

Quantum Computing for Quantum Chemistry

Module 1

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The lab introduced the electronic Hamiltonian for an N electron system with N_n fixed nuclei, written as $\hat{\mathcal{H}} = \hat{h} + \hat{g} + v_{nn}$, where \hat{h} is the one-electron term, \hat{g} the two-electron interaction, and v_{nn} the nucleus-nucleus repulsion. The coordinate representation was introduced first, then the Hamiltonian was expressed in an AO basis through the integrals $h_{\mu\nu} = \langle \mu | \hat{h}_1 | \nu \rangle_{\mathbf{r}}$ and $g_{\mu\mu'\nu\nu'} = (\mu\mu' | \nu\nu')$ used in practical calculations. For H_2 with bond length $R_{HH} = 1 \text{ \AA}$ in the STO-3G minimal basis, the core Hamiltonian integral matrix \mathbf{h} and the electron repulsion integral array \mathbf{g} were generated using PySCF. STO-3G is a minimal Gaussian basis set in which each basis function is formed by contracting three Gaussian primitives to approximate a Slater-type orbital. In a minimal basis, it assigns a single contracted function to each occupied atomic orbital of the isolated atom [1]. The output convention for \mathbf{g} was the chemists convention $g_{\mu\mu'\nu\nu'} = (\mu\mu' | \nu\nu')$.

Orientation dependence was then examined by placing the same H_2 bond length along different Cartesian directions, including rotated geometries. The computed \mathbf{h} and \mathbf{g} values were found to be unchanged up to small differences due to rounding. This supported the expectation that the integrals depend on internal geometry rather than absolute orientation.

Second quantisation was then introduced, treating electrons as excitations in a spin-orbital basis, which simplifies many-body problems. Instead of working with continuous coordinates, the system is described in a discrete set of spin orbitals using fermionic creation and annihilation operators. The occupation number picture makes the state space explicit, and the fermionic operator algebra automatically enforces antisymmetry. A `FermionicOperator` data structure was implemented to represent these creation and annihilation operators, ordered strings of operators, and sums of these strings with complex coefficients.

Correctness was checked in two ways. The additive and multiplicative examples provided in the lab book were reproduced, confirming that identical strings combined by coefficient addition and that multiplication produced the expected coefficient product with the operator strings concatenated in the correct order. For the integral generation, the rotation invariance test confirmed that the geometry, units, and integral calls were consistent.

References

- [1] David C. Young. *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*. Wiley-Interscience, New York, 2001.