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

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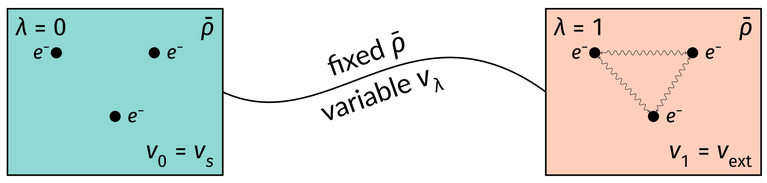
QUEST

1. The Exact Adiabatic Connection

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** is defined by $\mathcal{W}_\lambda(\bar{\rho}) = \mathrm{tr}\,\hat{\gamma}_\lambda(\bar{\rho})\hat{W}$, which we calculate 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 adiabatic connection, 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.

The higher the quality of the wavefunction method M:

- the better $\bar{\rho}_1^{\mathrm{M}}$ approximates the true reference density $\bar{\rho}$;
- the lower the Lieb-variational errors $\|\bar{\rho}_\lambda^{\mathrm{M}} - \bar{\rho}_1^{\mathrm{M}}\|_p$ where $1 \le p \le 3$; and
- the better v_λ^{M} approximates the true potential v_λ.

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** $\bar{\rho}_\lambda^{\mathrm{M}}(\boldsymbol{r};v)$.

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 $\bar{\rho}_\lambda^{\mathrm{M}}(\boldsymbol{r};v)$ is invariant only under a proper subgroup of $\mathcal{G}_\lambda(v)$, the functional derivative $\delta E_\lambda^{\mathrm{M}}(v)/\delta v(\boldsymbol{r})$ is **not unique**:

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

Symmetry of potential?

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

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

Is **equality** in the following condition

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

necessary for $v_\lambda^{\mathrm{M}} \in \mathcal{X}^*$? In other words, should the **auxiliary systems respect** the symmetry of the **physical system**?

Guarantee of *v*-representability?

The existence of the adiabatic connection $\mathcal{W}_\lambda(\rho)$ requires the **reference density** ρ to be ***v*-representable** $\forall\lambda \in [0,1]$. However, general v-representability conditions for $\rho \in \mathcal{X}$ are not well-established. In particular:

- Is $\bar{\rho}_1^{\mathrm{M}}$ **pure-state** v-representable $\forall\lambda \in [0,1]$?
- Is the ensemble density

$$\bar{\rho}_{1,\mathrm{en}}^{\mathrm{M}} = \frac{1}{|\mathcal{G}_1|}\sum_{i=1}^{|\mathcal{G}_1|} \hat{g}_i \bar{\rho}_1^{\mathrm{M}}$$

ensemble-state v-representable $\forall\lambda \in [0,1]$?

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

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