(R)\right] n_{\Psi_\nu^{elec.}(R)}(\mathbf{r})$$

$$E_\nu^{elec.}(R) \equiv E_\nu^{elec.}\left[n^{[\xi_\nu(R)]}\right]$$