Single Double Well in DVR

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Consider a quantum mechanical particle trapped inside a double-well potential. The system Hamiltonian is given by

$$\mathbf{H}_{\mathrm{DW}} = \frac{\mathbf{p}^2}{2\mathcal{M}} + \frac{\mathcal{M}^2\omega_0^4}{64\Delta U}\mathbf{q}^4 - \frac{\mathcal{M}\omega_0^2}{4}\mathbf{q}^2 - \mathbf{q}\varepsilon, \tag{1}$$

where $\mathbf{q}$ and $\mathbf{p}$ are the position and respectively the momentum operators of the particle, $\mathcal{M}$ is the mass of the particle, ω_0 is the classical oscillation frequency around the well minima, ΔU is the barrier height and ε is the bias factor of the potential. For simplicity, we first introduce dimensionless quantities according to

$$\tilde{t} = \omega_0 t, \qquad \tilde{\mathbf{q}} = \sqrt{\frac{\mathcal{M}\omega_0}{\hbar}}\mathbf{q}, \qquad \tilde{\mathbf{p}} = \sqrt{\frac{1}{\mathcal{M}\hbar\omega_0}}\mathbf{p}, \tag{2}$$

$$E_{\mathrm{B}} = \frac{\Delta U}{\omega_0}, \qquad \tilde{\varepsilon} = \frac{1}{\hbar\omega_0}\sqrt{\frac{\hbar}{\mathcal{M}\omega_0}}\varepsilon, \qquad \tilde{\mathbf{H}}_{\mathrm{DW}} = \frac{1}{\hbar\omega_0}\mathbf{H}_{\mathrm{DW}}. \tag{3}$$

Inserting the tilded expressions and consequently omitting the tildes the dimensionless Hamiltonian, in units of $\hbar\omega_0$, reads

$$\mathbf{H}_{\mathrm{DW}} = \frac{1}{2}\mathbf{p}^2 + \frac{1}{64E_{\mathrm{B}}}\mathbf{q}^4 - \frac{1}{4}\mathbf{q}^2 - \mathbf{q}\varepsilon. \tag{4}$$

Exploiting the similarity of (1) with the Hamiltonian of a simple harmonic oscillator, it is a good starting point to rewrite $\mathbf{H}_{\mathrm{DW}}$ in the basis of the energy eigenstates of the SHO. Denoting by $\{|\psi_i\rangle\}_{i\in I}$, $I = \{0, 1, 2, ...\}$ the set of energy eigenstates of the SHO and using the known action of $\mathbf{q}$ and $\mathbf{p}$ on these states, it is straightfoward to calculate that

$$\begin{aligned}
\langle\psi_m|\,\mathbf{p}^2\,|\psi_n\rangle &= \frac{1}{2}\left[(2n+1)\delta_{m,n} + \sqrt{n(n-1)}\delta_{m,n-2} - \sqrt{(n+2)(n+1)}\delta_{m,n+2}\right],\\
\langle\psi_m|\,\mathbf{q}^4\,|\psi_n\rangle &= \frac{1}{4}\Big[\sqrt{n(n-1)(n-2)(n-3)}\delta_{m,n-4} + (4n-2)\sqrt{n(n-1)}\delta_{m,n-2}\\
&\quad + (6n^2+6n+3)\delta_{m,n} + (4n+6)\sqrt{(n+2)(n+1)}\delta_{m,n+2}\\
&\quad + \sqrt{(n+4)(n+3)(n+2)(n+1)}\delta_{m,n+4}\Big],\\
\langle\psi_m|\,\mathbf{q}^2\,|\psi_n\rangle &= \frac{1}{2}\Big[(2n+1)\delta_{m,n} + \sqrt{n(n-1)}\delta_{m,n-2} + \sqrt{(n+2)(n+1)}\delta_{m,n+2}\Big],\\
\langle\psi_m|\,\mathbf{q}\,|\psi_n\rangle &= \frac{1}{\sqrt{2}}\Big[\sqrt{n}\delta_{m,n-1} + \sqrt{n+1}\delta_{m,n+1}\Big].
\end{aligned} \tag{5}$$

From these formulars one can easily compute the matrix elements of the Hamiltonian in the SHO basis, $H_{mn}^{\mathrm{SHO}} = \langle\psi_m|\,\mathbf{H}_{\mathrm{DW}}\,|\psi_n\rangle$. Since this matrix is in principle infinite-dimensional, we have to truncate it after its first K rows and columns. Indeed, we have to choose K large enough such that the first four eigenvalues of the truncated Hamiltonian matrix have converged closely enough to their actual value. Diagonalizing this $K \times K$-matrix yields a set of energy eigenvalues and eigenstates. Since we are interested in the dynamics of the energetically lowest doublet-doublet system, we now restrict the system to its first four energy eigenstates, leaving a diagonal Hamiltonian and its four eigenstates,

$$H_{\mathrm{DW}}^{\mathrm{Eig}} = \mathrm{diag}(\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4), \quad H_{\mathrm{DW}}^{\mathrm{Eig}} |n\rangle = \mathcal{E}_n |n\rangle . \tag{6}$$

As our interest lies in the decay of states localized in one of the wells, it is instructive to define so-called localized states via

$$\begin{aligned} |L_1\rangle &= \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle), \quad |L_2\rangle = \frac{1}{\sqrt{2}}(|3\rangle - |4\rangle), \\ |R_1\rangle &= \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle), \quad |R_2\rangle = \frac{1}{\sqrt{2}}(|3\rangle + |4\rangle). \end{aligned} \tag{7}$$

In this basis, the Hamiltonian takes the form

$$H_{\mathrm{DW}}^{\mathrm{Loc}} = \sum_{i=1,2} \Big[\bar{\mathcal{E}}_i (|L_i\rangle \langle L_i| + |R_i\rangle \langle R_i|) - \frac{\Delta_i}{2} (|L_i\rangle \langle R_i| + |R_i\rangle \langle L_i|) \Big], \tag{8}$$

where $\bar{\mathcal{E}}_1 = (\mathcal{E}_1 + \mathcal{E}_2)/2$, $\bar{\mathcal{E}}_2 = (\mathcal{E}_3 + \mathcal{E}_4)/2$, $\Delta_1 = \mathcal{E}_2 - \mathcal{E}_1$ and $\Delta_2 = \mathcal{E}_4 - \mathcal{E}_3$. Similarly, the position operator $\mathbf{q}$ can be expressed as

$$\begin{aligned} \mathbf{q}^{\mathrm{Loc}} &= q_{12}(|R_1\rangle \langle R_1| - |L_1\rangle \langle L_1|) + q_{34}(|R_2\rangle \langle R_2| - |L_2\rangle \langle L_2|) \\ &+ \frac{q_{14} + q_{23}}{2}(|R_1\rangle \langle R_2| + |R_2\rangle \langle R_1| - |L_1\rangle \langle L_2| - |L_2\rangle \langle L_1|) \\ &+ \frac{q_{14} - q_{23}}{2}(|R_2\rangle \langle L_1| + |L_1\rangle \langle R_2| - |L_2\rangle \langle R_1| - |R_1\rangle \langle L_2|). \end{aligned} \tag{9}$$