

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

Bang C. Huynh<sup>1</sup>, Andrew M. Teale<sup>1</sup>

<sup>1</sup>School of Chemistry, University of Nottingham, United Kingdom



University of  
Nottingham  
UK | CHINA | MALAYSIA



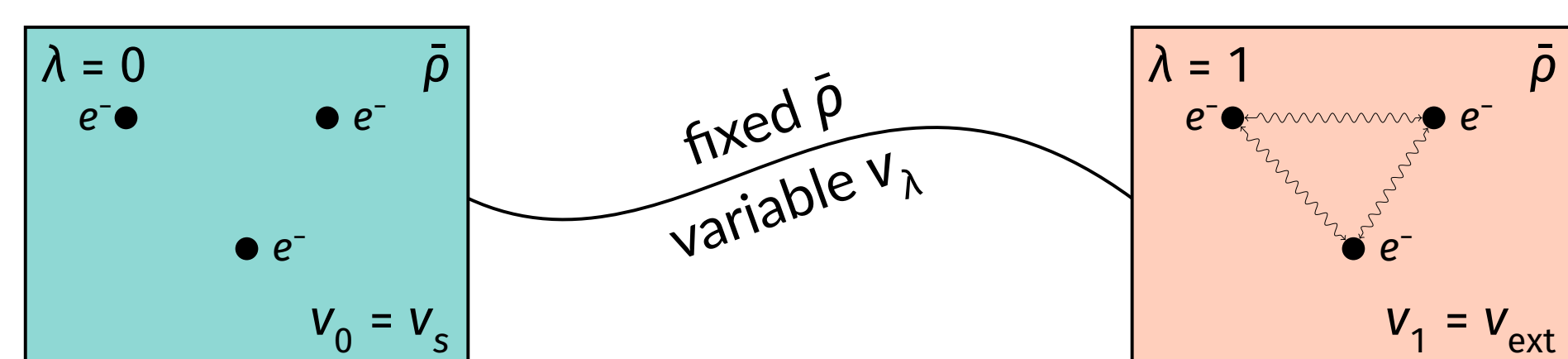
QUEST

## 1. The Exact Adiabatic Connection (AC)

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

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

one obtains the **M-optimal potential**  $v_\lambda^{\mathbf{M}}$  that

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

How well  $v_\lambda^{\mathbf{M}}$  approximates the true potential  $v_\lambda$  depends on the **quality of the method**  $\mathbf{M}$  and on **whether**  $v_\lambda$  **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**  $\bar{\psi}_\lambda^{\mathbf{M}}(v)$  with **energy**  $E_\lambda^{\mathbf{M}}(v)$  and **density**  $\bar{\rho}_\lambda^{\mathbf{M}}(\mathbf{r}; v)$ .

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

### Well-defined gradient?

The Lieb optimisation procedure to obtain the  $\mathbf{M}$ -optimal potential  $v_\lambda^{\mathbf{M}}$  requires the functional derivative

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

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

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

### Density alignment

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

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

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

### Symmetry of potential?

At all  $\lambda$ , the  $\mathbf{M}$ -optimal potential  $v_\lambda^{\mathbf{M}}$  determines the **symmetry group** of the Hamiltonian:

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

Is **equality** in the following condition

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

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

### Potential symmetry constraint

In the simplest Ansatz, at any  $\lambda \in [0, 1]$ , the constraint

$$\mathcal{G}_1(v_{\text{ext}}) = \mathcal{G}_\lambda(v)$$

is imposed for **all trial potentials**  $v$  to assist convergence in the Lieb optimisation. The necessity of this constraint can then be systematically investigated by relaxing to subgroups of  $\mathcal{G}_1(v_{\text{ext}})$ .

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

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

### Totally symmetric ensemble density

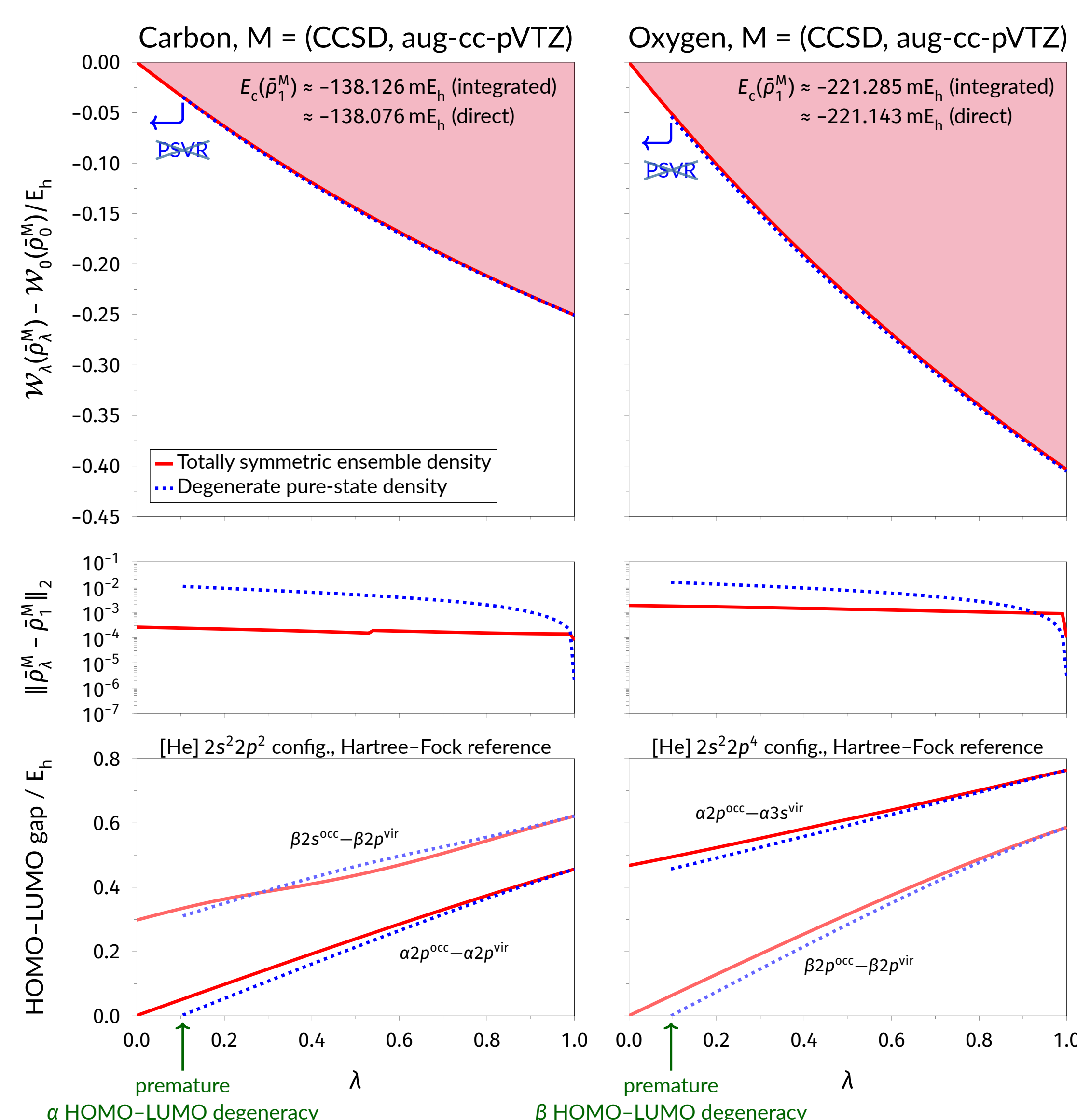
Consider instead the ensemble density

$$\frac{1}{|\mathcal{G}_1|} \sum_{i=1}^{|\mathcal{G}_1|} \hat{g}_i \bar{\rho}_1^{\mathbf{M}}(\mathbf{r}), \quad g_i \in \mathcal{G}_1(v_{\text{ext}}) \equiv \mathcal{G}_1$$

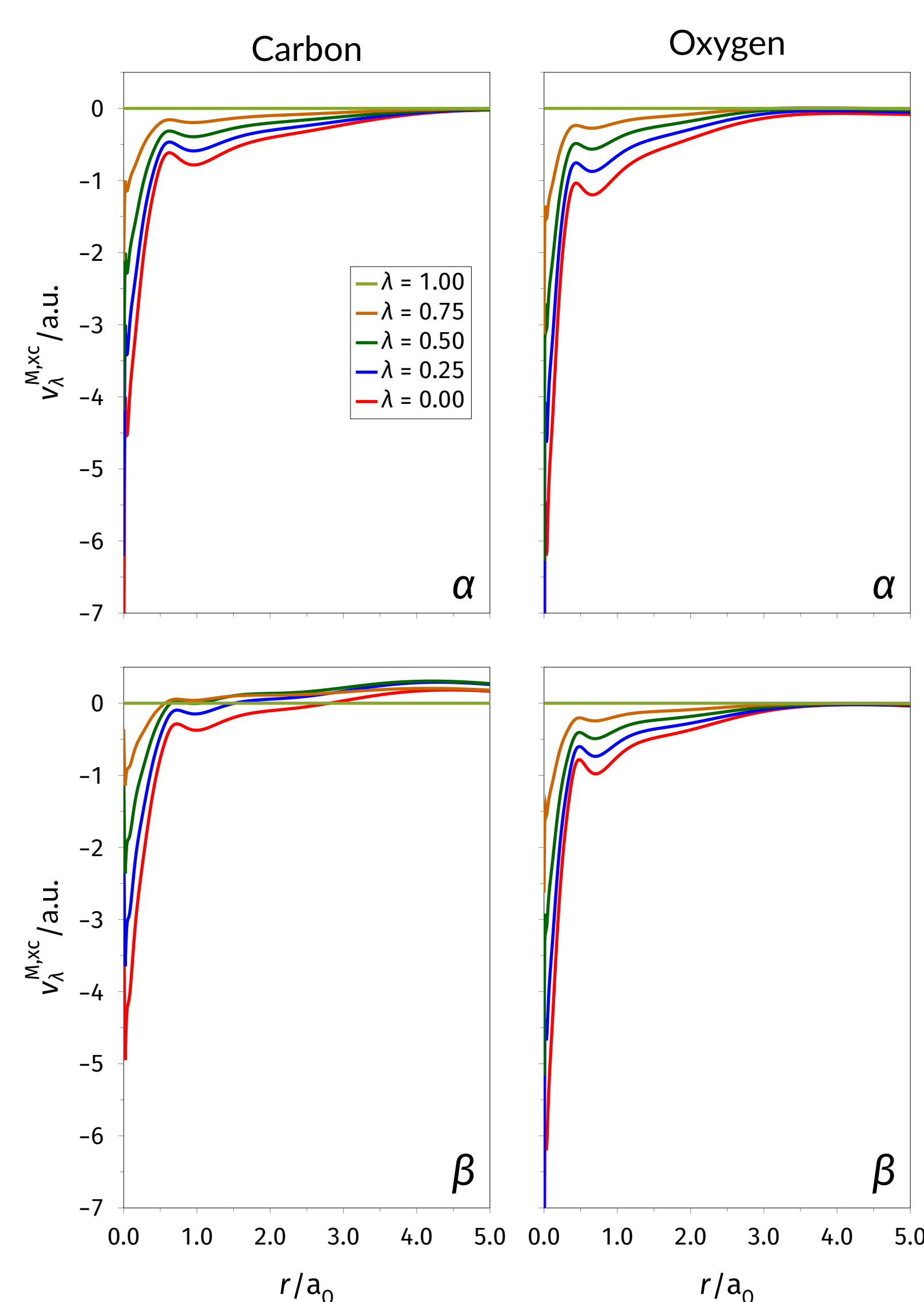
as the reference density, which is invariant under all of  $\mathcal{G}_1(v_{\text{ext}})$  and **not skewed** towards any particular degenerate component.

## 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-sensible 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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