Mathematics 32: Orientational kinetic energy

A description for orientational motion is developed, including a mean-field approximation for separating the longitudinal from the azimuthal motion. The single-particle kinetic energy in spherical polar coordinates is:

$$H = \frac{\hat{\mathbf{p}}^2}{2m} \mapsto -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\nabla^2_\Omega\right]$$

where the angular contribution is:

$$\nabla^2_\Omega = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

and in the more 'natural' coordinate, $u = \cos\theta$:

$$\nabla^2_\Omega = \frac{\partial}{\partial u}(1-u^2)\frac{\partial}{\partial u} + \frac{1}{1-u^2}\frac{\partial^2}{\partial\phi^2}$$

The physical problem in mind is a molecule in a hole: The centre of mass of the molecule describes the position of the molecule in the hole, but there is also the *orientation* of the molecule which provides an independent angular motion. The quantisation of the position of the molecule would be controlled by the size of the hole and a tight-fitting molecule would have a high energy scale for motional excitations. The orientational motion of the molecule involves the moment of inertia of the molecule and is moderated by the irregularities in the mismatch between the shapes of the molecule and hole.

After rescaling, the orientational problem becomes:

$$H = -\frac{\partial}{\partial u}(1-u^2)\frac{\partial}{\partial u} - \frac{1}{1-u^2}\frac{\partial^2}{\partial\phi^2} + V(u,\phi)$$

where $V(u,\phi)$ is the orientational potential. An estimate for this can be obtained from an expansion:

$$V(\mathbf{R}) = V(\mathbf{0}) + \mathbf{R}.\nabla V(\mathbf{0}) + \frac{1}{2}\left[\mathbf{R}.\nabla\right]^2 V(\mathbf{0}) + \frac{1}{6}\left[\mathbf{R}.\nabla\right]^3 V(\mathbf{0}) + ...$$

where:

$$\mathbf{R} = (X,Y,Z) \equiv R\left[(1-u^2)^{\frac{1}{2}}\cos\phi, (1-u^2)^{\frac{1}{2}}\sin\phi, u\right]$$

and we can employ $R \mapsto 0$ combined with point-group symmetry to provide an orientational potential.

The general solution to this problem involves the two dimensions of the two angles, but it is possible to provide a variational mean-field solution where the two angles are separated. The basic idea is to *force* a solution of the form:

$$\psi(u,\phi) = U(u)\Phi(\phi)$$

and then minimise the energy subject to this restriction. We will analyse the simplified Hamiltonian:

$$H = -\frac{\partial}{\partial u}(1-u^2)\frac{\partial}{\partial u} - \frac{1}{1-u^2}\frac{\partial^2}{\partial\phi^2} + V_0(u) + V_1(u)\cos 2m\phi$$

and then taking averages over each of the two variables we find:

$$H_u \equiv -\frac{\partial}{\partial u}(1-u^2)\frac{\partial}{\partial u} + \frac{\alpha^2}{1-u^2} + V_0(u) + \beta V_1(u)$$

where:

$$\alpha^2 \int_0^{2\pi} \frac{d\phi}{2\pi} \left[\Phi(\phi)\right]^2 = \int_0^{2\pi} \frac{d\phi}{2\pi} \left[\frac{d\Phi}{d\phi}\right]^2 (\phi)$$

$$\beta^2 \int_0^{2\pi} \frac{d\phi}{2\pi} \left[\Phi(\phi)\right]^2 = \int_0^{2\pi} \frac{d\phi}{2\pi} \left[\Phi(\phi)\right]^2 \cos 2m\phi$$

and:

$$H_\phi = -\frac{\partial^2}{\partial\phi^2} + \gamma\cos 2m\phi$$

where:

$$\gamma \int_{-1}^{1} \frac{du}{2} \left[U(u)\right]^2 (1-u^2)^{-1} = \int_{-1}^{1} \frac{du}{2} \left[U(u)\right]^2 V_1(u)$$

The mean-field theory is obtained by solving these equations for the wavefunctions, $U(u)$ and $\Phi(\phi)$, self-consistently with the parameters; α, β and γ.

Given a value for γ, the equation for ϕ can be solved and then a prediction for α^2 and β can be provided. Note that the associated eigenvalue of the ϕ equation satisfies:

$$E_\phi = \alpha^2 + \beta\gamma$$

which can be used to provide one of α^2 or β. These values then provide an equation for u which can be solved to provide an estimate for the energy and then a new value of γ can be predicted. The cycle is then closed and can be iterated to convergence.

The boundary conditions on the ϕ equation are straightforward, but the u equation is *singular* and requires some analysis. The wavefunction takes the form:

$$U(u) = \left(1-u^2\right)^{\frac{\alpha}{2}} \tilde{U}(u)$$

close to $u \mapsto \pm 1$ with the associated Hamiltonian:

$$\tilde{H}_u = -(1-u^2)\frac{\partial^2}{\partial u^2} + 2(1+\alpha)u\frac{\partial}{\partial u} + V_0(u) + \beta V_1(u) + \alpha(\alpha+1)$$

combined with the restriction:

$$(\pm 1)2(1+\alpha)\frac{\partial\tilde{U}}{\partial u}(\pm 1) + \left[V_0(\pm 1) + \beta V_1(\pm 1) + \alpha(\alpha+1) - \epsilon\right]\tilde{U}(\pm 1) = 0$$

which is required to keep the wavefunction finite.

The final numerical complication is that the eventual integral:

$$\int_{-1}^{1} \frac{du}{2} \left(1 - u^2\right)^{\alpha - 1} \left[\tilde{U}(u)\right]^2$$

involves a *divergence* when $\alpha < 1$. The integral can be smoothed by an application of integration by parts:

$$\int_{-1}^{1} \frac{du}{2} \alpha \left(1 - u^2\right)^{\alpha - 1} \left[\tilde{U}(u)\right]^2 = \left[\left(1 - \left(1 - u^2\right)^{\alpha}\right) \frac{\tilde{U}(u)^2}{4u}\right]_{-1}^{1}$$

$$+ \int_{-1}^{1} \frac{du}{2} \left[\left(1 - u^2\right)^{\alpha} - 1\right] \frac{\partial}{\partial u} \left[\frac{\hat{U}(u)^2}{2u}\right]$$

and consequently:

$$\int_{-1}^{1} \frac{du}{2} \alpha \left(1 - u^2\right)^{\alpha - 1} \left[\tilde{U}(u)\right]^2 = \frac{\tilde{U}(1)^2 + \tilde{U}(-1)^2}{4}$$

$$+ \int_{-1}^{1} \frac{du}{2} \left[\left(1 - u^2\right)^{\alpha} - 1\right] \left(\frac{1}{u} \tilde{U}(u) \frac{d\tilde{U}}{du}(u) - \frac{1}{2u^2} \tilde{U}(u)^2\right)$$