

On Symmetry and Degeneracy in the Construction of the Adiabatic Connection Based on the Lieb Variational Principle

Bang C. Huynh¹, Andrew M. Teale¹

¹School of Chemistry, University of Nottingham, United Kingdom



University of
Nottingham
UK | CHINA | MALAYSIA

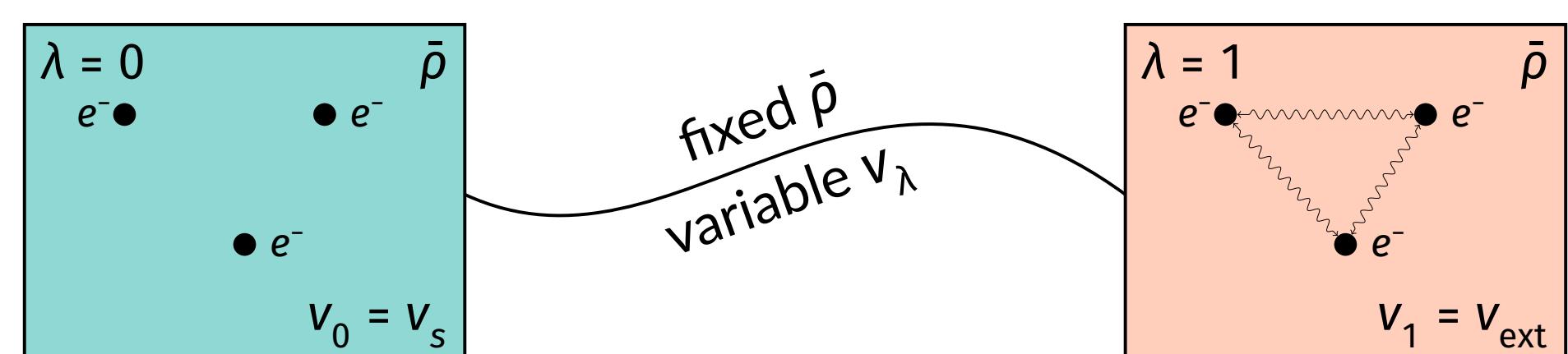


1. The Exact Adiabatic Connection (AC)

For an N -electron system, consider a λ -parametrised electronic Hamiltonian

$$\hat{\mathcal{H}}_\lambda(v_\lambda) = \hat{T} + \lambda \hat{W} + \sum_{i=1}^N v_\lambda(\mathbf{r}_i), \quad \text{where} \quad \hat{W} = \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

that continuously links the **physical system** to the **non-interacting system**.



The potential v_λ is chosen for $\hat{\mathcal{H}}_\lambda$ to admit the same **ground density** $\bar{\rho}$ as $\hat{\mathcal{H}}_1$ via the **ground density matrix** $\hat{\gamma}_\lambda(\bar{\rho})$.

The **adiabatic connection (AC)**, defined by $\mathcal{W}_\lambda(\bar{\rho}) = \text{tr } \hat{\gamma}_\lambda(\bar{\rho}) \hat{W}$, can be calculated accurately for small systems to form approximate models for larger systems.

2. The Lieb Variational Principle

Consider the space of densities \mathcal{X} and its dual, the space of potentials \mathcal{X}^* :

$$\mathcal{X} = L^3(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \quad \mathcal{X}^* = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3).$$

For every λ along the AC, given a **wavefunction method M** to compute the **M-ground energy** $E_\lambda^M(v)$ of $\hat{\mathcal{H}}_\lambda(v)$ and the M-reference density $\bar{\rho}_1^M \in \mathcal{X}$, by finding the **Lieb universal functional**

$$F_\lambda^M(\bar{\rho}_1^M) = \sup_{v \in \mathcal{X}^*} \left[E_\lambda^M(v) - \int v(\mathbf{r}) \bar{\rho}_1^M(\mathbf{r}) d\mathbf{r} \right] \equiv \sup_{v \in \mathcal{X}^*} G_\lambda^M(v; \bar{\rho}_1^M),$$

one obtains the **M-optimal potential** v_λ^M that

- supports $\bar{\rho}_\lambda^M$ as its ground density; and
- minimises the **Lieb-variational errors** $\|\bar{\rho}_\lambda^M - \bar{\rho}_1^M\|_p$, $1 \leq p \leq 3$.

How well v_λ^M approximates the true potential v_λ depends on the **quality of the method M** and on whether v_λ actually exists in \mathcal{X}^* .

3. Challenges of Degenerate Systems

Consider a Hamiltonian $\hat{\mathcal{H}}_\lambda(v)$ having a **symmetry group** $\mathcal{G}_\lambda(v)$ and admitting a **degenerate ground wavefunction** $\Psi_\lambda^M(v)$ with **energy** $E_\lambda^M(v)$ and **density** $\bar{\rho}_\lambda^M(r; v)$.

Non-convergence in Lieb optimisation at $\lambda \neq 1$.

Well-defined gradient?

The Lieb optimisation procedure to obtain the M-optimal potential v_λ^M requires the functional derivative

$$\frac{\delta G_\lambda^M(v; \bar{\rho}_1^M)}{\delta v(\mathbf{r})} = \frac{\delta E_\lambda^M(v)}{\delta v(\mathbf{r})} - \bar{\rho}_1^M(\mathbf{r}).$$

As the degenerate density $\bar{\rho}_\lambda^M(r; v)$ is not invariant under all of $\mathcal{G}_\lambda(v)$, $\delta E_\lambda^M(v)/\delta v(\mathbf{r})$ is **not unique**:

$$\frac{\delta E_\lambda^M(v)}{\delta v(\mathbf{r})} = \sum_{i=1}^{|\mathcal{G}_\lambda(v)|} c_i g_i \bar{\rho}_\lambda^M(\mathbf{r}; v), \quad g_i \in \mathcal{G}_\lambda(v), \quad c_i \geq 0, \quad \sum_{i=1}^{|\mathcal{G}_\lambda(v)|} c_i = 1.$$

Density alignment

The uniqueness of $\delta E_\lambda^M(v)/\delta v(\mathbf{r})$ is enforced by **choosing**

$$\frac{\delta E_\lambda^M(v)}{\delta v(\mathbf{r})} = \hat{g} \bar{\rho}_\lambda^M(\mathbf{r}; v), \quad g \in \mathcal{G}_1(v_{\text{ext}})$$

such that $\hat{g} \bar{\rho}_\lambda^M(\mathbf{r}; v)$ is in the **same symmetry gauge** as $\bar{\rho}_1^M(\mathbf{r})$, i.e. both densities are invariant under the same subgroup of $\mathcal{G}_1(v_{\text{ext}})$.

Symmetry of potential?

At all λ , the M-optimal potential v_λ^M determines the **symmetry group** of the Hamiltonian:

$$\begin{aligned} \lambda = 1 : \quad v_{\text{ext}} &\mapsto \mathcal{G}_1(v_{\text{ext}}) && \text{physical system,} \\ 0 \leq \lambda < 1 : \quad v_\lambda^M &\mapsto \mathcal{G}_\lambda(v_\lambda^M) && \text{auxiliary systems.} \end{aligned}$$

Is **equality** in the following condition

$$\mathcal{G}_1(v_{\text{ext}}) \geq \mathcal{G}_\lambda(v_\lambda^M), \quad \lambda \neq 1$$

necessary? In other words, do the **auxiliary systems** have to **respect** the symmetry of the **physical system**?

Pure-state v -representability (PSVR)?

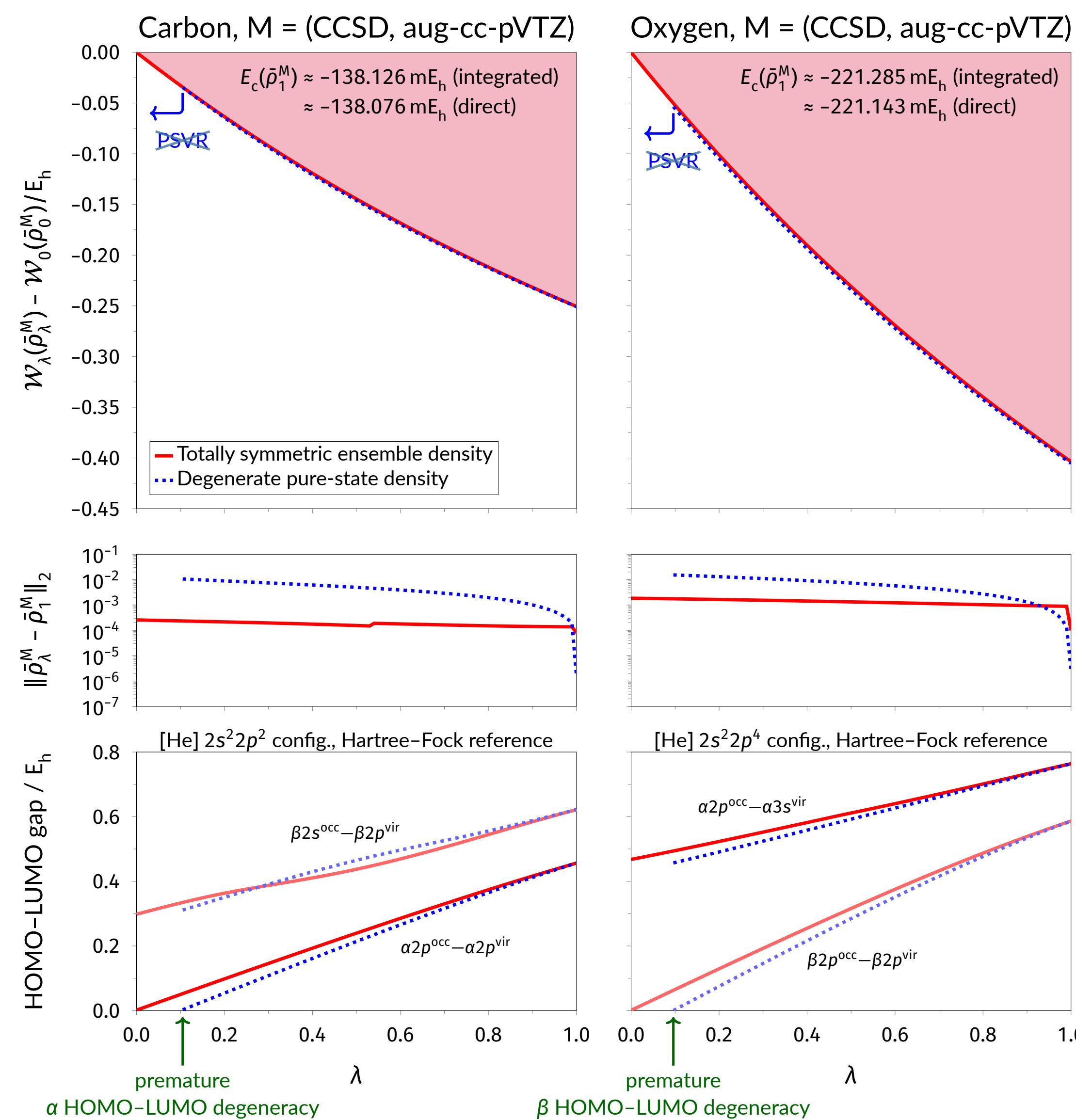
The **continuity** of the AC $\mathcal{W}_\lambda(\bar{\rho})$ requires the **reference density** $\bar{\rho}$ to be **v -representable** $\forall \lambda \in [0, 1]$. However, general v -representability conditions for densities in \mathcal{X} are not well-established.

In particular, consider the degenerate pure-state ground density $\bar{\rho}_1^M$ as the reference density: there is no guarantee that it is **pure-state v -representable** $\forall \lambda \in [0, 1]$.

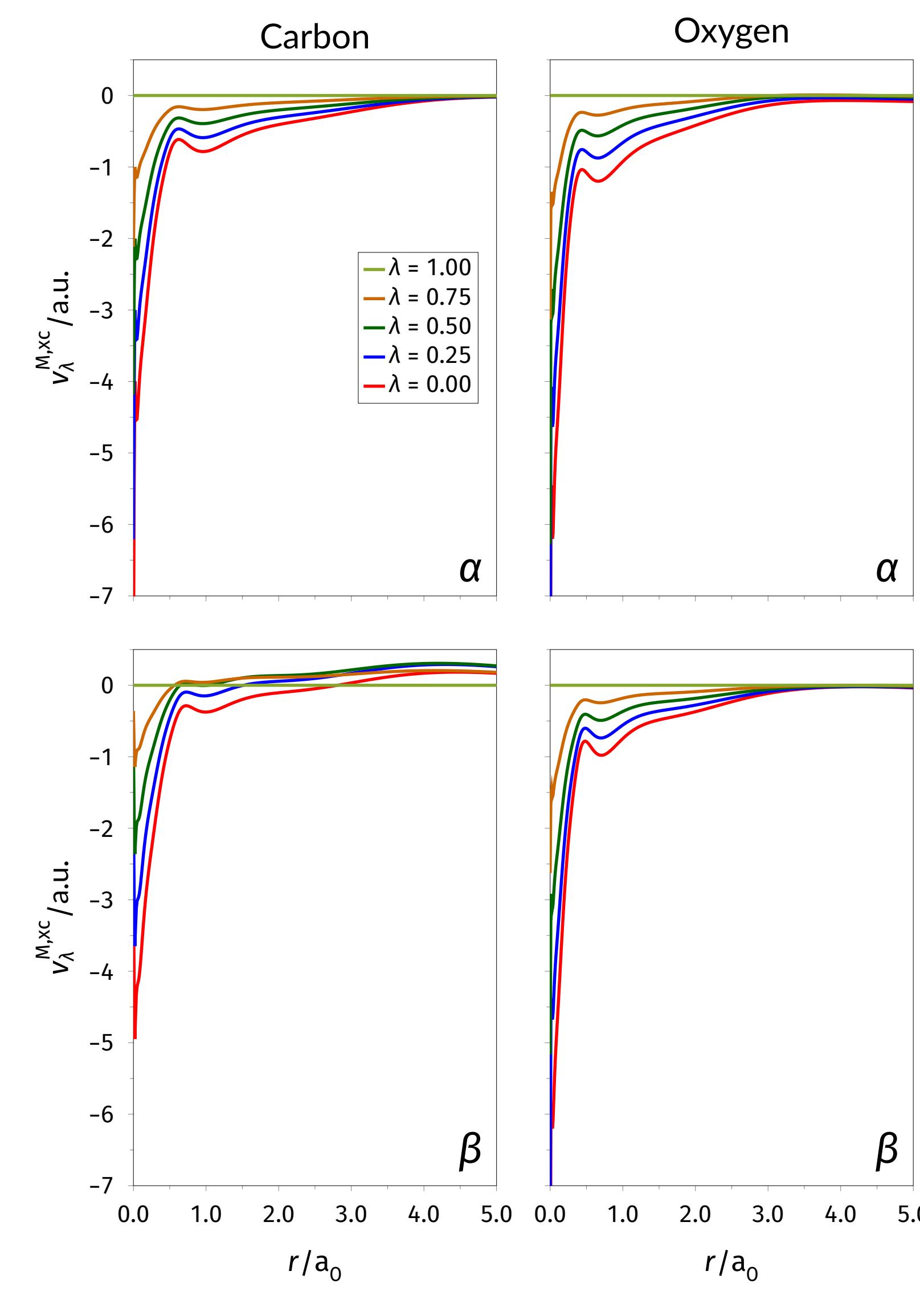
↔ There can exist λ values at which the M-optimal potential v_λ^M supports a ground density $\bar{\rho}_\lambda^M$ such that the Lieb-variational errors $\|\bar{\rho}_\lambda^M - \bar{\rho}_1^M\|_p$ can get arbitrarily large.

4. v -Representability in the Adiabatic Connection

(a) Pure-state density vs. ensemble density ACs.



(b) Exchange-correlation potentials in ensemble density ACs.



5. Discussion

Tackling the degeneracy challenges

- Density alignment** guarantees well-defined gradients for asymmetric densities.
- Constraining** the potential to be **totally symmetric** speeds up convergence by limiting \mathcal{X}^* to symmetry-sensitive subspaces.
- Totally symmetric ensemble densities** ensure v -representability by avoiding unphysical HOMO-LUMO inversions.

Results

- Smooth** ACs for open-shell degenerate atoms with **acceptable** Lieb-variational errors
- Exchange-correlation potentials with **qualitatively reasonable** features

References

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