FACULTY
OF SCIENCES

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# MODELLING MOLECULAR BEHAVIOUR IN A STRONG MAGNETIC FIELD BY EXPLOITING SPIN-SYMMETRY BREAKING

Emiel Vanden Berghe

GHENT
UNIVERSITY

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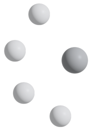
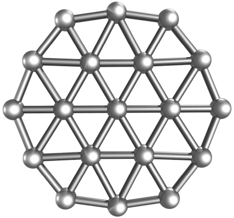
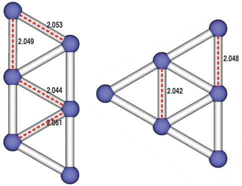


$H_{19}$



$He_6$

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- Spin-transitions to high-spin states associated with a **chemical regime-shift**:
  - Pauli exclusion **prohibits covalent bonding** between same spin electrons
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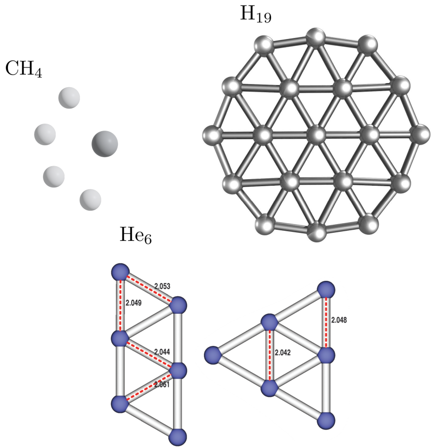
- Spin-transitions can **affect dissociation behaviour** even before the high-spin regime fully takes hold

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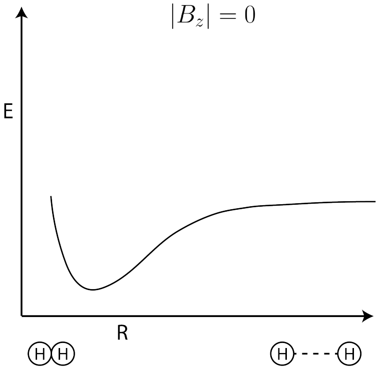


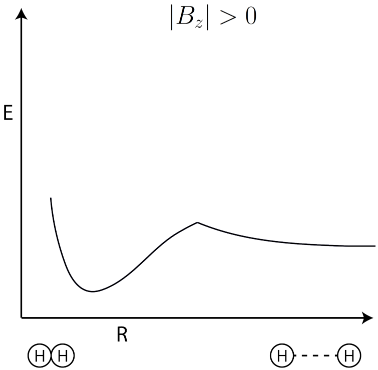

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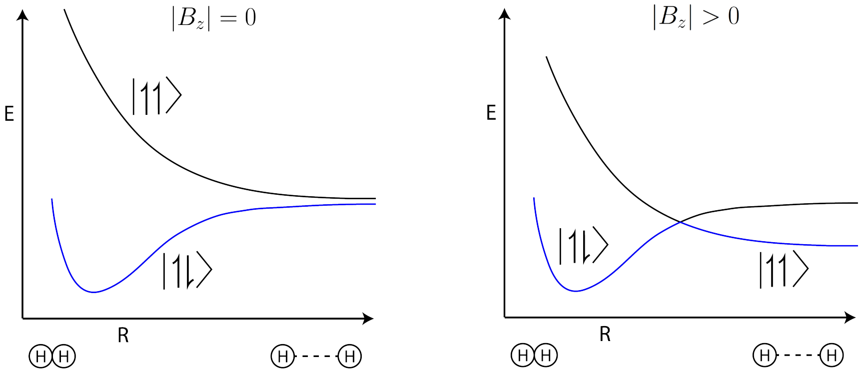

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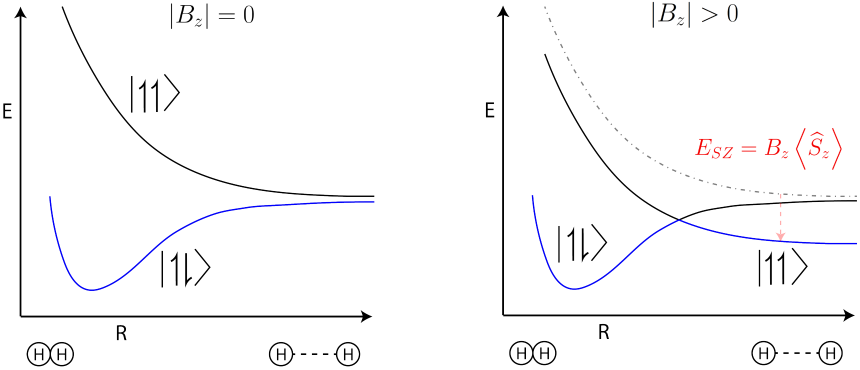

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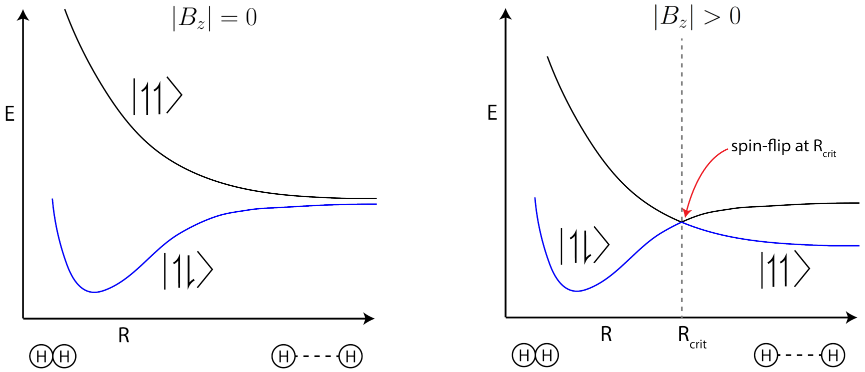


**Spin-transitions cause unexpected discontinuities in dissociation profiles**

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  - *Minimal-coupling*

$$\widehat{\mathcal{H}}(\boldsymbol{B}) = \widehat{\mathcal{H}}_0 + \underbrace{\boldsymbol{B}\cdot\widehat{\boldsymbol{S}}}_{\text{Spin-Zeeman}} + \underbrace{\frac{1}{2}\boldsymbol{B}\cdot\widehat{\boldsymbol{L}}_G}_{\text{Orbital-Zeeman}} + \underbrace{\frac{1}{8}(\boldsymbol{B}\times\boldsymbol{r}_G)^2}_{\text{Diamagnetic}} \tag{1}$$

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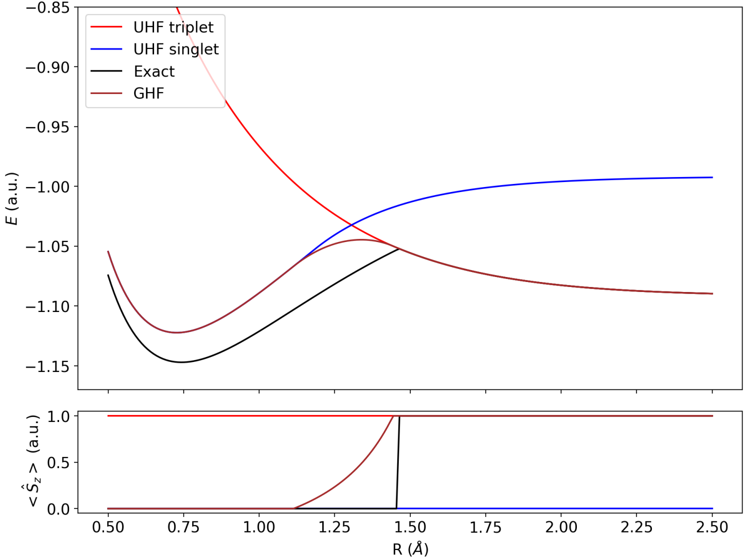

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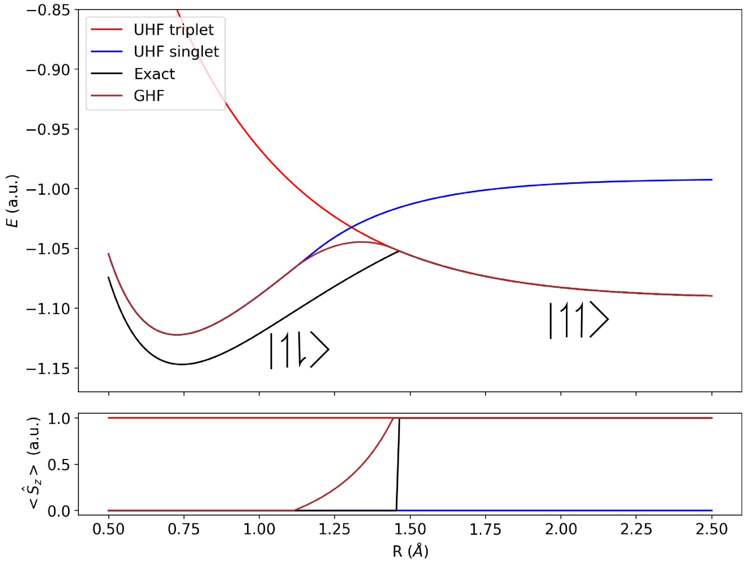

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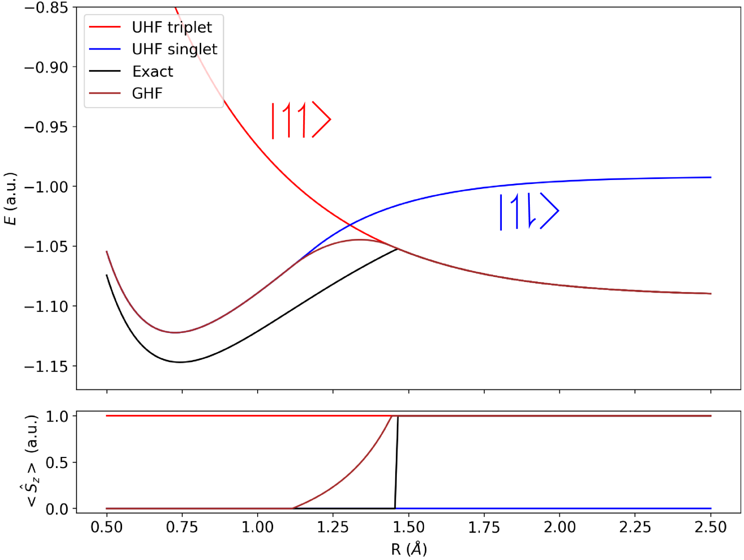

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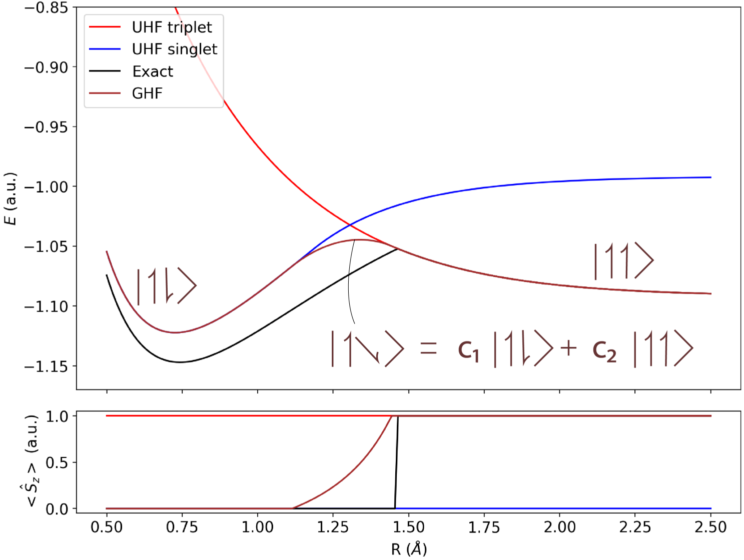
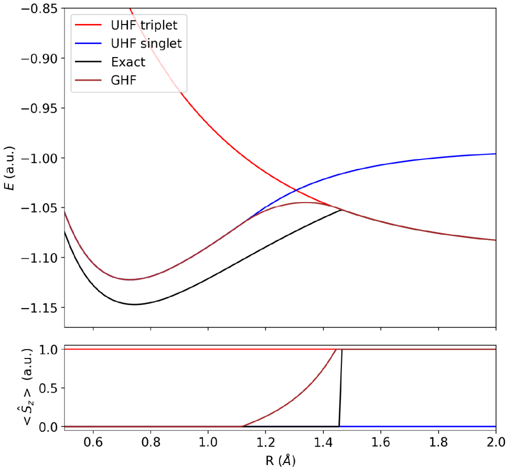


# Understanding spontaneous symmetry breaking: the symmetry-breaking potential



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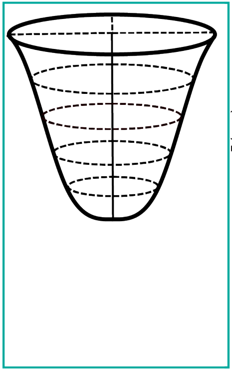

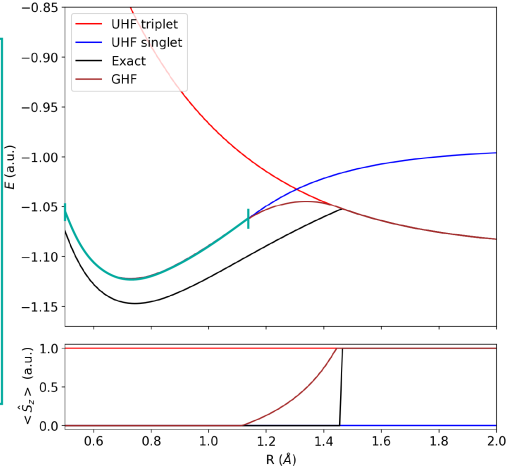

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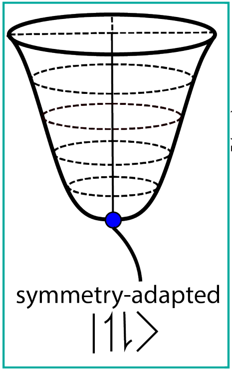


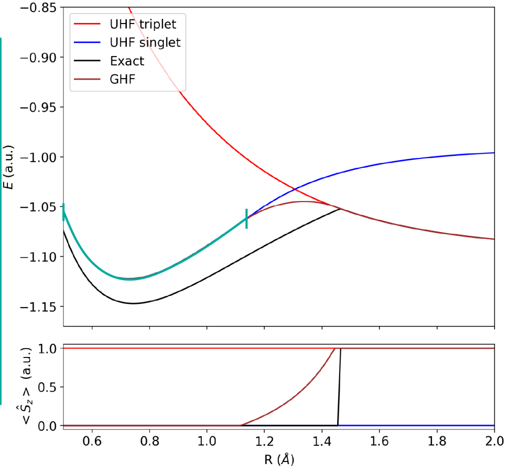

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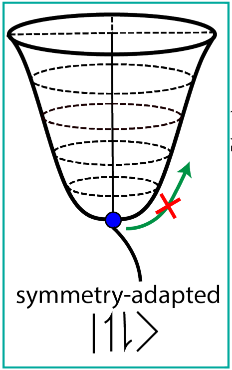


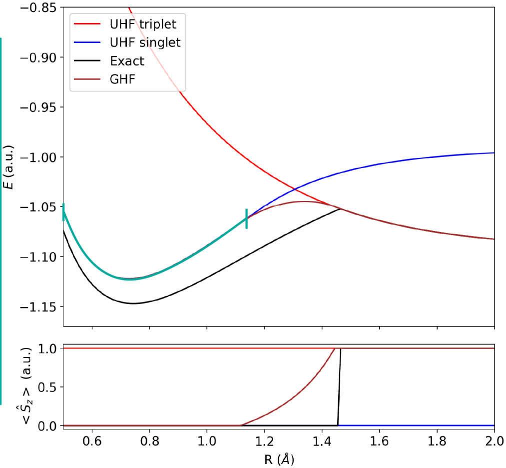

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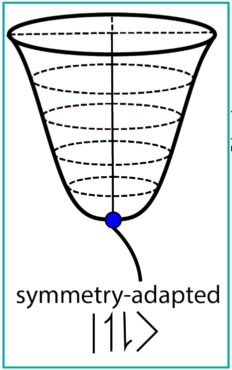


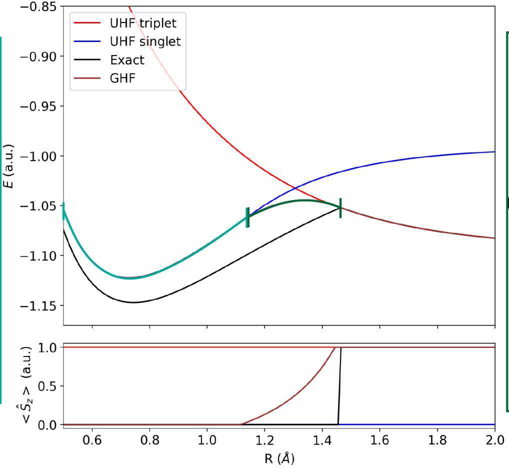


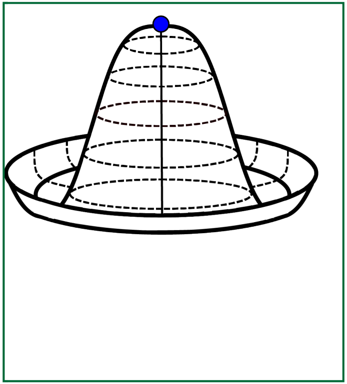

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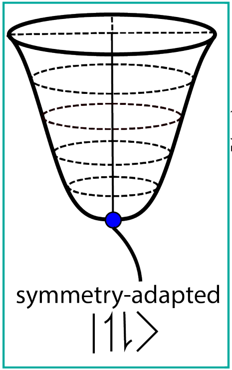


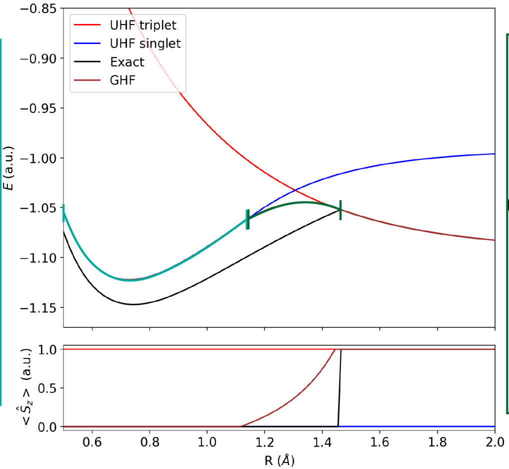


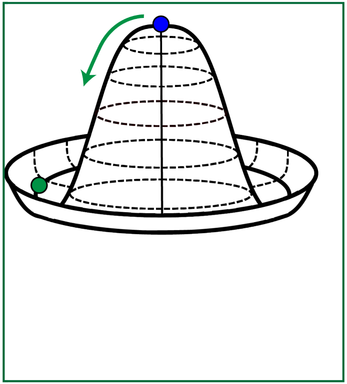

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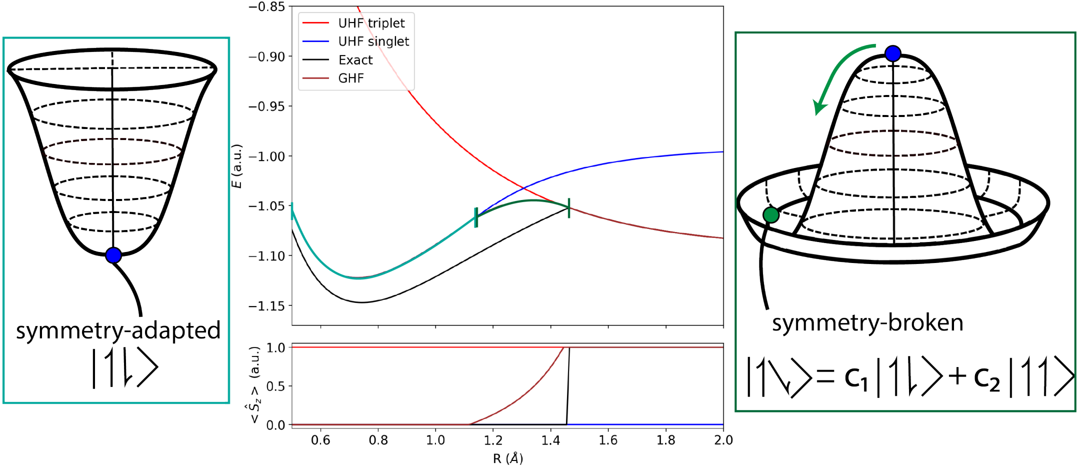

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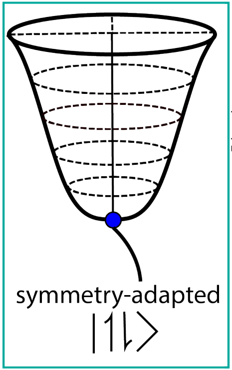


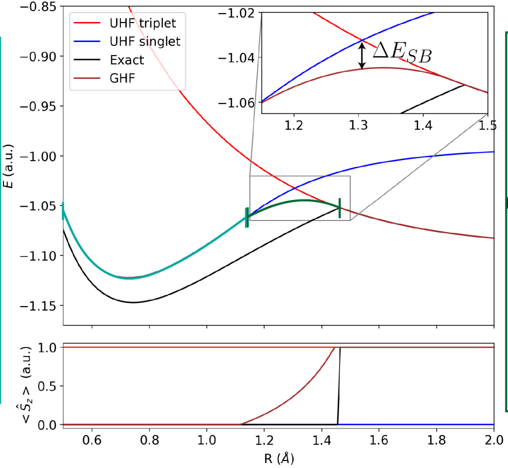


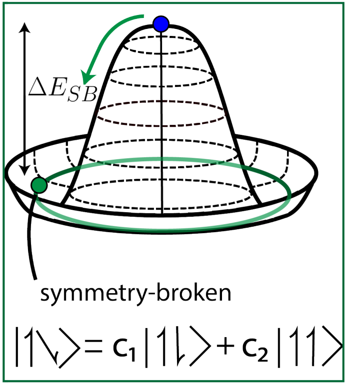

# ACCESSING THE GHF SYMMETRY-BREAKING POTENTIAL

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- The molecular **field-dependent Hamiltonian** (***B*** along $z$)

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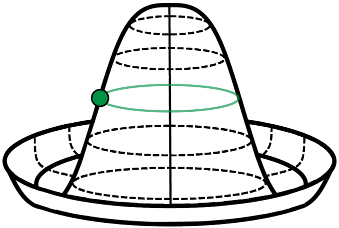

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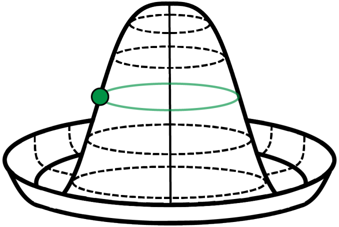
- We introduce the $\widehat{S}_z$-*level-shifted* Hamiltonian

$$\widehat{\mathcal{H}}_{\mathrm{LS}}^{S_z}(\boldsymbol{B}, \mu) = \widehat{\mathcal{H}}(\boldsymbol{B}) - \mu \widehat{S}_z, \tag{5}$$



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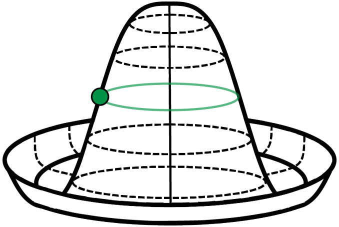

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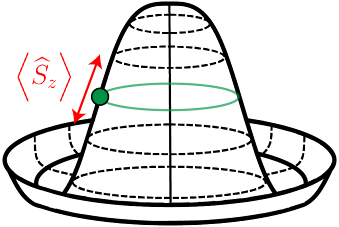
- Now we can tune $\langle \widehat{S}_z \rangle$ of the **LS-GHF** state $|\Phi_{\mathrm{LS}}^{S_z}(\mu)\rangle$.



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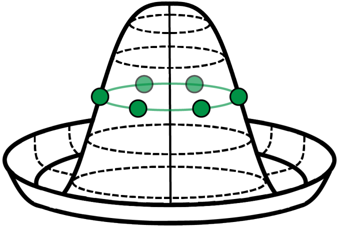
- From a given reference state $|\Phi\rangle$, we can **access** the corresponding **Goldstone manifold** through **spin-rotations**

$$\widehat{U}_{R,z}(\theta)\,|\Phi\rangle = \exp\left(i\theta\widehat{S}_z\right)|\Phi\rangle\,. \qquad (7)$$



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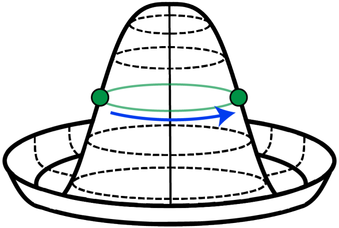
- We rotate to the other side of the Goldstone manifold

$$\widehat{U}_{R,z}(\theta = \pi)\,|\Phi\rangle = -i\widehat{\sigma}_z\,|\Phi\rangle\,. \tag{8}$$



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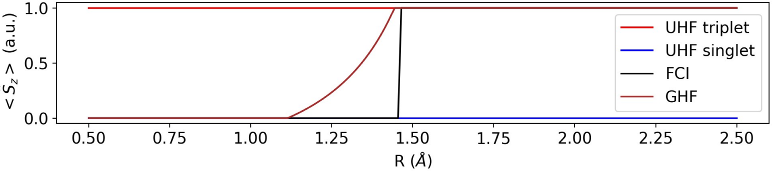

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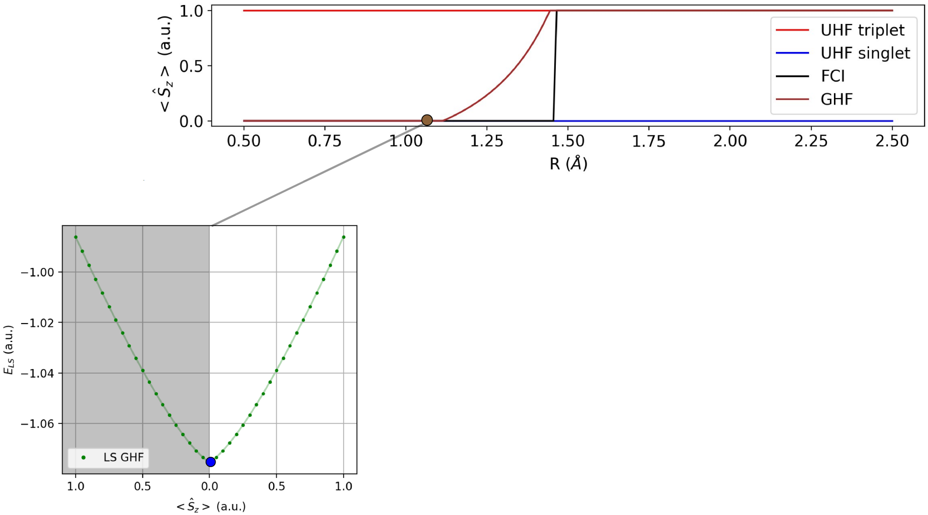

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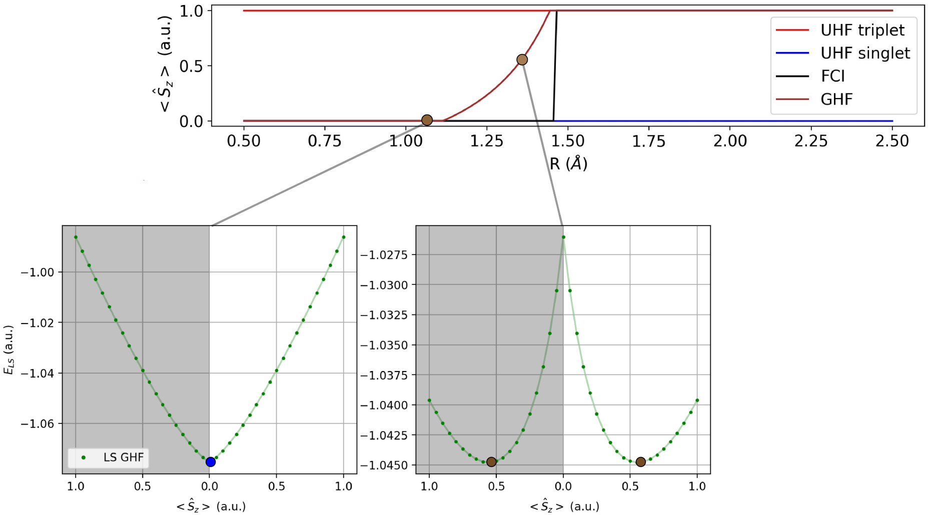

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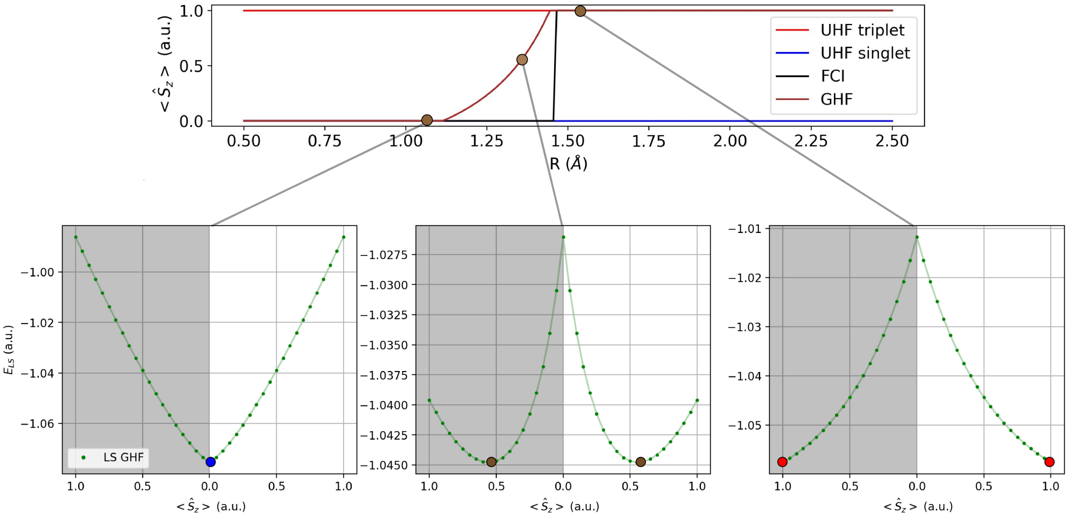

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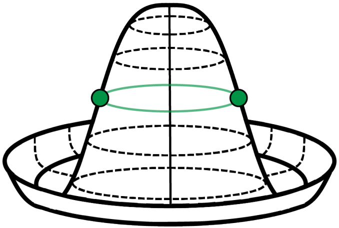

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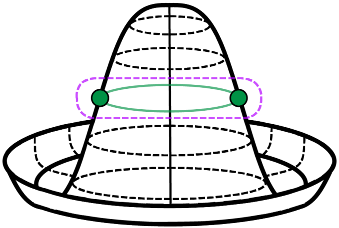
$$|\Phi_{\text{LS}}^{S_z}(\mu)\rangle \longrightarrow \{ |\Phi_{\text{LS}}^{S_z}(\mu)\rangle , -i\hat{\sigma}_z |\Phi_{\text{LS}}^{S_z}(\mu)\rangle \}. \tag{9}$$

- Diagonalising $\hat{\mathcal{H}}(\boldsymbol{B})$ in this basis gives a ***partial* symmetry-restored ansatz**

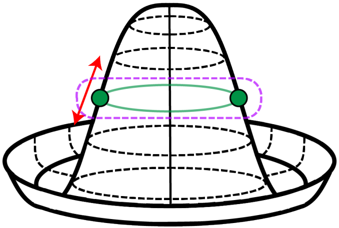
$$|\Psi_i^{S_z}(\mu)\rangle = c_{i,1} |\Phi_{\text{LS}}^{S_z}(\mu)\rangle + c_{i,2} \left(-i\hat{\sigma}_z |\Phi_{\text{LS}}^{S_z}(\mu)\rangle\right) . \tag{10}$$



# VARIATIONALLY TUNING THE UNDERLYING SYMMETRY-BREAKING: LS-VAP

- The LS-VAP ansatz energy is $\mu$-dependent,

$$E_{\Psi}(\boldsymbol{B}, \mu) = \left\langle \Psi_0^{S_z}(\mu) \middle| \widehat{\mathcal{H}}(\boldsymbol{B}) \middle| \Psi_0^{S_z}(\mu) \right\rangle . \quad (11)$$



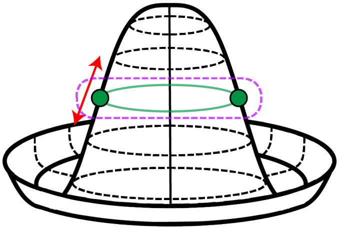
# Variationally tuning the underlying symmetry-breaking: LS-VAP

- The LS-VAP ansatz energy is $\mu$-dependent,

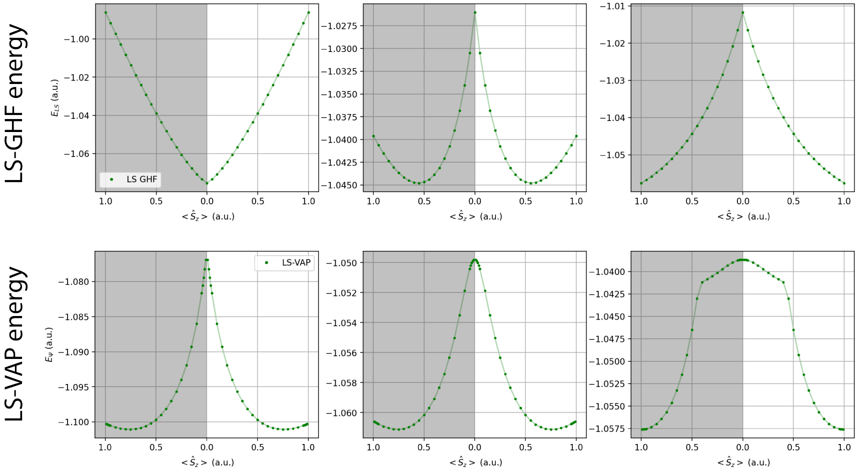
$$E_{\Psi}(\boldsymbol{B}, \mu) = \left\langle \Psi_0^{S_z}(\mu) \middle| \widehat{\mathcal{H}}(\boldsymbol{B}) \middle| \Psi_0^{S_z}(\mu) \right\rangle . \tag{11}$$

- We can tune the height of the sampled Goldstone manifold through variationally optimising the ansatz energy,

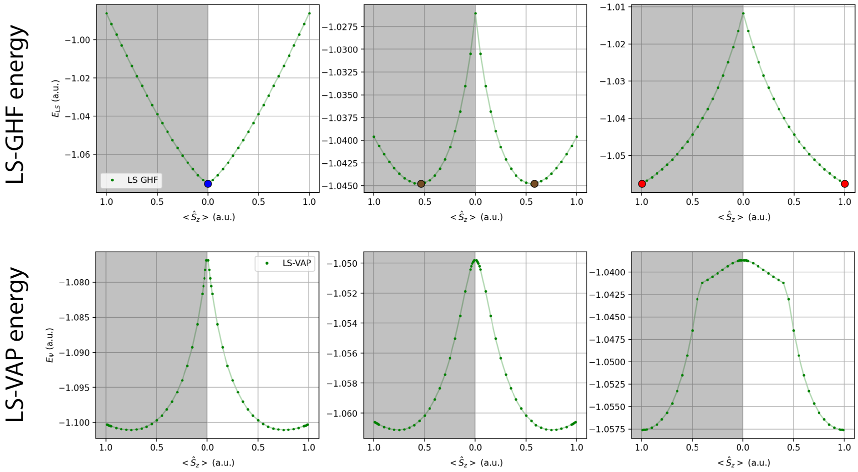
$$\left. \frac{\partial E_{\Psi}(\boldsymbol{B}, \mu)}{\partial \mu} \right|_{\mu^{\star}} = 0. \tag{12}$$



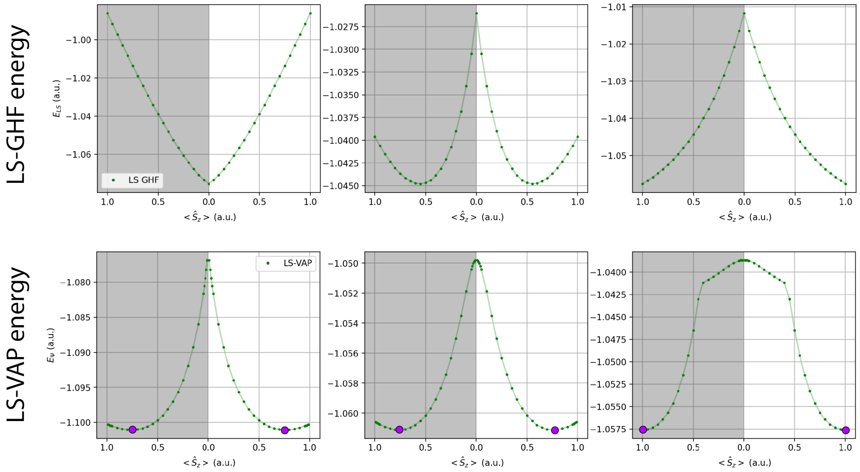
# Variationally tuning the underlying symmetry-breaking: LS-VAP



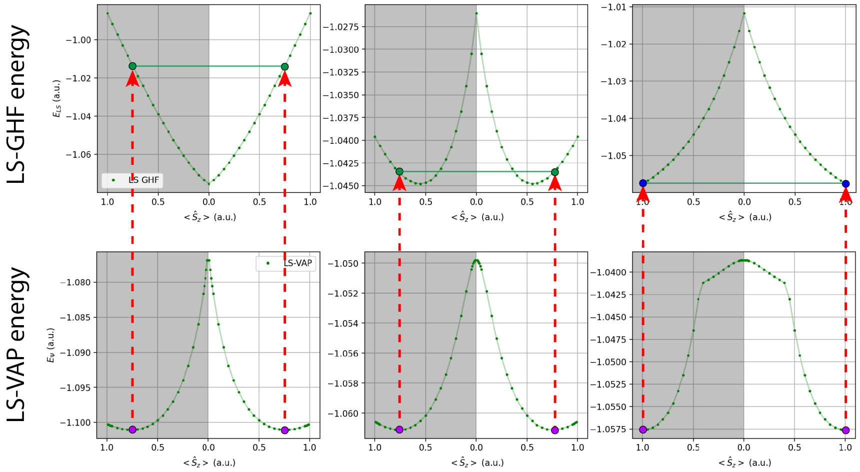
# Variationally tuning the underlying symmetry-breaking: LS-VAP



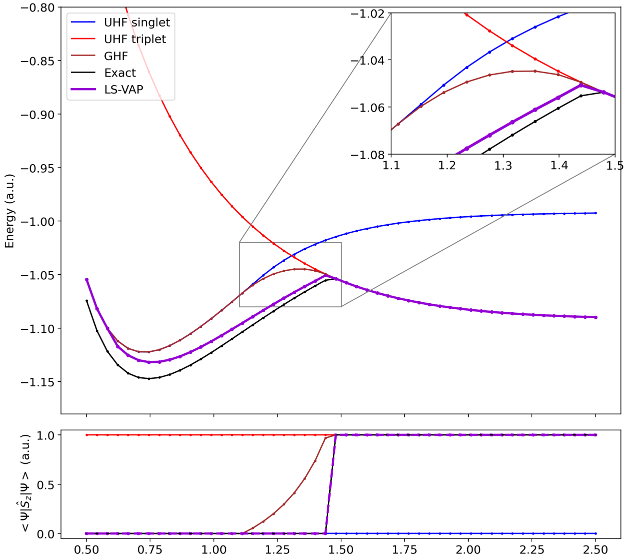
# Variationally tuning the underlying symmetry-breaking: LS-VAP



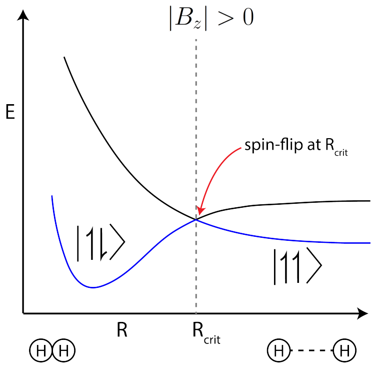
# Variationally tuning the underlying symmetry-breaking: LS-VAP

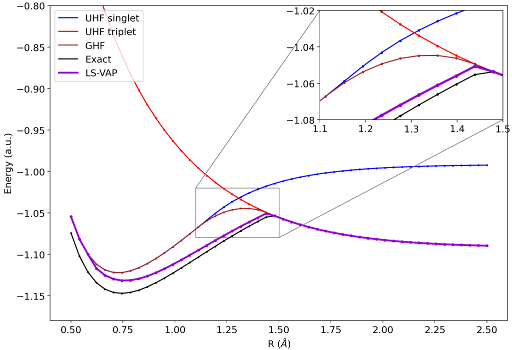


# LS-VAP PROVIDES AN ACCURATE SPIN-TRANSITION PREDICTION



# CONCLUSIONS




Spin-transitions cause unexpected **discontinuities throughout dissociation**

Symmetry-breaking can be **exploited** to gain **dynamic correlation** and **accurately describe spin-transitions**