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

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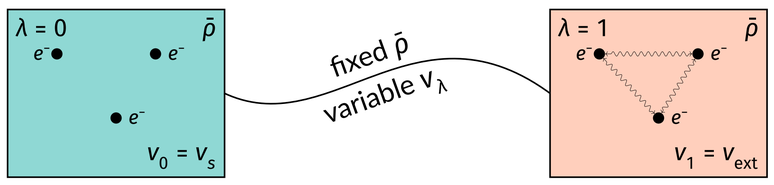
1. The Exact Adiabatic Connection (AC)

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

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

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 $\mathcal{W}_\lambda(\bar{\rho}) = \mathrm{tr}\,\hat{\gamma}_\lambda(\bar{\rho})\hat{W}$, 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** $E_\lambda^{\mathrm{M}}(v)$ of $\hat{\mathcal{H}}_\lambda(v)$ and the M-reference density $\bar{\rho}_1^{\mathrm{M}} \in \mathcal{X}$, by finding the **Lieb universal functional**

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

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

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

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** $\bar{\Psi}_\lambda^{\mathrm{M}}(v)$ with **energy** $E_\lambda^{\mathrm{M}}(v)$ and **density** $\bar{\rho}_\lambda^{\mathrm{M}}(\boldsymbol{r};v)$.

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

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

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

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

Density alignment

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

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

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

Symmetry of potential?

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

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

Is **equality** in the following condition

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

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

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

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 $\mathcal{G}_1(v_{\mathrm{ext}})$.

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 $\bar{\rho}_1^{\mathrm{M}}$ as the reference density: there is no guarantee that it is **pure-state v-representable** $\forall\lambda \in [0,1]$.
$\Leftrightarrow$ There can exist λ values at which the M-optimal potential v_λ^{M} supports a ground density $\bar{\rho}_\lambda^{\mathrm{M}}$ such that the Lieb-variational errors $\|\bar{\rho}_\lambda^{\mathrm{M}} - \bar{\rho}_1^{\mathrm{M}}\|_p$ can get arbitrarily large.

Totally symmetric ensemble density

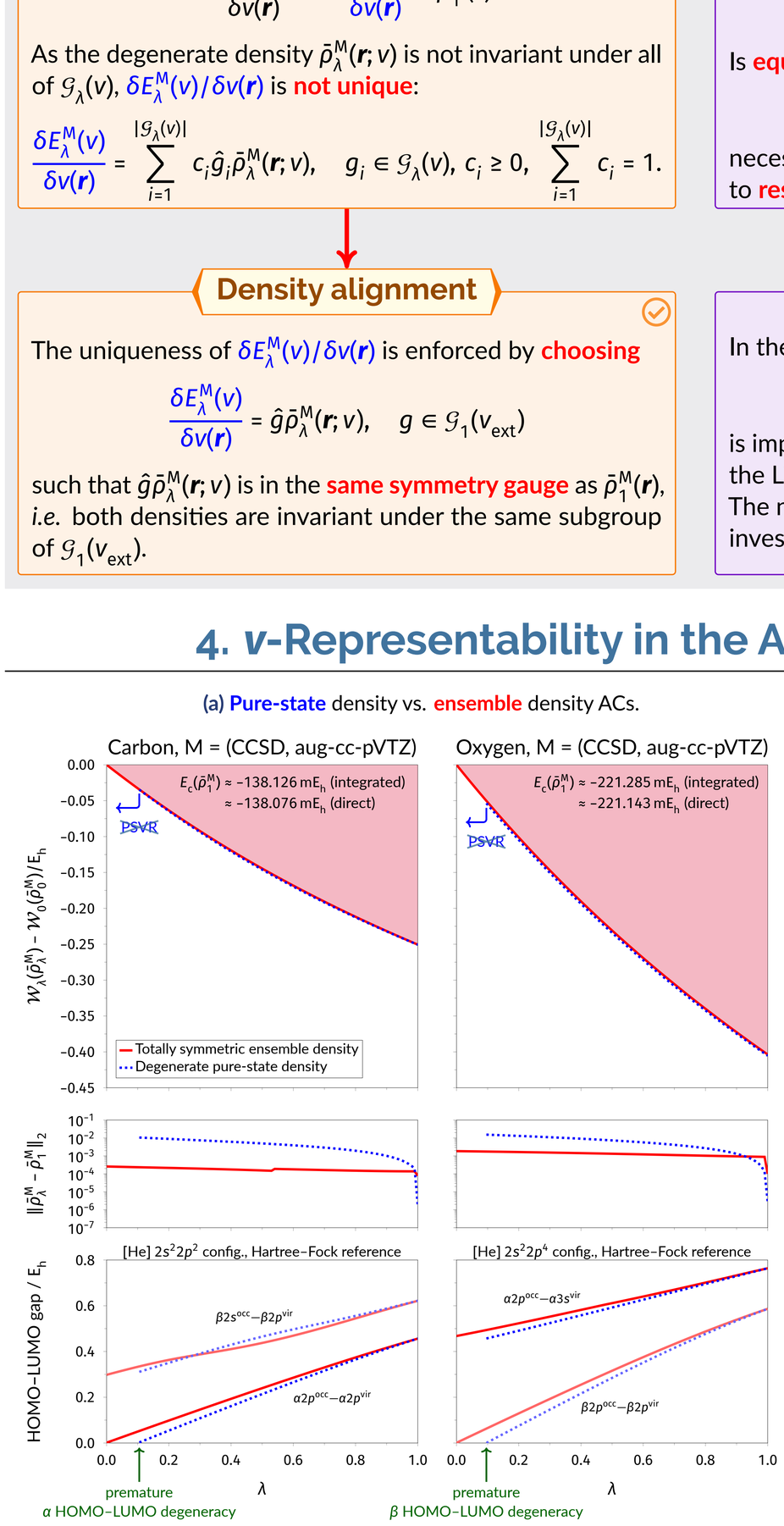
Consider instead the ensemble density

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

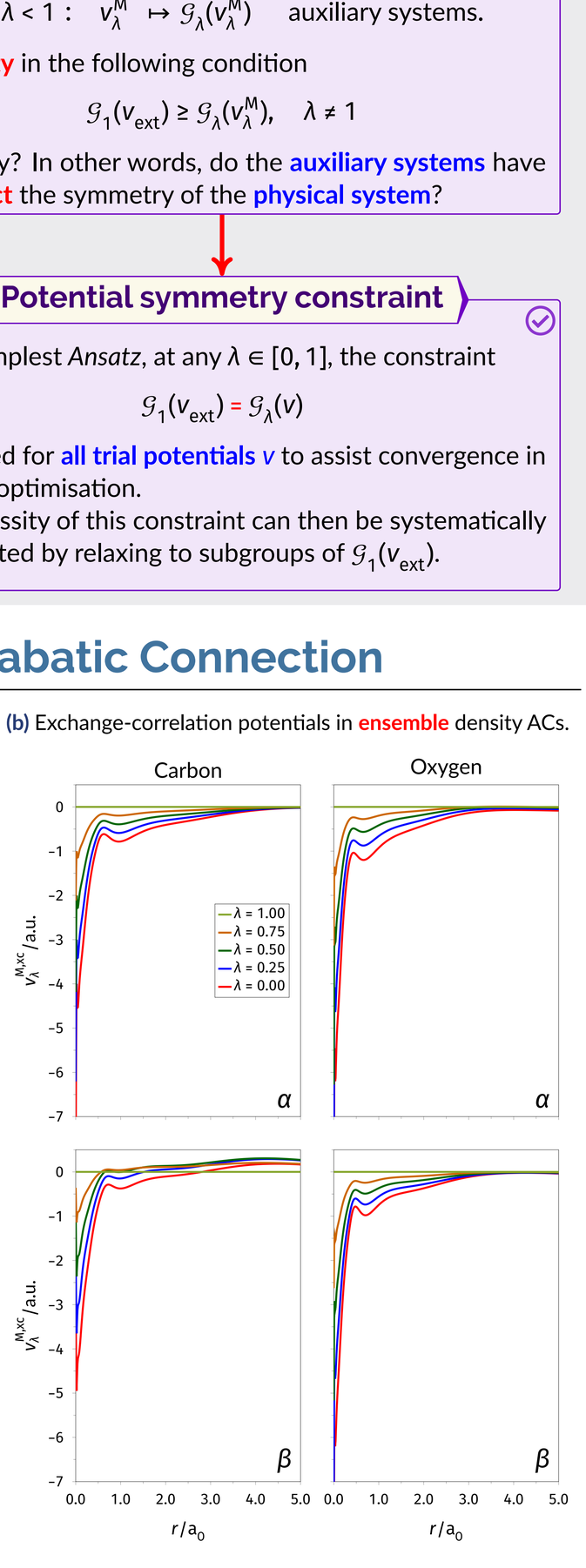
as the reference density, which is invariant under all of $\mathcal{G}_1(v_{\mathrm{ext}})$ and **not skewed** towards any particular degenerate component.

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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