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Spectroscopy Duplication I

Ronald Lovett
Washington University in St. Louis

Separable Problems

References

Quantum Chemistry, D.A. McQuarrie, §6-2 – §6-11, (Chem QD462 M25).

General Formulation

A system is *separable* if the coordinates which fix the configuration of the system can be divided into two groups, $q_1, \ldots \oplus Q_1, \ldots$ (say) and there are no coupling terms in the Hamiltonian between the two groups. That is, for a separable system, the Hamiltonian can be written as a sum of two terms,

$$\begin{aligned} \hat{H} =& \hat{H}_a(q_1, \ldots) + \hat{H}_b(Q_1, \ldots), \\ =& \hat{H}_a(\underline{q}) + \hat{H}_b(\underline{Q}). \end{aligned} \tag{1}$$

In this case, the energy eigenfunction problem can be broken into two smaller problems. If

$$\hat{H}_a \varphi_m(\underline{q}) = \epsilon_m \varphi_m(\underline{q})$$

and

$$\hat{H}_b \phi_n(\underline{Q}) = E_n \phi_n(\underline{Q}),$$

then the functions

$$f_{mn}(\underline{q}, \underline{Q}) = \varphi_m(\underline{q})\, \phi_n(\underline{Q}) \tag{2}$$

are eigenfunctions of (1) with eigenvalues

$$\mathcal{E}_{mn} = \epsilon_m + E_n.$$

Since $\{\varphi_m\}$ forms a basis set in the $\underline{q}$-space and $\{\phi_n\}$ forms a basis set in the $\underline{Q}$-space, $\{f_{mn}(\underline{q}, \underline{Q})\}$ forms a basis set in the full space. Thus the set of eigenfunctions of the form (2) is a complete set of eigenfunctions.

The Standard Argument

Textbooks argue for this result by starting with the assumption that the solutions to

$$\hat{H} f(\underline{q}, \underline{Q}) = E f(\underline{q}, \underline{Q}) \tag{3}$$

are of the form

$$f(\underline{q}, \underline{Q}) = \varphi(\underline{q})\,\phi(\underline{Q}).$$

With Hamiltonian (1), (3) becomes

$$\phi(\underline{Q})\,\hat{H}_a\varphi(\underline{q}) + \varphi(\underline{q})\,\hat{H}_b\phi(\underline{Q}) = E\,\varphi(\underline{q})\phi(\underline{Q})$$

which can be rearranged to

$$\frac{\hat{H}_a\varphi(\underline{q})}{\varphi(\underline{q})} = E - \frac{\hat{H}_b\phi(\underline{Q})}{\phi(\underline{Q})}.$$

In this expression the variables have been "separated" because the left hand side depends upon $\underline{q}$ alone and the right hand side on $\underline{Q}$ alone. That is, the two sides of this equation can depend upon *neither* $\underline{q}$ *nor* $\underline{Q}$. If E_1 is the actual (constant) value of this expression, we find

$$\hat{H}_a\,\varphi(\underline{q}) = E_1\,\varphi(\underline{q}),$$

$$\hat{H}_b\,\phi(\underline{Q}) = (E - E_1)\,\phi(\underline{Q}).$$

Degeneracy ~ 2 dimensions but not with 1 dimension

In one dimensional problems the energy eigenvalues increase as the number of nodes ($\sim$ the quantum number) of the eigenfunction/eigenvector increases. Each eigenvalue can only be associated with one eigenvector. The eigenvalues are *non-degenerate*. The eigenvalues cannot be ordered this way, however, in greater than one dimension. It is possible to have more than one eigenvector associated with an eigenvalue. If there are n distinct eigenfuctions with the *same* eigenvalue,

$$\hat{H}\psi_k = \mathcal{E}\psi_k \qquad \text{for } k = 1, \ldots, n,$$

the eigenvalue (level) $\mathcal{E}$ is described as being n-fold *degenerate*.

Applications

The energy eigenfunction problems for which explicit analytic solutions are known all have Hamiltonians for which the initial N-dimensional problem can be "separated" into N one-dimensional problems. It is experience with problems of this type which forms the basis of our image of real three-dimensional problems.

The separability of a problem is a property of the coordinate system used: A coordinate transformation $\underline{q}, \underline{Q} \rightarrow \underline{q}', \underline{Q}'$ usually destroys the separability in (1). There are often more than one coordinate systems in which a problem can be separated, however. For these problems we have more than one image of the solutions.

1. What is a basis set ?
2. Normalized eigenvectors
3. eigenvectors
   eigenvalues
   eigenfunction
4. Unitary Transformations
   coordinate Transformation
   = Transformation of representation

(Ammonia maser) → (Reduced the state Vector) ← Towns Gorden Ziegler.

Problem Set #6

1. The simple harmonic oscillator in one dimension has

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2.$$

The energy eigenvalue problem $\hat{H}\psi = E\psi$ has solutions

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-m\omega x^2/2\hbar}$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

for $n = 0, 1, 2, \ldots$ in which $H_n(z)$ is the n^{th} Hermite polynomial.

If you ask *Mathematica* for the solution to the energy eigenvalue problem for the SHO (if you give the second order differential equation to DSolve) you get the "answer"

$$\psi[x] \to e^{-m\omega x^2/2\hbar} C[1]\,\text{HermiteH}\left[\frac{2\mathcal{E} - \hbar\omega}{2\hbar\omega}, \sqrt{\frac{m\omega}{\hbar}}x\right] + e^{-m\omega x^2/2\hbar} C[2]\,\text{Hypergeometric1F1}\left[-\frac{2\mathcal{E} - \hbar\omega}{2\hbar\omega}, \frac{1}{2}, \frac{m\omega}{\hbar}x^2\right]$$

The HermiteH[n,z] are the *Hermite* polynomials,

$$H_0(z) = 1$$
$$H_1(z) = 2\,z$$
$$H_2(z) = -2 + 4\,z^2$$
$$H_3(z) = -12\,z + 8\,z^3$$
$$H_4(z) = 12 - 48\,z^2 + 16\,z^4$$
$$H_5(z) = 120\,z - 160\,z^3 + 32\,z^5$$
$$etc,$$

but a complete identification of the "allowed" solutions requires a knowledge of the asymptotic form for the functions HermiteH and Hypergeometric1F1 as $z \to \pm\infty$ for *all* $\mathcal{E}$. This is a somewhat more sophisticated question!

Note that the argument of the Hermite polynomial in this solution is dimensionless. What is the physical dimension of $\psi_n(x)$?

An isotropic oscillator in two dimensions has

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}m\omega^2(x^2 + y^2) \tag{4}$$

in Cartesian coordinates. Show that (4) is separable. Determine the energy eigenfunctions and eigenvalues for this problem. Turn in a level diagram (showing the eigenvalues of $\hat{H}$) on which the degeneracies of the energy eigenstates are marked.

2. In cylindrical coordinates,

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial^2}{\partial \theta^2}.$$

Show that the eigenvalue problem for the isotropic two-dimensional oscillator can also be separated in the R, θ coordinate system. What are the solutions to the θ-subproblem? What do the eigenvalues of the θ-subproblem correspond to physically?

The R-dependent factor is determined by the ordinary differential equation

$$F''(R) + \frac{1}{R}F'(R) + F(R)\left(-\frac{\ell^2}{R^2} + \frac{2mE}{\hbar^2} - \frac{m^2\omega^2R^2}{\hbar^2}\right) = 0$$

with $\ell = 0, \pm 1, \pm 2, \ldots$. If , for $\ell \geq 0$, we set

$$F(R) = R^\ell e^{-m\omega R^2/2\hbar} G\left(\frac{m\omega}{\hbar}R^2\right),$$

then $G(x)$ is determined by

$$x\,G''(x) + (\ell + 1 - x)\,G'(x) + \frac{1}{2}\left(\frac{E}{\hbar\omega} - \ell - 1\right) G(x) = 0.$$

Use Table 22.6 of *Abramowitz and Stegun* to identify polynomial solutions to this differential equation. Turn in plots of $\psi(R,\theta)$ and $|\psi(R,\theta)|^2$ for all the eigenfunctions associated with the three lowest energies of this system. [Recall that bound state eigenfunctions can always be made *real*.] Turn in an explicit representation (i.e., a formula) for these eigenfunctions in terms of the solutions found in problem (1).

> An image of a surface in 3D is constructed by Plot3D. If $f[x, y] = \exp[-(x^2 + y^2)]$, for example, Plot3D[$f[x, y]$, $\{x, -2, 2\}$, $\{y, -2, 2\}$, PlotRange → All,PlotPoints→ 25] will produce a plot of this function.

3. Show that

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}m\omega^2(x^2 + y^2) + m\lambda^2 x\,y$$

is separable in a Cartesian coordinate system which is rotated $\pi/4$ radians. Turn in a formula for the energy eigenvalues and an energy level diagram for the $\lambda = 0.1\omega$ case.