

Linear system of the Schrödinger equation

Notes on Quantum Mechanics

<http://quantum.bu.edu/notes/QuantumMechanics/LinearSystems.pdf>
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Department of Chemistry, Boston University, Boston MA 02215

In numerical applications of quantum mechanics in chemistry, a powerful method of solving the Schrödinger equation,

$$H \Psi_\alpha = E_\alpha \Psi_\alpha$$

is to express the unknown wavefunction, Ψ_α , in terms of known basis functions, ψ_j , as

$$\Psi_\alpha = \sum_j \psi_j c_{j\alpha}.$$

The result is a linear system of equations for the expansion coefficients, $c_{j\alpha}$.

Here is what the linear system looks like for an expansion in terms of three basis functions.

$$\begin{pmatrix} H_{11} - E_\alpha & H_{12} & H_{13} \\ H_{21} & H_{22} - E_\alpha & H_{23} \\ H_{31} & H_{32} & H_{33} - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ c_{3\alpha} \end{pmatrix} = 0$$

where

$$H_{jk} = \int \psi_j(x)^* H \psi_k(x) dx.$$

For this example, we have three equations in four unknowns: the three expansion coefficients, $c_{j\alpha}$, and the energy, E_α .

The way to proceed is to first determine the values of the energy by requiring that the matrix

$$\begin{pmatrix} H_{11} - E_\alpha & H_{12} & H_{13} \\ H_{21} & H_{22} - E_\alpha & H_{23} \\ H_{31} & H_{32} & H_{33} - E_\alpha \end{pmatrix}$$

does *not* have an inverse, for if it did have an inverse, then the solution would be

$$\begin{pmatrix} H_{11} - E_\alpha & H_{12} & H_{13} \\ H_{21} & H_{22} - E_\alpha & H_{23} \\ H_{31} & H_{32} & H_{33} - E_\alpha \end{pmatrix}^{-1} \begin{pmatrix} H_{11} - E_\alpha & H_{12} & H_{13} \\ H_{21} & H_{22} - E_\alpha & H_{23} \\ H_{31} & H_{32} & H_{33} - E_\alpha \end{pmatrix} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ c_{3\alpha} \end{pmatrix} = \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ c_{3\alpha} \end{pmatrix} = 0,$$

that is, all of the expansion coefficients would be equal to 0 and so the wavefunction, Ψ_α , would vanish!

Now, the inverse of a matrix is proportional to the reciprocal of its determinant, and so we can ensure that a matrix does not have an inverse by arranging for its determinant to be equal to 0. We do this by finding those values of E_α at which the determinant vanishes. For an $n \times n$ matrix, the determinant is an n -th order polynomial in E_α and so there will be as many values of the energy at which the determinant vanishes as there are basis functions.

Once the values of the energy, E_α , have been determined, we are left with a homogeneous system of equations for the unknown expansion coefficients, $c_{j\alpha}$. The way to solve this system of equations is to set one of the expansion coefficients equal to 1, set aside the corresponding equation of the linear system, and then solve the remaining set of equations. For the 3×3 example, setting $c_{1\alpha} = 1$, the remaining equations to solve are

$$\begin{pmatrix} H_{22} - E_\alpha & H_{23} \\ H_{32} & H_{33} - E_\alpha \end{pmatrix} \begin{pmatrix} c_{2\alpha} \\ c_{3\alpha} \end{pmatrix} = - \begin{pmatrix} H_{21} \\ H_{31} \end{pmatrix}.$$

We can solve this to for the remaining coefficients, $c_{2\alpha}$ and $c_{3\alpha}$.

The result is

$$\Psi_\alpha = N (\psi_1 + \psi_2 c_{2\alpha} + \psi_3 c_{3\alpha})$$

where the normalization constant, N , corrects for the fact that we have set $c_{1\alpha} = 1$. The last step is to determine the value of N using

$$\int |\Psi_\alpha|^2 dx = N^2 \int |\psi_1 + \psi_2 c_{2\alpha} + \psi_3 c_{3\alpha}|^2 dx = N^2 (1 + c_{2\alpha}^2 + c_{3\alpha}^2),$$

where in the second equality we have assumed the orthonormality of the basis functions, ψ_j . The final result is that

$$\Psi_\alpha = \frac{1}{\sqrt{1 + c_{2\alpha}^2 + c_{3\alpha}^2}} (\psi_1 + \psi_2 c_{2\alpha} + \psi_3 c_{3\alpha})$$

is the normalized wavefunction corresponding to the energy E_α .

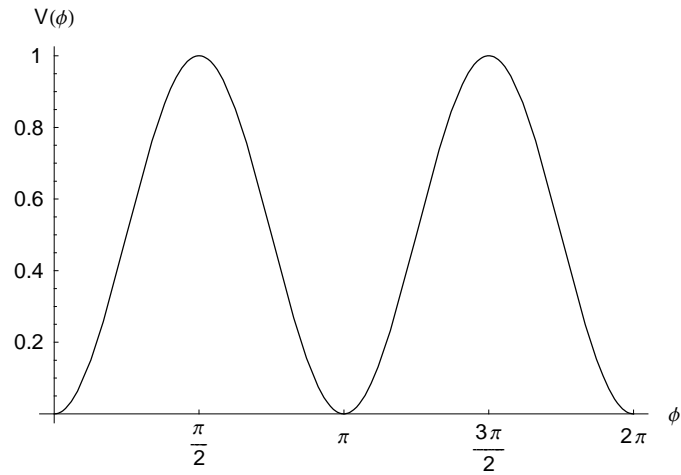
■ Particle on a bumpy ring

To see how this method of solving the Schrödinger equation works, let's consider a particle moving on a bumpy ring.

A particle on a smooth ring has only kinetic energy, since the potential energy is zero on the ring. We can make the ring "bumpy" by adding the potential energy

$$V(\phi) = \frac{\hbar^2}{2I} \sin^2(\phi).$$

Here is a plot of this potential energy, in units $\hbar^2/(2I)$.



Potential energy, in units $\hbar^2/(2I)$, of a bumpy ring.

The potential energy has minima along the $\pm x$ directions and maxima along the $\pm y$ directions. To construct the linear system of the Schrödinger equation for a particle moving on a ring in this potential energy, we need the integrals

$$V_{mm'} = \int_0^{2\pi} \Phi_m(\phi)^* \left(\frac{\hbar^2}{2I} \sin^2(\phi) \right) \Phi_{m'}(\phi) d\phi.$$

The value of such integrals, in units $\hbar^2/(2I)$, is $1/2$ for $m = m'$, $-1/4$ for $m = m' \pm 2$, and 0 otherwise. This means that the integrals of the hamiltonian,

$$H_{mm'} = \frac{\hbar^2}{2I} \left(-\frac{d^2}{d\phi^2} + \sin^2(\phi) \right)$$

of a particle on this bumpy ring for basis functions with $m = 0, 1$ and 2 , are, in units $\hbar^2/(2I)$,

	$m' = 0$	$m' = 2$	$m' = 1$
$m = 0$	$\frac{1}{2}$	$-\frac{1}{4}$	0
$m = 2$	$-\frac{1}{4}$	$\frac{9}{2}$	0
$m = 1$	0	0	$\frac{3}{2}$

Use the values of the integrals $V_{mm'}$ to show these values are correct.

If we express the wavefunction of the particle on the bumpy ring as the expansion

$$\Psi_\alpha(\phi) = \Phi_0(\phi) c_{0\alpha} + \Phi_1(\phi) c_{1\alpha} + \Phi_2(\phi) c_{2\alpha},$$

then the normalized wavefunctions, $\Psi_\alpha(\phi)$, and corresponding energies, E_α , in units $\hbar^2/(2I)$, are

α	Ψ_α	E_α
1	$0.398942 e^{1 \cdot i \phi}$	1.5
2	$0.398171 + 0.0247893 e^{2 \cdot i \phi}$	0.484436
3	$-0.0247893 + 0.398171 e^{2 \cdot i \phi}$	4.51556

Normalized wavefunctions, $\Psi_\alpha(\phi)$, and corresponding energies, E_α , in units $\hbar^2/(2I)$, for a particle in a ring in a potential energy $\hbar^2/(2I) \sin^2(\phi)^2$, using an expansion in ring basis functions, $\Phi_m(\phi)$, for $m = 0, 1$ and 2 .

Show that these results are correct.

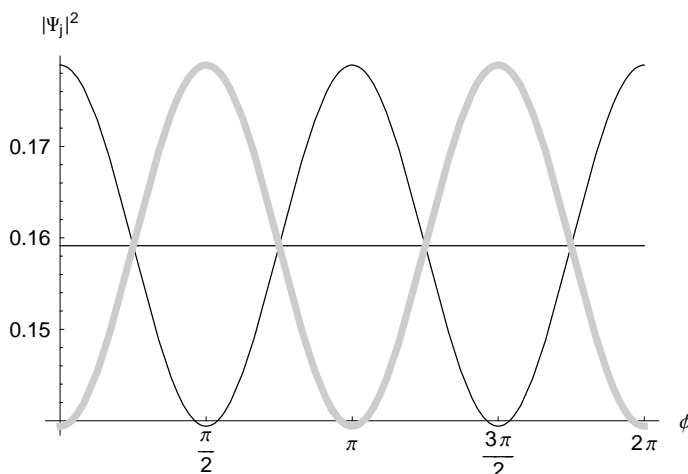
Here is the composition of each wavefunction, $\Psi_\alpha(\phi)$, in terms of the percentage contribution of the three ring basis functions, $\Phi_0(\phi)$, $\Phi_1(\phi)$ and $\Phi_2(\phi)$.

	Φ_0	Φ_2	Φ_1
Ψ_1	0.	0.	100.
Ψ_2	99.6	0.386	0.
Ψ_3	0.386	99.6	0.

Percentage composition of each bumpy ring wavefunction, $\Psi_\alpha(\phi)$, in terms of the five ring basis states, $\Phi_m(\phi)$, for $m = 0, 1$ and 2 .

Show that these results are correct.

Finally, here are the probability densities corresponding to the three wavefunctions, $\Psi_1(\phi)$, $\Psi_2(\phi)$ and $\Psi_3(\phi)$.



Probability densities corresponding to the three wavefunctions $\Psi_1(\phi)$ (horizontal line), $\Psi_2(\phi)$ (oscillating thin grey line) and $\Psi_3(\phi)$ (oscillating thick grey line).

Show that these results are correct.

The horizontal line is for energy $E_1 = 1.5 \hbar^2 / (2I)$; this energy is just the sum of the kinetic energy and the potential energy expectation values for $m = 1$.

The oscillating thin grey line is for energy $E_2 = 0.484 \hbar^2 / (2I)$. This energy is slightly less than the sum of the kinetic energy and the potential energy expectation values for $m = 0$. The decrease is due to the probability density being slightly larger in the potential valleys (along $\pm x$) and slightly smaller at the potential peaks (along $\pm y$).

The oscillating thick grey line is for energy $E_3 = 4.516 \hbar^2 / (2I)$; this energy is slightly more than the sum of the kinetic energy and the potential energy expectation values for $m = 2$. The increase is due to the probability density being slightly larger at the potential peaks (along $\pm y$) and slightly smaller in the potential valleys (along $\pm x$).

■ Improving the energies and eigenvalues

In this method of solving the Schrödinger equation, as additional basis functions are added, the more accurate the energies and wavefunctions become. To illustrate this, we can resolve the particle on a bumpy ring using a five-member basis consisting of the ring functions $\Phi_m(\phi)$ with $m = 0, 1, 2, 3$ and 4 .

The integrals of the hamiltonian,

$$H_{mm'} = \frac{\hbar^2}{2I} \left(-\frac{d^2}{d\phi^2} + \sin^2(\phi) \right)$$

of a particle on this bumpy ring for basis functions with $m = 0, 1, 2, 3$ and 4 , are, in units $\hbar^2/(2I)$,

	$m' = 0$	$m' = 2$	$m' = 4$	$m' = 1$	$m' = 3$
$m = 0$	$\frac{1}{2}$	$-\frac{1}{4}$	0	0	0
$m = 2$	$-\frac{1}{4}$	$\frac{9}{2}$	$-\frac{1}{4}$	0	0
$m = 4$	0	$-\frac{1}{4}$	$\frac{33}{2}$	0	0
$m = 1$	0	0	0	$\frac{3}{2}$	$-\frac{1}{4}$
$m = 3$	0	0	0	$-\frac{1}{4}$	$\frac{19}{2}$

The normalized wavefunctions, $\Psi_\alpha(\phi)$, and corresponding energies, E_α , in units $\hbar^2/(2I)$, are

α	Ψ_α	E_α
1	$0.398748 e^{1 \cdot i\phi} + 0.0124487 e^{3 \cdot i\phi}$	1.4922
2	$-0.0124487 e^{1 \cdot i\phi} + 0.398748 e^{3 \cdot i\phi}$	9.5078
3	$0.00012978 - 0.00830859 e^{2 \cdot i\phi} + 0.398856 e^{4 \cdot i\phi}$	16.5052
4	$-0.0248159 + 0.398083 e^{2 \cdot i\phi} + 0.00830057 e^{4 \cdot i\phi}$	4.51037
5	$0.39817 + 0.0248132 e^{2 \cdot i\phi} + 0.000387329 e^{4 \cdot i\phi}$	0.48442

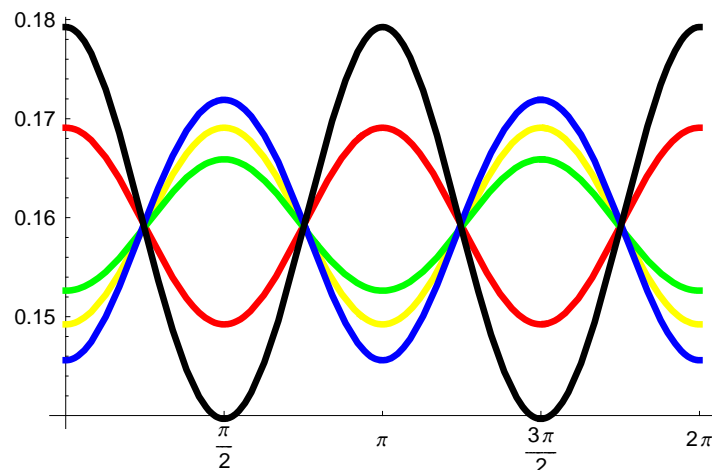
Normalized wavefunctions, $\Psi_\alpha(\phi)$, and corresponding energies, E_α , in units $\hbar^2/(2I)$, for a particle in a ring in a potential energy $\hbar^2/(2I) \sin^2(\phi)^2$, using an expansion in ring basis functions, $\Phi_m(\phi)$, for $m = 0, 1, 2, 3$ and 4 .

Here is the composition of each wavefunction, $\Psi_\alpha(\phi)$, in terms of the percentage contribution of the five ring basis functions.

	Φ_0	Φ_2	Φ_4	Φ_1	Φ_3
Ψ_1	0	0	0	99.9	0.09737
Ψ_2	0	0	0	0.09737	99.9
Ψ_3	0.00001058	0.04337	99.96	0	0
Ψ_4	0.3869	99.57	0.04329	0	0
Ψ_5	99.61	0.3869	0.00009426	0	0

Percentage composition of each bumpy ring wavefunction, $\Psi_\alpha(\phi)$, in terms of the five ring basis states, $\Phi_m(\phi)$, for $m = 0, 1, 2, 3$ and 4 .

Finally, here are the probability densities corresponding to the five wavefunctions, $\Psi_\alpha(\phi)$.



Probability densities corresponding to the five wavefunctions $\Psi_\alpha(\phi)$. At $\phi = \pi/2$, the ordering of the curves and predominant ring basis function contribution, from bottom to top, are $(\alpha, m) = (5, 0)$ (black curve), $(\alpha, m) = (1, 1)$ (red curve), $(\alpha, m) = (3, 4)$ (green curve), $(\alpha, m) = (2, 3)$ (yellow curve), and $(\alpha, m) = (4, 2)$ (blue curve).

The first thing to note is that, as in the three-member basis, the densities ($\alpha = 1$ and 5) that are reduced at the potential bumps and enhanced at the potential valleys correspond to lower energies than the sum of the kinetic energy and the potential energy expectation values for dominant value of m for the given Ψ_α , and the densities ($\alpha = 2, 3$ and 4) that are enhanced at the potential bumps and reduced at the potential valleys correspond to higher energies than the sum of the kinetic energy and the potential energy expectation values for dominant value of m for the given Ψ_α .

The second thing to note is that whereas in the three-member basis the density of the level with $m = 1$ remained constant and its energy did not change from the sum of the kinetic energy and the potential energy expectation values for $m = 1$, now the density is shifted away from the bumps into the valleys, and the energy is correspondingly lowered. This is balanced by a shift of the predominantly $m = 3$ density away from the valleys and onto the bumps, and its corresponding increased energy, relative to the sum of the kinetic energy and the potential energy expectation values for $m = 3$.

■ Comparing the three- and five-member basis results

It is *very* instructive to compare the energy changes that result using the three-member basis with those that result using the five member basis.

Here is a tabulation of the three-member basis results,

m	E_m	$E_m + V_m$	E_α	$E_\alpha - (E_m - V_m)$
0	0	0.5	0.484	-0.0156
2	4	4.5	4.52	0.0156
4	16	—	—	—
1	1	1.5	1.5	0.
3	9	—	—	—

Ring function kinetic energies, E_m , ring function kinetic energies plus potential bump potential energies, V_m , energies E_α , and the change in energy, $E_\alpha - (E_m - V_m)$, for a particle on a ring in a potential energy $\sin^2(\phi)^2$, using an expansion in ring basis functions, $\Phi_m(\phi)$, for $m = 0, 1$ and 2. All energies are in units $\hbar^2/(2I)$.

and here is a tabulation of the five-member basis results,

m	E_m	$E_m + V_m$	E_α	$E_\alpha - (E_m - V_m)$
0	0	0.5	0.484	-0.0156
2	4	4.5	4.51	0.0104
4	16	16.5	16.5	0.00521
1	1	1.5	1.49	-0.0078
3	9	9.5	9.51	0.0078

Ring function kinetic energies, E_m , ring function kinetic energies plus potential bump potential energies, V_m , energies E_α , and the change in energy, $E_\alpha - (E_m - V_m)$, for a particle on a ring in a potential energy $\sin^2(\phi)^2$, using an expansion in ring basis functions, $\Phi_m(\phi)$, for $m = 0, 1, 2, 3$ and 4. All energies are in units $\hbar^2/(2I)$.

The key thing to note in these results and their comparison is that the energies, E_α , for the five-member basis are lower than those for the three member basis. This is an example of a general result known as the *separation theorem*. The theorem has two parts: First, unless we use all of the basis functions of a complete set, the resulting energies, E_α , will be higher than the exact energies; second, the more basis functions we include, the closer will be the energies, E_α , to the exact energies, that is, enlarging a linear system always lowers energies, E_α .

This property of linear systems of the Schrödinger equation means that we can get good approximations to exact energies of at least the lowest several levels without having to use a huge number of basis functions. The reason is that adding more and more basis functions results in smaller and smaller improvement to the energies of the lowest levels. It is for this reason that this method of working with the Schrödinger equation is so powerful and so widespread in applications of quantum mechanics to chemical systems.