

Numerical Methods for Finding Momentum Space Distributions

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For chemists, quantum mechanics consists to a large extent in solving Schrödinger's equation in its position representation for a wide variety of problems of varying complexity. This activity yields quantized energy levels and their associated wave functions, $\Psi(q)$, where q represents the position coordinates (x, y, z) , (r, θ, ϕ) , etc. Once obtained, $\Psi(q)$ can be used to examine the probability distribution in position space or to calculate the expectation value of some observable property such as momentum. Though not as familiar to chemists, an equivalent form of Schrödinger's equation in momentum space also exists (1). Solving this equation yields the momentum-space wave function, $\Phi(p)$, which can be used to examine the probability distribution in momentum space or calculate the expectation value of some observable property such as position. In other words, $\Psi(q)$ and $\Phi(p)$ are equivalent representations of the system under study.

However, for most cases the momentum version of Schrödinger's equation is significantly more difficult to solve than its position-space counterpart. Because of the equivalency of the position and momentum representations of Schrödinger's equation, $\Psi(q)$ and $\Phi(p)$ are related by the Fourier transformation given in atomic units for a one-dimensional problem in eq 1 (1).

$$\Phi(p) = \frac{1}{\sqrt{2\pi}} \int e^{ipx} \Psi(x) dx \quad (1)$$

Therefore, when the momentum wave function is required it is generally found by a Fourier transform of the more easily obtainable position wave function.

Recently Liang et al. (2) discussed the importance of the momentum representation of the wave function and demonstrated how to transform the spatial wave function for the particle in the box into momentum space using analytical methods. Prior to this work the subject of the momentum wave function for the particle in the box was given a brief treatment by Markley (3) in the physics literature. There have also been several discussions of the momentum-space wave functions for the hydrogen atom (4, 5). The purpose of this note is to expand on these presentations by showing that momentum-space wave functions can be obtained quite easily and economically using numerical techniques and widely available computer software. The program employed in this presentation is Mathcad and versions 3.x or higher can be used.

Figure 1 shows how the momentum-space wave function is obtained numerically for the $n = 3$ state for a particle in a 1 Bohr box using Mathcad. The Fourier transform is typed, then evaluated numerically for a range of momentum values, and displayed graphically. The result illustrated in Figure 1 is identical to that shown in ref 2.

Numerical solutions have two major attractive features: they are relatively easy to obtain, as Figure 1 illustrates, and it is very easy to move from one problem to the next. This is demonstrated in Figure 2, where the same Mathcad template has been edited to handle the harmonic oscillator problem. As Pauling and Wilson (6) noted in their classic text, and as Figure 2 shows, the momentum and space wave functions are the same for the simple harmonic oscillator. This is because the momentum operator in position space is $-i(d/dx)$, whereas the position operator in mo-

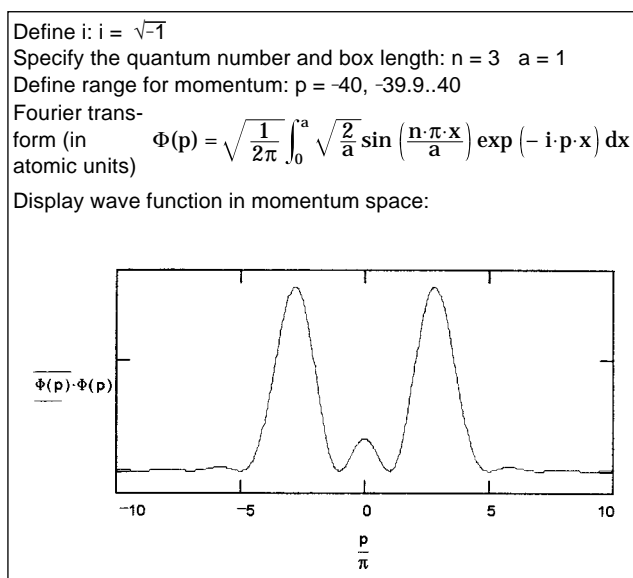


Figure 1. Momentum distribution function for the $n = 3$ state of a particle in the box.

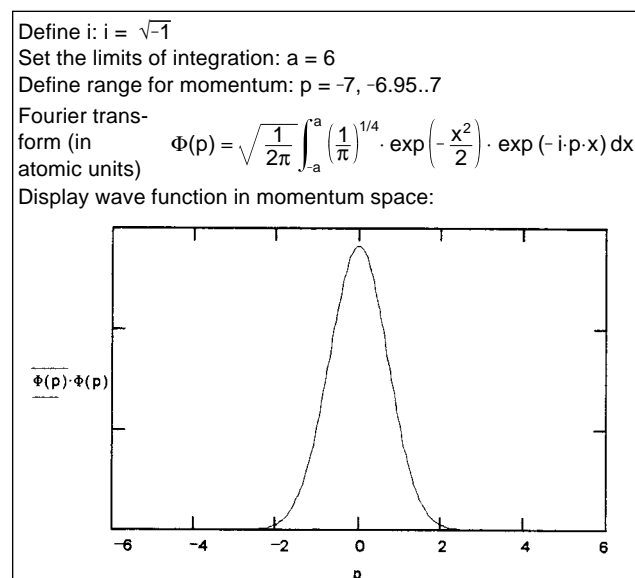


Figure 2. Momentum distribution function for the ground state of the harmonic oscillator.

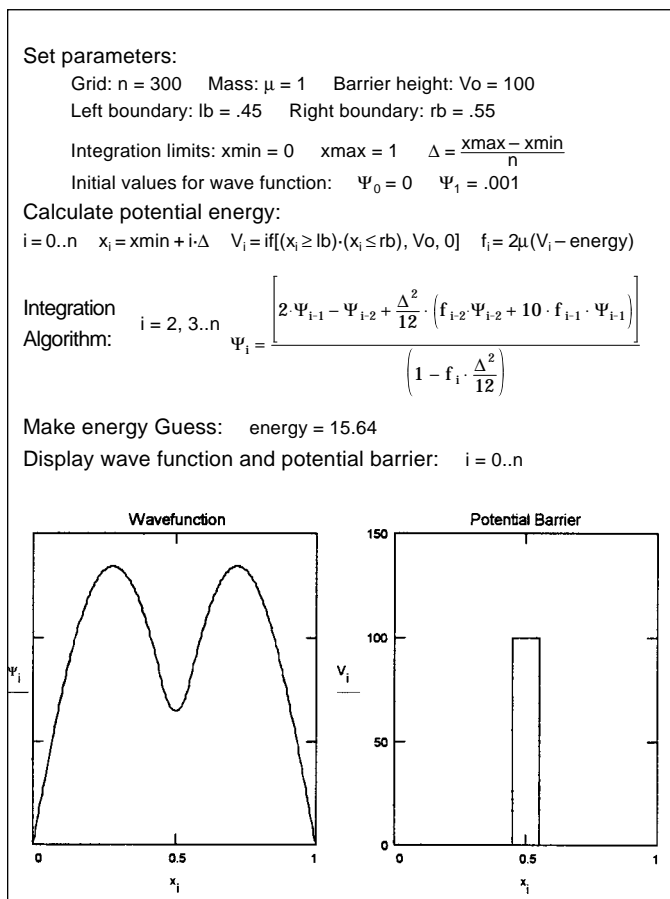


Figure 3a. Numerical solution for the particle in a box with internal barrier.

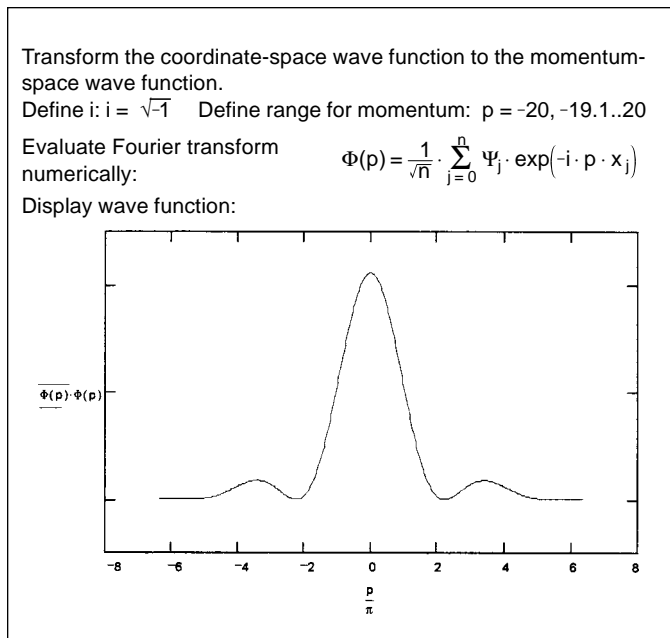


Figure 3b. Momentum distribution function for the particle in a box with internal barrier.

mentum space is $i(d/dp)$. Using the usual methods to convert the classical expression for the harmonic oscillator energy into Schrödinger's equation in position and momentum space yields eqs 2 and 3, respectively. Thus, for the harmonic potentials in one dimension, Schrödinger's equation is just as easy to solve in momentum space as in position space.

$$\Psi''(x) = 2\mu \left[\frac{1}{2} kx^2 - E \right] \Psi(x) \quad (2)$$

$$\Phi''(p) = \frac{2}{k} \left[\frac{p^2}{2\mu} - E \right] \Phi(p) \quad (3)$$

A striking exploitation of this symmetry for harmonic potentials was reported recently by Anderson et al. (7). These researchers created a Bose-Einstein condensate (the first direct experimental confirmation of a state predicted by Einstein in 1925) of several thousand rubidium atoms confined to the ground state of a three-dimensional harmonic potential well. In such a condensate the rubidium atoms are all in the same quantum state and as such represent the material equivalent of a laser. Anderson and co-workers used spectroscopic measurements on the expanded condensate to obtain the velocity (and momentum, $\mathbf{p} = m\mathbf{v}$) distribution of the original condensate. Owing to the position/momentum symmetry mentioned above, this is equivalent to the spatial distribution. Thus, a single spectroscopic measurement provides both the momentum and position wave functions of the Bose-Einstein condensate.

In the examples discussed so far, the momentum wave function is found by a numerical Fourier transform of the analytical form of the position wave function. However, there are many examples for which analytical solutions are unavailable or very difficult to obtain. Figures 3a and 3b show how the position wave function for the particle in the box with internal barrier is obtained by numerical integration of Schrödinger's equation (8) and then transformed numerically into a momentum-space wave function. This Mathcad document can serve as a template for any one-dimensional problem and is especially useful for those that require a numerical solution for Schrödinger's equation.

In summary it can be stated that the preference for the position or momentum formulation of quantum mechanics is guided by the uncertainty principle. Because chemistry deals with the behavior of the valence electrons of discrete atomic and molecular species whose electrons are localized in space (small Δq , large Δp), chemists are mainly interested in $\Psi(q)$. Among the accomplishments of solid state physics is the elucidation of the electronic structure of metals (9). In the most elementary theory of metals the electrons are essentially completely delocalized (large Δq , small Δp) and the organizing principles are the Fermi surface and the momentum space wave function, $\Phi(p)$.

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