PHASG473 - Electronic Structure Methods for Materials Modelling

Exercises

1.1 Introducing Molecular Dynamics

You are looking at an ion of mass m embedded in a particularly viscous liquid solvent. The above mentioned ion is sitting on top of an atomically flat surface. The interaction between the ion and the surface can be described by a harmonic potential U_h:

$$U_h = \frac{1}{2}kx^2 \tag{1}$$

where k is the stiffness of the "bond" between the ion and the surface and x is the bond length (we assume the bond extends along the normal with respect to the surface). Because of the viscous solvent, there is also an additional dissipation function U_s of the form:

$$U_s = \frac{1}{2}b\dot{x}^2 \tag{2}$$

- Write down the Newton's equation of motion for the ion using $\beta = \frac{b}{2m}$ and $\omega_0 = \sqrt{\frac{k}{m}}$ (hint: divide every term by $/m$ first). Note that the force due to the dissipation function can be obtained by taking the *velocity* gradient of Eq. 2.

- Solve the Newton's equation of motion for the ion (hint: perform the substitution $x = e^{i\gamma t}$ first), obtaining:

$$x = e^{-\beta t \pm i\sqrt{\omega_0^2 - \beta^2}\cdot t} \tag{3}$$

- Picking the positive solution only, using $\alpha = \sqrt{\omega_0^2 - \beta^2}$, applying Eulero's rule ($e^{ix} = \cos(x) + i\sin(x)$) and considering the real part of the solution only (we are allowed to do that, as the real and imaginary part separately satisfy the equation of motion) you should end up with:

$$x = e^{-\beta t} \cdot [A\cos(\alpha t) + B\sin(\alpha t)] \tag{4}$$

- Choosing $A = 1$ and $B = 0$, derive the expression for $\dot{x}$

- Perform the following linear transformations: ($u = x$ and $w = x + \dot{x}$). Now you have a parametric expression for the position x and the momentum (well, just the velocity here...) $\dot{x}$. Plot these guys for $\alpha = 10$ and $\beta = 1$ to obtain the phase space plot depicted in Fig. 1 - the same logarithmic spiral of the Nautilus.

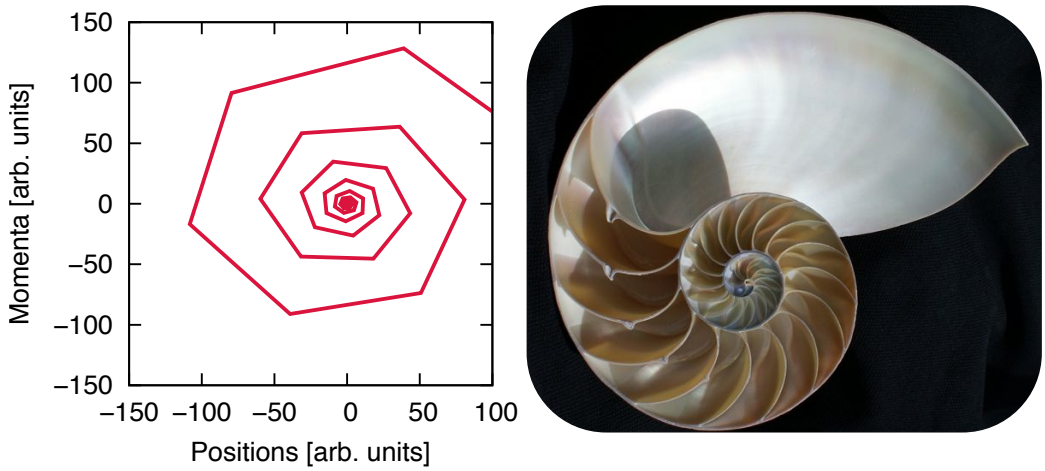

Figure 1: Phase space for the system introduced in Exercise 1.1 - a nicer counterpart on the right.

1.2 Ab initio Molecular Dynamics

Given a rather peculiar quantum system described by the following Hamiltonian:

$$\hat{H}_{fake} = \sum_{i=1}^{N_{el}} \sum_{j=1}^{N_{nu}} \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} + \log[(R_j^x)^2] \tag{5}$$

where $\mathbf{r}_i$, $\mathbf{R}_j$ and R_j^x are the position vector for the i-th electron, the position vector for the j-th nucleus and the component along the x direction of the latter respectively, demonstrate that the x component of the force acting on a particular nucleus λ can be written as:

$$F_{R_{\lambda^x}} = -\langle \psi_{fake} | \sum_{i=1}^{N_{el}} \frac{r_i^x - R_\lambda^x}{|\mathbf{r}_i - \mathbf{R}_\lambda|^3} + \frac{2}{R_{\lambda^x}} | \psi_{fake} \rangle \tag{6}$$

where ψ_{fake} are eigenfunctions of $\hat{H}_{fake}$ (hint: use the Hellmann-Feynamn theorem).

1.3 Ensembles Medley

Derive the partition function Γ for the isoenthalpic-isobaric ensemble:

$$\Gamma(N, \beta p, H) = \int_0^\infty dV \int dx \; \delta(\mathcal{H}(x) + PV - H) \tag{7}$$

performing the (inverse! Mind the minus sign...) Laplace transform $\beta \to H$ from the isothermal-isobaric ensemble partition function $\Delta(N, \beta p, \beta)$ (hint: the fact that you end up with a Dirac delta function suggests you'll have to backtrack till the partition function of the NVE ensemble).