# Molecular quantum dynamics: Exercise series 1

## Problem 1: Two-level quantum dynamics

In a quantum control experiment, a diatomic molecule was prepared in a superposition of its ground and first excited vibrational states, $\psi(t=0) = \frac{1}{2}\psi_0 + \frac{\sqrt{3}}{2}\psi_1$. Assume that the corresponding energies are $E_0$ and $E_1$.
(a) What is the wave function $\psi(t)$ at time $t$?
(b) What is the probability $P_g(t)$ that the molecule will be in the ground state at time $t$?
(c) What is the expectation value for the measurement of energy at time $t$?
(d) In general, will the expectation value for the measurement of the bond length ($q$) and therefore of the electric dipole $d$ depend on time? Recall that $d = Qq$ where $+Q$ and $-Q$ are the partial charges on the two atoms and assume, for simplicity, that $Q$ does not depend on $q$.

## Problem 2: Commutator

The **commutator** $[A, B] := AB - BA$ of two quantum-mechanical operators is an important concept in quantum mechanics. In this exercise, you will prove several identities that will be useful throughout the course. Below $A$, $B$, $C$ are operators, $\lambda$ a complex number. (Hats are not indicated on the operators, especially because it will save you time writing the solution, but if you prefer, add the hats to operators—consistently!)
(a) Prove that the commutator is skew-symmetric,

$$[B, A] = -[A, B],$$

bilinear,

$$[\lambda A, B] = \lambda [A, B],$$
$$[A, B + C] = [A, B] + [A, C],$$

and satisfies the **Jacobi identity**:

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0.$$

*Remark*: These three conditions express that the set of operators together with addition and commutator form a **Lie algebra**.
(b) Show that a commutator $[A, \cdot]$ with a fixed operator $A$ satisfies the **Leibniz rule**

$$[A, BC] = B [A, C] + [A, B] C.$$

The name comes from the analogy with the Leibniz rule for a derivative of a product of functions.
*Remark*: Mathematicians, therefore, call a linear mapping that satisfies the Leibniz rule a **derivation** on the associative algebra of operators with the usual multiplication of operators, $AB$. (In an **associative algebra**, the product $AB$ must be again bilinear, but the associative law

replaces the Jacobi identity. The product does not have to be symmetric or skew-symmetric.) A set that is both an associative algebra (with respect to $\cdot$ operation) and Lie algebra (with respect to $[\cdot, \cdot]$), and, in addition, satisfies the Leibniz rule, is called a **Poisson algebra**.
(c) One of the pillars of quantum mechanics is the expression for the commutator of the position and momentum operators:

$$[q, p] = i\hbar.$$

Using the Leibniz rule (b), show that if functions $f$ and $g$ can be expanded in convergent power series of their arguments, then

$$[p, f(q)] = -i\hbar \frac{df}{dq} \quad \text{and} \quad [q, g(p)] = i\hbar \frac{dg}{dp}.$$

Read Chapters 1 and 2 of Tannor.