5 Quantum Mechanics

5.1 Introduction

Quantum mechanics compared with mechanics is a very young theory. The theory emerged at 1900 when Max Planck (see Figure 5.1.1) examined the blackbody radiation in thermodynamics. The discovery by Planck was that the blackbody radiation can be described by a unified relation interpolating between the high-frequency limit proposed by Wien and the low-frequency limit favored by Rayleigh. The major assumption by Planck was that the energy in this relation is linear in frequency and discrete \( E = h \omega \). Planck believed that this quantization applied only to the absorption and emission of energy by matter, not to electromagnetic waves themselves. However, it turned out to be much more general than he could have imagined.
Another anchorman in quantum mechanics was Erwin Schrödinger (see Figure 5.1.2) who invented wave mechanics in 1926. Reading the thesis of Louis de Broglie, he was inspired to write down a wave equation which established a second approach to mathematically describe quantum mechanics.
It was Werner Heisenberg (see Figure 5.1.3) who first gave a sound description of quantum mechanics with his matrix mechanics in 1925. Heisenberg was studying a set of quantized probability amplitudes when he used a matrix algebra. These amplitudes formed a noncommutative algebra. It was Max Born and Jordan in Göttingen who recognized this noncommutative algebra to be a matrix algebra. Another fundamental achievement by Heisenberg in 1927 was the uncertainty principle which governs all quantum mechanical systems.

Today, quantum mechanics is a central theory in physics to describe micro and nano phenomena in atomic systems or semiconductors, for example. Quantum mechanics in its field-theoretic extensions is important in discussions of the unification of fundamental forces. The application of quantum mechanics ranges from nano systems up to large-scale systems such as black holes. Quantum mechanics is, in terms of its application, by no means a self-contained theory. The major open question in quantum theory is the unification with the theory of gravitation.

The current chapter introduces basic concepts of wave functions and demonstrates the application of the Schrödinger equation to different examples. In Section 5.2 the Schrödinger equation is introduced. Section 5.3 is concerned with the one-dimensional quantum dot model. Section 5.4 discusses the harmonic oscillator as a basic system to carry out quantum
mechanical calculations. The harmonic oscillator is extended to an anharmonic oscillator, which is important in the solution of nonlinear field equations. Section 5.6 discusses the motion of a particle in a central force field. The last section is concerned with the calculation of the second virial coefficient and its quantum mechanical correction.

5.2 The Schrödinger Equation

The development of quantum mechanics as a field of study required an equation that would adequately describe experimentally observed quantum mechanical properties, such as the spectroscopic properties of atoms and molecules. In 1926, Schrödinger wrote down the equation of motion for a complex field in close analogy to the eikonal equation of optics [5.1]. Today, it is known as the Schrödinger equation. The Schrödinger equation for a single particle reads

\[ i \hbar \psi_t = -\frac{\hbar^2}{2m} \Delta \psi(\vec{x}, t) + V(\vec{x}) \psi(\vec{x}, t), \]

where \( \psi(\vec{x}, t) \) denotes the wave function, \( V(\vec{x}) \) is an external potential representing the source of forces in the quantum system, \( \hbar \) is Planck's constant, and \( m \) the mass of the particle under consideration.

The Schrödinger equation is a linear equation. It is well known that linear partial differential equations allow a superposition of their solutions to construct general solutions. Using this information with the two solutions \( \psi_1 \) and \( \psi_2 \) of the Schrödinger equation (5.2.1) allows us to construct the solution \( \psi = c_1 \psi_1 + c_2 \psi_2 \). We can identify Schrödinger's equation as a diffusion equation if we define an imaginary diffusion constant. To solve Schrödinger's equation, we can use, in principle, the same solution procedure as for the diffusion equation. For certain initial values and known boundary values, we find the evolution of the wave function \( \psi \) by Eq. (5.2.1).

The main problem at the outset of quantum mechanics was the interpretation of the wave function \( \psi \). Although Schrödinger's linear equation of motion (5.2.1) is completely deterministic, its solution \( \psi(\vec{x}, t) \) is not a measurable quantity. In fact, the only observable quantities in
quantum mechanics are the probability $\psi^*\psi$ and any mean value based on the distribution function $\psi$ denoted by $\langle \psi | \Theta | \psi \rangle$.

Another consequence of the linearity of the Schrödinger equation is the property of dispersion. It is well known that linear equations of motion have dispersive waves as solutions. Since Schrödinger's equation (5.2.1) contains an imaginary factor $i$, we can expect the solutions for a free particle to undergo oscillations in the time domain. Plane waves are the simplest solutions to $\psi$. A particular solution of Eq. (5.2.1) with $V(\bar{x}) = 0$ is given by

$$\psi_k(\bar{x}, t) = \frac{1}{(\sqrt{2\pi})^3} e^{i[\bar{k}\bar{x} - \omega(k)t]}.$$  \hspace{1cm} (5.2.2)

The superposition of this particular solution delivers the general solution by

$$\psi(\bar{x}, t) = \frac{1}{(\sqrt{2\pi})^3} \int_{\mathbb{R}^3} A(k) e^{i[\bar{k}\bar{x} - \omega(k)t]} d^3 k.$$ \hspace{1cm} (5.2.3)

For simplicity's sake, we limit our consideration to one spatial dimension. The solution (5.2.3) of the Schrödinger equation (5.2.1) is known as a wave packet. The spectral density $A(k)$ of the packet is completely determined by the initial condition $\psi(x, t = 0) = \psi_0(x)$. The representation (5.2.3) follows from the Fourier transform of the initial condition

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi_0(x) e^{-ikx} dx.$$ \hspace{1cm} (5.2.4)

Inserting the spectral density into the general solution (5.2.3), we get the representation

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_0(x') e^{i(k(x-x')-\omega(k)t)} dk dx',$$

$$= \int_{-\infty}^{\infty} \psi_0(x') G(x, x', t) dx',$$ \hspace{1cm} (5.2.5)

where the Green's function $G$ is defined by

$$G(x, x', t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')-\omega(k)t} dk.$$ \hspace{1cm} (5.2.6)

The dispersion relation $\omega(k)$ of a dispersive wave is given by the defining equation of motion. For the Schrödinger equation with vanishing external potential $V(x) = 0$, the dispersion relation is $\omega(k) = \hbar k^2 / (2m)$. Assuming a localized distribution $\psi_0(x) = \delta(x)$ for the initial condition of the wave function, we can write the related solution as follows:

$$\psi(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-\alpha k t)} dk.$$ \hspace{1cm} (5.2.7)
This initial condition (assumed to derive the wave function \( \psi \)) cannot be normalized. Although this assertion contradicts the quantum mechanical interpretation, our only interest here is to show the dispersive behavior of the wave function. The constant \( \alpha = \hbar / (2m) \) is purely numerical. The relation (5.2.7) represents a solution of the Schrödinger equation (5.2.1) for the case of a free particle located at \( x = 0 \) with \( t = 0 \). Since the Schrödinger equation describes dispersive phenomena, we can observe a broadening of the wave packet diminishing for \( t \to \infty \). Its shape is studied in the following. Replacing \( k \) by \( k = \sqrt{\alpha t} \) in Eq. (5.2.7), we obtain

\[
\psi(x, t) = \frac{1}{\sqrt{\alpha t}} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\kappa/\sqrt{\alpha t} - x^2)} d\kappa. \tag{5.2.8}
\]

Computing the square in the exponent, we get

\[
\psi(x, t) = \frac{1}{\sqrt{\alpha t}} \frac{1}{2\pi} e^{i x^2/(4 \alpha t)} \int_{-\infty}^{\infty} e^{-i (x^2 - \kappa^2)/(4 \alpha t)} d\kappa. \tag{5.2.9}
\]

Substituting \( \Gamma = x / (2 \sqrt{\alpha t}) - \kappa \) gives us

\[
\psi(x, t) = \frac{1}{2 \sqrt{\alpha \pi t}} e^{i x^2/(4 \alpha t)} \int_{-\infty}^{\infty} e^{i \Gamma^2} d\Gamma = \frac{1}{2 \sqrt{\alpha \pi t}} e^{i(x^2/(4 \alpha t) + \pi/4)}. \tag{5.2.10}
\]

This representation of the wave function for a free particle can be used to determine the probability of locating the particle at a certain time. As discussed earlier, \( \psi \) is not a function directly observable by experiment. To locate a particle at a certain location at a certain time, we have to study the probability distribution \( |\psi|^2 \) of the particle. The probability distribution of solution (5.2.10) is given by the expression

\[
|\psi(x, t)|^2 = \frac{1}{4 \alpha \pi t}. \tag{5.2.11}
\]

This result shows that the probability of finding a free particle as described by Schrödinger’s equation vanishes as time goes on. The probability of finding a particle at any location decreases with time and vanishes as \( t \to \infty \). The dispersion process of the particle can be represented using *Mathematica* in a sequence of pictures. To animate the dispersion process, we first define the wave function \( \psi \) of the free particle:
where mass $m$ and $\hbar$ are set to unity. By an appropriate scaling of the coordinates, we can eliminate these constants in the equation of motion. The probability distribution $|\psi|^2$ in relation (5.2.11) is only a function of time and does not show any spatial dependence. However, if we examine the wave function itself, we observe the spatial dispersion of the wave.

In Figure 5.2.4 a time sequence of the real part of the wave function is plotted. The pictures are created by

\begin{verbatim}
Psi[x_, t_, hbar_:1, mass_:1] :=
  Block[{
    alpha,
    alpha = hbar/(2 mass);
    Exp[I (x^2/(4 alpha t) + Pi/4)]/(2 Sqrt[alpha t Pi])
  ]

Re[Psi]
 t=0.5
 0.4 0.2 0.2 0.4 2 4 6
 Re[Psi]
 t=1.5
 0.2 0.1 0.2 0.1 0.3 2 4 6
 Re[Psi]
 t=2.5
 0.2 0.1 0.2 0.1 0.2 2 4 6
 Re[Psi]
 t=3.
 0.2 0.1 0.2 0.1 0.2 2 4 6

Figure 5.2.4. Time evolution of a wave packet for the Schrödinger equation. Initial conditions are $\psi_0(x) = \delta(x)$.
\end{verbatim}
The plots show that the amplitude of the wave function decreases from about 0.5 to about 0.1 in a time range of 0.5 to 3.0. The dispersion of the wave packet is observable in the wave function. The wave function exhibits a reduced amplitude and a broadening of the initial packet.

The Schrödinger equation (5.2.1) not only describes time-dependent properties of quantum mechanical systems but also stationary properties of these systems. Contrary to our observations about free particles, we now find that Schrödinger's equation describes stable particles. One central question for such a system is how to uncover its intrinsic characteristics such as the spectral properties. In the following, we examine one of the fundamental models of quantum mechanics—the harmonic oscillator.

Before discussing the spectral properties of the harmonic oscillator, we first summarize the solution steps for the time dependent Schrödinger equation by a short graphical representation given in Figure 5.2.5.

1. Starting point of the solution procedure is the partial differential equation (PDE) (5.2.1) and the initial solution of the wave function $\psi(x, 0)$.

2. The use of the Fourier transform allows us to derive the spectral density $A(k)$ from the initial conditions.

3. A complete representation in Fourier space is attained when considering the time evolution, which is given by the dispersion relation $\omega(k)$.

4. The inversion of the representation in Fourier space delivers the solution of the Schrödinger equation.
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Figure 5.2.5. Solution steps for a linear PDE by using the Fourier transform.

A similar solution procedure for nonlinear PDEs is discussed in Chapter 3 on nonlinear dynamics.

5.3 One-Dimensional Potential

In quantum mechanics, the measurement of a physical quantity $A$ can result only in one of the eigenvalues of the corresponding operator $\hat{A}$. The eigenvalues of $\hat{A}$ forming the spectrum of the operator might be discrete, continuous, or both. The eigenfunctions of $\hat{A}$ form a complete basis that can be used to expand an arbitrary wave function. The expansion coefficients can be used to determine the probability of finding the system in an eigenstate of the operator $\hat{A}$ with eigenvalue $a$. Central to quantum mechanics is the determination of these eigenvalues and their related eigenfunctions.

One of the fundamental quantities of a quantum dynamical system is its energy. The operator corresponding to energy is the Hamiltonian operator of the system. The Hamiltonian for a particle with mass $m$ located in a potential $V$ is represented by $\hat{H} = -\hbar^2 / (2m) \Delta + V(x)$. The determination of eigenvalues and eigenfunctions is demonstrated with a one-dimensional model, the potential well. The potential well of depth $V = -V_0$ discussed in the following extends between $-a \leq x \leq a$ where $a$ is the maximum
extension. Beyond the maximum extension, the potential vanishes. A graphical representation of the potential is given in Figure 5.3.6.

We study the case for which the kinetic energy of the particle is smaller than the minimal potential value \( V_0 \) (i.e., \( T < V_0 \)). The total energy \( E \) of the system is \( E = T - V_0 < 0 \). The particle has a negative total energy in the domains 1 and 3 depicted in Figure 5.3.6. In classical mechanics, the particle cannot be found in these regions. Contrary to classical mechanics, however, quantum mechanics allows the existence of particles in regions where they are classically forbidden. The domains 1 and 3 are governed by the eigenvalue equations \( \hat{H} \psi = E \psi \), which are given in a differential representation by

\[
\psi'' - \kappa^2 \psi = 0, \quad (5.3.12)
\]

where \( \kappa^2 = -2mE/\hbar^2 > 0 \) is a positive constant containing the total energy. Primes denote differentiation with respect to the spatial coordinate.

The solution of Eq. (5.3.12) represents the domains 1 and 3 by

\[
\psi_1 = A_1 e^{\kappa x} + B_1 e^{-\kappa x} \quad \text{for} \quad -\infty < x \leq -a, \quad (5.3.13)
\]

\[
\psi_3 = A_3 e^{\kappa x} + B_3 e^{-\kappa x} \quad \text{for} \quad a \leq x < \infty. \quad (5.3.14)
\]

The related Mathematica result reads
\[ s13 = \text{DSolve}[\partial_x x \psi[x] - x^2 \psi[x] == 0, \psi, x] // \text{Flatten} \]

\{\psi \to \text{Function}[\{x\}, e^{x x} c_1 + e^{-x x} c_2]\}

In domain 2 the eigenvalue equation takes the form

\[ \psi'' + k^2 \psi = 0, \quad (5.3.15) \]

where \( k^2 = 2 m(V_0 + E)/\hbar^2 > 0 \). The complete solution of (5.3.15) is given by

\[ \psi_2 = A_2 \cos k x + B_2 \sin k x \quad \text{for} \quad -a \leq x \leq a. \quad (5.3.16) \]

The computer algebra result is

\[ s2 = \text{DSolve}[\partial_x x \psi[x] + k^2 \psi[x] == 0, \psi, x] // \text{Flatten} \]

\{\psi \to \text{Function}[\{x\}, c_1 \cos(k x) + c_2 \sin(k x)]\}

From the normalization condition, it follows that the eigenfunctions given by relations (5.3.13) and (5.3.14) require that the coefficients \( B_1 \) and \( A_3 \) vanish (i.e., \( B_1 = A_3 = 0 \)). The remaining parameters \( A_1, B_2, A_2 \) and \( B_3 \) are determined by applying the continuity condition of the wave function and its first derivative at the end points of the potential well (\( x = -a \) and \( x = a \)).

The normalization condition requires

\[ ps1 = \psi[x] /. s13 /. \{C[1] \to A1, C[2] \to B1\} /. B1 \to 0 \]

\[ A1 e^{x x} \]

and

\[ ps3 = \psi[x] /. s13 /. \{C[1] \to A3, C[2] \to B3\} /. A3 \to 0 \]

\[ B3 e^{-x x} \]
The conditions on the domain boundaries read

\[ \begin{align*}
\psi_1 &= \psi_2 \quad \text{and} \quad \psi'_1 = \psi'_2 \quad \text{for} \quad x = -a, \\
\psi_2 &= \psi_3 \quad \text{and} \quad \psi'_2 = \psi'_3 \quad \text{for} \quad x = a
\end{align*} \]  

which can be given as

\[ \begin{align*}
eq 1 &= \psi_1 = \psi_2 = \psi_3 = \psi_4 = 0 \\
\psi'_1 &= \psi'_2 = \psi'_3 = \psi'_4 = 0
\end{align*} \]

The four equations form a homogeneous system of equations for the unknowns \( A_1, B_3, A_2, \) and \( B_2 \). In a matrix representation, we get

\[
\begin{pmatrix}
e^{-\kappa a} & -\cos(k a) & \sin(k a) & 0 \\
\kappa e^{-\kappa a} & -k \sin(k a) & -k \cos(k a) & 0 \\
0 & -\cos(k a) & -\sin(k a) & e^{-\kappa a} \\
0 & k \sin(k a) & -k \cos(k a) & -\kappa e^{-\kappa a}
\end{pmatrix}
\begin{pmatrix}
A_1 \\
A_2 \\
B_1 \\
B_2
\end{pmatrix} = 0. \quad (5.3.19)
\]
A nontrivial solution of Eq. (5.3.19) exists if the determinant of the matrix vanishes. This condition delivers the relation

\[ \kappa^2 - k^2 + 2 \kappa k \cot(2 ka) = 0 \]  

(5.3.20)

with solutions

\[ \kappa = k \tan(ka), \]

(5.3.21)

\[ \kappa = -k \cot(ka). \]

(5.3.22)

If we consider the first of these relations (5.3.21), we find that \( B_2 = 0, B_3 = A_1, \) and \( A_2 \cos ka = A_1 e^{-\kappa a}. \) The second relation, (5.3.22), results in the conditions \( A_2 = 0, B_3 = -A_1, \) and \( B_2 \sin ka = -A_1 e^{-\kappa a}. \)
We can thus distinguish between two systems of eigenfunctions: a symmetric one and an antisymmetric one. The symmetry of the eigenfunctions is obvious if we exchange the coordinates by $x \rightarrow -x$. The symmetrical case is represented by

\begin{align*}
\kappa &= k \tan(k a), \\
\psi_1 &= A_1 e^{k x}, \\
\psi_2 &= A_1 e^{-k a} \frac{\cos(k x)}{\cos(k a)}, \\
\psi_3 &= A_1 e^{-k x} 
\end{align*}

The antisymmetric case follows from the relations

\begin{align*}
\kappa &= -k \cot(k a), \\
\psi_1 &= -A_1 e^{k x}, \\
\psi_2 &= A_1 e^{-k a} \frac{\sin(k x)}{\sin(k a)}, \\
\psi_3 &= A_1 e^{-k x} 
\end{align*}
From the normalization condition
\[ \int_{-\infty}^{\infty} \psi^2 \, dx = \int_{-a}^{a} \psi_1^2 \, dx + \int_{-a}^{a} \psi_2^2 \, dx + \int_{a}^{\infty} \psi_3^2 \, dx, \quad (5.3.31) \]
we get a relation for the undetermined amplitude \( A_1 \)
\[ \frac{1}{A_1^2} = a e^{-2\kappa a} \left( 1 + \frac{1}{\kappa a} + \frac{\kappa}{k^2 a} + \frac{\kappa^2}{k^4} \right). \quad (5.3.32) \]
Relation (5.3.32) is satisfied for both the symmetric and antisymmetric eigenfunctions. To calculate the eigenvalues, note that \( \kappa^2 + k^2 = 2 m V_0 / \hbar^2 > 0 \) is independent of the total energy \( E \). If we introduce the parameter
\[ C^2 = a^2 2 m \frac{V_0}{\hbar^2} = (k^2 + k^2) a^2, \quad (5.3.33) \]
we can eliminate \( \kappa \) from the eigenvalue equations. The equations determining the eigenvalues are now
\[ \frac{\sqrt{C^2-(k a)^2}}{k a} = \tan(k a), \quad (5.3.34) \]
\[ -\frac{k a}{\sqrt{C^2-(k a)^2}} = \tan(k a). \quad (5.3.35) \]
Using relation (5.3.34) or (5.3.35), we can calculate \( k a \) and \( E = \hbar^2 k^2 - 2 m V_0 \).
The problem with the potential well is not the derivation of its solution but the calculation of the eigenvalues determined by Eqs. (5.3.34) and (5.3.35). In the package \texttt{QuantumWell}' (see Section 5.8.1), we solve the problem numerically for varying well depths \( V_0 \) and well widths \( a \). Because the two determining equations of the eigenvalues are transcendent equations, we have to switch to numeric calculations. The left-hand and right-hand sides of Eqs. (5.3.34) and (5.3.35) are graphically represented in Figure 5.3.7 for \( V_0 = 12 \) and \( a = 1 \).

Figure 5.3.7 is created by means of the function \texttt{Spectrum[12,1]} defined in the package \texttt{QuantumWell}'. Also defined in the package \texttt{QuantumWell}' are the eigenfunctions \texttt{PsiSym[]} and \texttt{PsiASym[]}]. The function \texttt{Spectrum[]} provides us with a graphical representation of the eigenfunctions and prints out the related eigenvalues in a list. Some examples of these eigenfunctions are given in Figures 5.3.8 and 5.3.9. Function \texttt{Spectrum[]} creates a sequence of eigenfunction pictures starting with the symmetric ones followed by the antisymmetric ones. Figures 5.3.8 and 5.3.9 contain the superposition of these sequences into one picture.
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The symmetric eigenfunctions for a potential well with depth \( V_0 = 12 \) and width \( a = 1 \). For the given potential depth, there are a total of four eigenvalues, two of which are shown in this figure and the other two are shown in the next figure. The solid eigenfunction with a broad single maximum and no nodes is related to the lowest eigenvalue \( k = 1.30183 \) of the symmetric case. The second symmetric eigenvalue is \( k = 3.81858 \). The corresponding eigenfunction is dashed.

The antisymmetric eigenfunction for the potential with \( V_0 = 12 \) and \( a = 1 \). The two antisymmetric eigenfunctions are correlated with the eigenvalues \( k = 2.5856 \) and \( k = 4.85759 \). The first eigenfunction is represented by a solid curve and the second is dashed.

The sequence of eigenfunctions and eigenvalues for different potential depths \( V_0 \) are generated with the function `Spectrum[]`. For a potential depth of \( V_0 = 44 \) with a potential with \( a = 2 \) we find
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Spectrum[44, 2]

\[ \psi^s \]

\[ k_i = 0.745615 \]
\[ \psi^s \]

\[ k_i = 3.72294 \]

\[ \psi^s \]

\[ k_i = 3.72294 \]

\[ \psi^s \]

\[ k_i = 5.20377 \]
$\psi^s$

$k_i = 6.67289$

$x$

$\psi^s$

$k_i = 8.11658$

$x$

$\psi^a$

$k_i = 1.49099$

$x$
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\[ \psi^a \]

$k_i = 2.97996$

\[ \psi^a \]

$k_i = 4.46439$

\[ \psi^a \]

$k_i = 5.94032$
\[ \psi^a \]

\[ k_i = 7.39956 \]

\[ \psi^a \]

\[ k_i = 8.81407 \]

---- eigenvalues ----

sym eigenvalue k1 = 0.745615, asym eigenvalue k1 = 1.49099

sym eigenvalue k2 = 3.72294, asym eigenvalue k2 = 2.97996

sym eigenvalue k3 = 3.72294, asym eigenvalue k3 = 4.46439

sym eigenvalue k4 = 5.20377, asym eigenvalue k4 = 5.94032

sym eigenvalue k5 = 6.67289, asym eigenvalue k5 = 7.39956

sym eigenvalue k6 = 8.11658, asym eigenvalue k6 = 8.81407
The result is a system allowing 12 eigenvalues corresponding to 6 symmetric and 6 antisymmetric eigenfunctions.

5.4 The Harmonic Oscillator

The potential energy for a stable system exhibits a local minimum. One of the standard methods of physics is to expand the potential energy around the point of a local minimum in a Taylor series,

\[ V = V_0 + \left. \frac{1}{2} \left( \frac{\partial^2 V}{\partial x^2} \right) \right|_{x=0} x^2 + \ldots, \tag{5.4.36} \]

where \( x \) denotes the displacement from the equilibrium point. The potential satisfies \( \frac{\partial V}{\partial x} = 0 \) at the stable equilibrium point. If the particle of mass \( m \) only undergoes small oscillations around the equilibrium point, the first two terms of relation (5.4.36) are sufficient to describe the potential energy. Choosing the origin of the energy to be identical with \( V(0) \) of the expansion, we can express the Hamiltonian of the harmonic oscillator

\[ H_{\text{cl}} = \frac{p^2}{2m} + \frac{k}{2} x^2, \tag{5.4.37} \]

where \( k = \left. \frac{\partial^2 V}{\partial x^2} \right|_{x=0} \) is the spring constant of the oscillator. We already know that the classical solution for the harmonic oscillator is given by a periodic function

\[ x(t) = A \cos(\omega t + \beta) \text{ where } \omega = \sqrt{\frac{k}{m}}, \tag{5.4.38} \]

and the system undergoes harmonic oscillations around the equilibrium point. The time average of the total energy follows from relations (5.4.37) and (5.4.38)
\[
\langle E \rangle_T = \frac{1}{2} A^2 \omega^2
\]

\[
\langle E \rangle_T = \frac{1}{2} m A^2 \omega^2 = m \omega^2 x^2,
\]  \hspace{1cm} (5.4.39)

where \( T \) denotes the period of the oscillation; that is, the time-averaged energy depends quadratically on the amplitude \( A \) of the oscillations.

In this section, our aim is to examine the quantum mechanical properties of the harmonic oscillator and compare them with the classical situation. The transition from classical to quantum mechanics is formally achieved by replacing the classical coordinates with quantum mechanical operators: \( x \rightarrow \hat{x} \) and \( p \rightarrow \hat{p} = \hbar / i \partial_x \). Using the transformations in the Hamiltonian yields the timeless Schrödinger equation in the form of an eigenvalue problem given by

\[
\left( \frac{d^2}{dx^2} - \frac{\omega^2 m^2}{\hbar^2} x^2 + \frac{2mE}{\hbar^2} \right) \psi(x) = 0,
\]  \hspace{1cm} (5.4.40)

where \( \psi \) denotes the set of eigenfunctions of the Hamiltonian. By an appropriate scaling of the spatial coordinate \( \xi = \sqrt{m \omega / \hbar} x \) and of the eigenvalue \( \varepsilon = 2E / (\hbar \omega) \), we get the eigenvalue problem in a standard form

\[
\left( \frac{d^2}{d\xi^2} - \xi^2 + \varepsilon \right) \psi(\xi) = 0.
\]  \hspace{1cm} (5.4.41)

The question here is what type of function \( \psi(\xi) \) satisfies Eq. (5.4.41). As a solution, we try the expression

\[
\psi(\xi) = v(\xi) e^{-\xi^2/2}.
\]  \hspace{1cm} (5.4.42)
\[
\text{ansatz} = \psi \rightarrow \text{Function} \left[ \xi, v[\xi] e^{-\frac{\xi^2}{2}} \right] \\
\psi \rightarrow \text{Function} \left[ \xi, v(\xi) e^{-\frac{\xi^2}{2}} \right]
\]

From Eq. (5.4.41), it follows that the amplitude \( v \) has to satisfy the ODE

\[
v'' - 2 \xi v' + (\epsilon - 1) v(\xi) = 0, \tag{5.4.43}
\]

where primes denote differentiation with respect to \( \xi \). To be physically acceptable, the wave function \( \psi(\xi) \) must be continuous and finite. The amplitude \( v(\xi) \) defined by Eq. (5.4.43) is a finite function if \( v \) is a polynomial of finite order.

\[
\text{solution} = \text{DSolve}[\text{transformedEVeEq}, v, \xi] \text{// Flatten}
\]

\[
\left\{ v \rightarrow \text{Function} \left[ \{\xi\}, c_1 H_{\frac{1}{2}n+1}(\xi) + c_2 \, _1F_1\left( \frac{1 - \epsilon}{4}; \frac{1}{2}; \xi^2 \right) \right] \right\}
\]

This type of solutions exists if

\[
\epsilon = 2n + 1, \text{ where } n = 0, 1, 2, \ldots \tag{5.4.44}
\]

For each value \( n \) there exists a polynomial of order \( n \) which satisfies Eq. (5.4.43). These polynomials are known as Hermite polynomials, defined by

\[
H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}. \tag{5.4.45}
\]

In Mathematica, the Hermite polynomials are identified by the function \text{HermiteH}[\cdot]. The solutions of the eigenvalue problem become with the eigenvalues
a two-component solution determined by \( c_1 \) and \( c_2 \), the integration constants

\[
\text{ve} = v[\xi] / \text{. solution / . eigenValues}
\]

\[
c_1 H_n(\xi) + c_2 \, _1F_1\left(-\frac{n}{2}; \frac{1}{2}; \xi^2\right)
\]

it is known that the hypergeometric function \( _1F_1 \) is divergent for \( \xi \to \pm \infty \). Thus, we can choose \( c_2 = 0 \). The eigenfunctions thus are determined by

\[
\text{ve} = v \to \text{Function}[\xi, \$v] / \text{. } \$v \to (\text{ve} / \text{. } C[2] \to 0)
\]

\[
v \to \text{Function}[\xi, c_1 \, H_n(\xi)]
\]

The eigenfunctions thus can be written

\[
\text{ps} = \psi[x] / \text{. ansatz / . ve}
\]

\[
e^{-\frac{x^2}{2}} \, c_1 \, H_n(x)
\]

where \( c_1 \) is a constant determined by the normalization. The wave function \( \psi \) of the harmonic oscillator is represented in scaled coordinates by

\[
\psi_n(\xi) = \frac{1}{\sqrt{n! \, 2^n \, \sqrt{\pi}}} \, H_n(\xi) \, e^{-\xi^2/2}.
\]  

(5.4.46)

The corresponding eigenvalues of the harmonic oscillator are

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

(5.4.47)

Each eigenvalue has its own eigenfunction which is either even or odd with respect to coordinate reflections in \( \xi \). Note that the eigenvalues and
eigenfunctions have a one-to-one correspondence (i.e. the spectrum is non-degenerate). The first four even and odd eigenfunctions of the harmonic oscillator are depicted in figures 5.4.10 and 5.4.11.

The probability distribution $|\psi|^2$ of finding the harmonic oscillator in a certain state $n$ in the range $\xi \pm d\xi$ is given by

$$|\psi|^2 d\xi = \frac{1}{n! 2^n \sqrt{\pi}} H_n^2(\xi) e^{-\xi^2} d\xi = w_{\text{qm}}(\xi) d\xi.$$  \hfill (5.4.48)

The classical probability of finding a particle in the range $x \pm dx$ is determined by the period $T$ of the oscillator.

$$w_{\text{cl}}(x) = \frac{dt}{T} = \frac{\omega}{2\pi} d\frac{x}{|v|},$$  \hfill (5.4.49)

where $x(t)$ is represented by the classical solution (5.4.38). The corresponding velocity $v$ follows from the time derivative of $x$:

$$v = -A \omega \sqrt{1 - \left(\frac{x}{A}\right)^2}.$$  \hfill (5.4.50)

In scaled variables $\xi$ we find for the classical probability the relation

$$w_{\text{cl}}(\xi) = \frac{1}{2\pi \sqrt{2n+1}} \frac{1}{\sqrt{1-\xi^2/(2n+1)}}.$$  \hfill (5.4.51)

Specifying either the energy or the eigenvalue of the harmonic oscillator enables us to compare the classical probability with the quantum mechanical result. A graphical representation of these two quantities is given in Figures 5.4.12 and 5.4.13. Figure 5.4.12 shows the ground state and Figure 5.4.13 shows the eigenvalue with $n = 5$. It can be clearly seen that the quantum mechanical behavior of the probability density is different from its classical behavior. In the classical case, the particle spends most of its time near the two turning points, where the density $|\psi|^2$ is large. Quantum mechanically, there is a high probability that the particle is located near the center of the potential (ground state). In an excited state, we observe regions where the particle cannot be found (see Figure 5.4.13). This is due to the fact that the quantum mechanical probability density oscillates for $n > 0$, which, in turn, is a consequence of the oscillations of the wave function.

At the classical turning points, a completely different behavior of the quantum particle is apparent. Where the classical particle cannot be found
in quantum mechanics, there is a finite probability for locating a particle outside the potential well. This tunneling of the particle into the potential barrier is unusual and cannot be explained by classical mechanics.

The eigenfunctions and the harmonic potential $V(\xi)$ are superimposed on each other in Figures 5.4.10 and 5.4.11. The related classical and quantum mechanical probabilities are shown in Figures 5.4.12 and 5.4.13. The functions to create these figures for certain eigenvalues are contained in the package `HarmonicOscillator` (see Section 5.8.2).

Symmetric eigenfunctions of the harmonic oscillator $V(x) = x^2$ for eigenvalues $n = 0, 2, 4, 8$. The eigenfunctions are centered around the energetic levels $E = \hbar \omega (n + 1/2)$ corresponding to the eigenvalues $n$. 

Figure 5.4.10.
Antisymmetric eigenfunctions of the harmonic oscillator $V(x) = x^2$ for eigenvalues $n = 1, 3, 5, 9$. The eigenfunctions are centered around the energy levels $E = \hbar \omega (n + 1/2)$ corresponding to the eigenvalues $n$.

Classical and quantum mechanical probability density for the harmonic oscillator in the ground state. The classical probability shows a singular behavior at the turning points of the motion.
The given derivation of the wave function is based on the defining equation of the Hermite polynomials (5.4.41). The solution of the scaled equation (5.4.41) delivers the complete set of eigenfunctions in one step. In the following, we show how the set of eigenfunctions can be derived by an iterative procedure involving creation and annihilation operators $a^+$ and $a^-$. All of the eigenfunctions are created out of the ground state of the harmonic oscillator,

$$\psi_0(x) = \frac{1}{\sqrt{\pi}} e^{-x^2/2}.$$  (5.4.52)

The whole set of eigenfunctions can be created using the following creation and annihilation operators $a^+$ and $a^-$, which act in the spatial and momentum space:

$$a^+ = \frac{1}{\sqrt{2}} \left( \xi - \frac{\partial}{\partial \xi} \right) = \frac{1}{\sqrt{2}} (\hat{\xi} - i \hat{p}),$$ (5.4.53)

$$a^- = \frac{1}{\sqrt{2}} \left( \xi + \frac{\partial}{\partial \xi} \right) = \frac{1}{\sqrt{2}} (\hat{\xi} + i \hat{p}).$$ (5.4.54)

The name of the operators stems from the action of the wave functions respectively creating and annihilating a quantum mechanical state. The actions of operators $a^+$ and $a^-$ can be demonstrated by introducing two functions $\text{aminus}[\cdot]$ and $\text{across}[\cdot]$. The definitions are given below and use the representations of Eqs. (5.4.53) and (5.4.54).
If we apply the defined functions to the ground state, we get the first excited state or, simply, zero. The definition of the ground state is contained in the function $\psi_n$.

$$\psi_n[\xi] := \frac{1}{\sqrt{n!} 2^n \sqrt{\pi}} \text{HermiteH}[n, \xi] e^{-\frac{\xi^2}{2}}$$

We get from the application of the generating operator

$$\sqrt{2} e^{-\frac{\xi^2}{2}} \xi$$

The anhilation operator applied to the ground state gives

$$0$$

Comparing the Mathematica result with the first excited state $\psi_1$, we find that they are equivalent.
This is also true if we incorporate the factor $\sqrt{n!}$ on the right-hand side for higher $n$. The higher eigenfunctions are derived from the ground state by the relation

$$\psi_n(\xi) = \frac{1}{\sqrt{n!}} (a^+)^n \psi_0(x). \quad (5.4.55)$$

Repeatedly applying an operator is achieved by using the function \texttt{Nest[]}.

\texttt{Nest[across, \psi_0[\xi], 5] // Simplify}

$$\sqrt{2} e^{-\xi^2/2} \xi (4 \xi^4 - 20 \xi^2 + 15) \over \sqrt{\pi}$$

We assume that $\psi_n$ is a function of $\xi$. When using \texttt{Nest[]}, we can repeatedly apply the function \texttt{across[]} to the wave function \texttt{Psi[]}. The number of applications of \texttt{across[]} to $\psi_n$ is controlled by the second argument of \texttt{Nest[]}. In the above example, we applied \texttt{across[]} five times to $\psi_n$. The result is the representation of $\psi_5$. If we are interested in the functions preceding $\psi_5$, we can use \texttt{NestList[]} instead.

\texttt{\psiList = NestList[across, \psi_0[\xi], 5] // Simplify}

$$\left\{ e^{-\xi^2/2} \over \sqrt{\pi}, \sqrt{2} e^{-\xi^2/2} \xi \over \sqrt{\pi}, e^{-\xi^2/2} (2 \xi^2 - 1) \over \sqrt{\pi}, \sqrt{2} e^{-\xi^2/2} \xi (2 \xi^2 - 3) \over \sqrt{\pi}, e^{-\xi^2/2} (4 \xi^4 - 12 \xi^2 + 3) \over \sqrt{\pi}, \sqrt{2} e^{-\xi^2/2} \xi (4 \xi^4 - 20 \xi^2 + 15) \over \sqrt{\pi} \right\}$$

The unnormalized wave functions contained in the list $\psiList$ are eigenfunctions of the harmonic oscillator. To determine the normalization factors, we integrate $\psiList$ over the total space:
The normalized eigenfunctions are now given by

\[ \psi_{\text{List}} = \psi_{\text{List norm}} \]

\[
\{ e^{-\frac{x^2}{2}} \sqrt{2} e^{-\frac{x^2}{2}} \xi, e^{-\frac{x^2}{2}} \xi (2\xi^2 - 1), e^{-\frac{x^2}{2}} \xi (2\xi^2 - 3), e^{-\frac{x^2}{2}} (4\xi^4 - 12\xi^2 + 3), e^{-\frac{x^2}{2}} \xi (4\xi^4 - 20\xi^2 + 15) \}
\]

The preceding functions are collected in the package HarmonicOscillator\(^*\). A complete listing is contained in Section 5.8.2.

### 5.5 Anharmonic Oscillator

So far, we have discussed problems which assume harmonic particle motion. In real systems, harmonic motion is the exception rather than the rule. In general, forces are not proportional to linear displacements. From the example of the pendulum in classical mechanics (see Section 2.4.8.6), we recall that the restoring force is not proportional to linear displacements. Another example is that of large molecules in quantum chemistry: In contrast to the binding potential of a diatomic molecule [5.2], the forces between atoms in a large molecule are anharmonic.

The classical work on anharmonic forces in quantum mechanics was initiated by Pöschel and Teller [5.3], who examined the single anharmonic oscillator. Lotmar [5.4] in 1935 studied an ensemble of anharmonic oscillators and established their connection with large molecules. We examine here an altered Pöschel–Teller potential, which today is used in the inverse scattering method of solving nonlinear evolution equations (see
Chapter 3). The interaction potential for a quantum mechanical system was given by Flügge [5.5] in the form

\[ V(x) = -V_0 \text{sech}^2 x, \]

(5.5.56)

where \( V_0 \) is a constant determining the depth of the potential well. The related stationary Schrödinger equation in scaled variables reads

\[ \left( \frac{d^2}{dx^2} + \lambda + V_0 \text{sech}^2 x \right) \psi(x) = 0. \]

(5.5.57)

In our examination, we determine the eigenvalues \( \lambda = 2 \frac{mE}{\hbar^2} \), which depend on the potential depth \( V_0 \). Another point of our study is the form of the wave functions in the asymptotic range \( |x| \rightarrow \infty \). We first introduce some changes in the notation of Eq. (5.5.57). Substituting for the independent variable \( x \) using the relation \( x = \tanh \xi \) in Eq. (5.5.57), we can carry out the transformation by

\[
\text{t1} = \text{PTEVproblem} /. \psi \rightarrow \text{Function}[y, \psi[\xi[y]]]
\]

\[ \psi''(\xi(x)) \xi'(x)^2 + (V_0 \text{sech}^2(x) + \lambda) \psi(\xi(x)) + \psi'(\xi(x)) \xi''(x) = 0 \]

then we replace the new dependent variable \( \xi \) by

\[
\text{t2} = \text{t1} /. \xi \rightarrow \text{Function}[x, \tanh[x]]
\]

\[ \psi''(\tanh(x)) \tanh^4(x) - 2 \tanh(x) \psi'(\tanh(x)) \text{sech}^2(x) + (V_0 \text{sech}^2(x) + \lambda) \psi(\tanh(x)) = 0 \]

Using the inverse of the hyperbolic tan, we get
\[ t3 = t2 \over \pi \rightarrow \text{ArcTanh}[\xi] \over \pi \rightarrow -\lambda \]

\[ \psi''(\xi) (1 - \xi^2) - 2 \xi \psi'(\xi) (1 - \xi^2) + ((1 - \xi^2) V_0 - \lambda) \psi(\xi) = 0 \]

which in traditional representation is

\[
(1 - \xi^2) \frac{d}{d\xi} \left( (1 - \xi^2) \frac{d\psi}{d\xi} \right) + (\lambda + V_0(1 - \xi^2)) \psi = 0 \text{ where } -1 < \xi < 1,
\]

or the equivalent standard representation of Eq. (5.5.58)

\[
\frac{d}{d\xi} \left( (1 - \xi^2) \frac{d\psi}{d\xi} \right) + \left( V_0 + \frac{\lambda}{1-\xi^2} \right) \psi = 0.
\]

Equation (5.5.59) is the defining equation for the associated Legendre polynomials, which is checked by the line

\[
\text{solution} = \text{DSolve}[t3, \psi, \xi] // \text{Flatten}
\]

\[
\{ \psi \rightarrow \text{Function}[[\xi], c_1 P_{1/2}^{\sqrt{\lambda}}(\sqrt{4V_0+1-1})(\xi) + c_2 Q_{1/2}^{\sqrt{\lambda}}(\sqrt{4V_0+1-1})(\xi)]\}
\]

A graphical check of the two Legendre polynomials shows that Legendre \( Q_n^m \) is divergent at the boundaries,
whereas the Legendre $P^n_m$ is finite at the boundaries,

Plot[Evaluate[
  (ψ[ξ] /. solution /. {V₀ → N (N + 1), λ → n²}) /. 
  {N → 25, n → 2, C[1] → 0, C[2] → 1}], 
  {ξ, -1, 1}, AxesLabel -> {"ξ", "ψ"}];
Thus, for a finite solution of the Pöschel–Teller problem we have to assume that $c_2 = 0$. The solution then becomes

$$\text{solution}_\text{PT} = \text{solution} / . \ C[2] \to 0$$

$$\left\{ \psi \to \text{Function}\left[\xi, c_1 P_{\lambda}^{N/2} (\sqrt{4 V_0 + 1} - 1) (\xi) + 0 Q_{\lambda}^{N/2} (\sqrt{4 V_0 + 1} - 1) (\xi)\right]\right\}$$

For the solution of Eq. (5.5.59), we assume, in addition, that the potential depth is given by positive integer $V_0 = N (N + 1)$, where $N$ is a positive number. Equation (5.5.59) possesses discrete bound solutions in the range $\xi \in [-1, 1]$ if and only if $\lambda = -n^2 < 0$ with $n = 1, 2, ..., N$. The eigenfunctions of the Schrödinger equation (5.5.59) are proportional to the associated Legendre functions $P_{\lambda}^n (\xi)$ defined mathematically by

$$P_{\lambda}^n (\xi) = (-1)^n (1 - \xi^2)^{n/2} \frac{d^n}{d \xi^n} P_N (\xi), \quad (5.5.60)$$

where $P_N (\xi)$ are the Legendre polynomials of degree $N$:

$$P_N (\xi) = \frac{1}{N! \sqrt{2}^N} \frac{d^n}{d \xi^n} (\xi^2 - 1)^N. \quad (5.5.61)$$

The constant connecting the Legendre functions with the eigenfunctions of the Pöschel–Teller problem is a product of the normalization condition and the eigenfunctions. The following function represents the eigenfunctions of the Pöschel–Teller system. The associated Legendre polynomials are given by the function \texttt{LegendreP[\]}. 
The eigenfunctions for $N = 4$ are

\[
\text{Table} [\text{PoeschelTeller}[x, i, 4], \{i, 1, 4\}]
\]

\[
\left\{ \frac{1}{4} \sqrt{5} \sqrt{\cosh(2x) + \sinh(2x)} \left( \tanh(x) - 1 \right) \tanh(x) (7 \tanh^2(x) - 3), \right. \\
\frac{1}{4} \sqrt{5} (3 \cosh(2x) - 4) \text{sech}^4(x), -\frac{1}{4} \sqrt{105} \sqrt{\cosh(2x) + \sinh(2x)} \\
\left. (\tanh(x) - 1)^2 \tanh(x) (\tanh(x) + 1), \frac{1}{4} \sqrt{\frac{35}{2}} \text{sech}^4(x) \right\}
\]

The results for $n = 1$ and $n = 3$ are graphically represented in Figure 5.5.14:
So far we derived the discrete spectrum of the modified Pöschel–Teller problem. In the following we consider the continuous eigenvalues \( \lambda = k^2 > 0 \) of the stationary Schrödinger Eq. (5.5.59). The eigenfunctions thus read

\[
\psi(x; k) = a(k) \left( \frac{1 - \xi^2}{4} \right)^{-ik/2} 2F_1 \left( \tilde{a}, \tilde{b}; \frac{1+\xi}{2} \right),
\]

where \( \tilde{a} = 1/2 - i k + \sqrt{V_0 + 1/4} \), \( \tilde{b} = 1/2 - i k - \sqrt{V_0 + 1/4} \) and \( \tilde{c} = 1 - i k \) are constants depending on the model parameters and the eigenvalues. The label \( 2F_1 \) denotes the Gaussian hypergeometric function. In the limit \( x \to \infty \) \( \text{sech}(x) = \sqrt{1 - \xi^2} = 2 e^x / (1 + e^{2x}) \sim 2 e^{-x} \) and the solution reduces to the form \( \psi \sim a(k) e^{-ikx} \). The explicit representation in the limit \( \xi \to -1 \) of the solution (5.5.62) is given by

\[
\psi(x; k) = a(k) e^{-ikx} \left( 1 + \frac{\tilde{a} \tilde{b}}{2 \tilde{c}} (1 + \xi) + O(\xi^2) \right).
\]

The asymptotic expansion of the hypergeometric function \( 2F_1 \) is carried out by first replacing the argument \( \frac{1}{2} (1 + \xi) \) with \( z \) and then by expanding \( 2F_1 \) up to first order around \( z = 0 \).
Series[Hypergeometric2F1[a, b, c, z], {z, 0, 1}]

\[1 + \frac{abz}{c} + O(z^2)\]

Hence, the leading term in the asymptotic representation of the eigenfunction \(\psi\) for \(x \to -\infty\) is

\[\psi \sim a(k) e^{-ikx}.\]  

(5.5.64)

In the other limit \(x \to \infty\), we first transform the hypergeometric function using the linear transformation \(\pFq{2}{1}{a, b, c, z}{d, 2F_1(a, b, c, 1-z)}\), yielding

\[\frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}},\]

\[\frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}}, 1 - ik; \quad \frac{1+\xi}{2}\]

\(= \left(\frac{1-\xi}{2}\right)^{ik}\)

\[\left(2F_1\left(\frac{1}{2} - \sqrt{V_0 + \frac{1}{4}}, \frac{1}{2} + \sqrt{V_0 + \frac{1}{4}} ; 1 - ik; \quad \frac{1-\xi}{2}\right)\right).\]

(5.5.65)

\[
\frac{\Gamma(1+ik)\Gamma(-ik)}{\Gamma\left(\frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}}\right)\Gamma\left(\frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}}\right)} +
\]

\[2F_1\left(\frac{1}{2} - \sqrt{V_0 + \frac{1}{4}}, \frac{1}{2} + \sqrt{V_0 + \frac{1}{4}} ; 1 + ik; \quad \frac{1-\xi}{2}\right).
\]

If the potential depth is of the form \(V_0 = N(N + 1)\), we observe that \(1/2 - \sqrt{V_0 + 1/4}\) is always a negative integer. Since the function \(\Gamma\) is
singular for these points, the second term on the right hand side always vanishes. Taking this into account (5.5.65) reduces to

\[ 2F_1 \left( \frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}}, \right) \]

\[ \frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}}; 1 - ik; \frac{1 + \xi}{2} \right) = \left( \frac{1 - \xi}{2} \right)^i \]

(5.5.66)

\[ 2F_1 \left( \frac{1}{2} - \sqrt{V_0 + \frac{1}{4}} \right) \right) \frac{\Gamma(1+ik) \Gamma(-ik)}{\Gamma(\frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}}) \Gamma(\frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}})} \]

In the limit \( x \to \infty \), the wave function \( \psi \) has the representation

\[ \psi \sim e^{-ikx} + b(k) e^{ikx}, \]  

(5.5.67)

where \( b(k) \) is the reflection coefficient of the wave. Relation (5.5.67) means that an incoming wave of amplitude 1 is reflected by a part determined by \( b(k) \).

An asymptotic expansion of the hypergeometric function for \( \xi \to 1 \) consequently gives us the representation in the form

\[ \psi \sim a(k) \frac{\Gamma(1+ik) \Gamma(-ik)}{\Gamma(\frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}}) \Gamma(\frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}})} e^{-ikx}. \]  

(5.5.68)

Comparing relation (5.5.68) with (5.5.67), we observe that the reflection coefficient of the wave vanishes. The transmission coefficient \( a(k) \) in the case \( V_0 = N (N + 1) \) takes the form

\[ a(k) = \frac{\Gamma(\frac{1}{2} - ik + \sqrt{V_0 + \frac{1}{4}}) \Gamma(\frac{1}{2} - ik - \sqrt{V_0 + \frac{1}{4}})}{\Gamma(1+ik) \Gamma(-ik)}. \]  

(5.5.69)

A wave is free of reflection if the potential takes the form \( V = V_0 \sech(x) \) and the depth of the potential is an integer number \( V_0 = N (N + 1) \).

For \( V_0 = N (N + 1) \), the entire calculation procedure can be activated by \texttt{AsymptoticPT[]} which is part of the package \texttt{Anharmonic-Oscillator} (see Section 5.8.3). By calling \texttt{AsymptoticPT[]} we get the asymptotic representation of the eigenfunction in the limits \( x \to \pm \infty \). The
results of the expansion are contained in the global variables \(w1a\) and \(w2a\). Function \texttt{AsymptoticPT[]} can also handle the case in which \(N\) is an integer. In addition to the eigenfunction, function \texttt{AsymptoticPT[]} delivers information about the reflection and transmission coefficients \(|b|^2\) and \(|a|^2\). These two characteristic properties of the scattering problem satisfy \(|a|^2 + |b|^2 = 1\).

\texttt{PlotPT[]}, which is also part of the package \texttt{AnharmonicOscillator\^{}}, gives a graphical representation of the reflection and transmission coefficients. This function plots five curves for different \(k\) values. The range of the \(k\) values is specified as first and second arguments in the function \texttt{PlotPT[]}. The third argument of \texttt{PlotPT[]} determines the coefficient. We can choose between two types of coefficient. Whereas "t" will create a plot for the transition coefficient, the "r" string will create the reflection plot. Two examples for \(k_{\text{ini}} = 0.05\) and \(k_{\text{end}} = 0.5\) are given in Figures 5.5.15 and 5.5.16. The pictures are created by

\begin{verbatim}
PlotPT[0.05, .5, "r"];
\end{verbatim}

![Graph of |b|^2 vs N](image)

The reflection coefficient \(|b|^2\) is plotted as a function of \(N\). The ensemble of curves represent the reflection coefficient for energy values \(k\) in the interval \(k \in [0.05, 0.5]\) for \(N \in [1, 2]\). The top curve represents the value \(k = 0.05\). The other \(k\) values > 0.05 follow below the top curve.

and

\begin{verbatim}
PlotPT[0.05, .5, "t"];
\end{verbatim}

Figure 5.5.15.
The transmission coefficient $|a|^2$ of the Pöschel–Teller potential is plotted across the depth parameter $N$ of the potential. The energy values $k$ are taken from the interval $k \in [0.05, 0.5]$ for $N \in [1, 2]$. The lowest curve corresponds to $k = 0.05$.

The structure represented in Figures 5.5.15 and 5.5.16 is repeated in each of the intervals $[N, N+1] \mid N \geq 1$. Two neighboring intervals for a potential depth ranging between $V_0 = 2$ and $V_0 = 6$ ($N = 1$ and $N = 2$) are represented in Figure 5.5.17. In this figure, the reflection coefficient is shown for a range of $k$ values by means of a surface plot. The pictures are created by the sequence

\[
\text{th} = \text{AsymptoticPT}[\text{NN}, \text{kk}];
\]

\[
\text{Plot3D}[	ext{Evaluate}[\text{th}[2]], \{\text{NN}, 1, 3\},
\{\text{kk}, 0.05, 0.75\}, \text{AxesLabel} \rightarrow \{"N", "k", "|b|^2\}];
\]

\[
\text{Plot3D}[	ext{Evaluate}[\text{th}[1]], \{\text{NN}, 1, 3\}, \{\text{kk}, 0.05, 0.75\},
\text{AxesLabel} \rightarrow \{"N", "k", "|a|^2\}];
\]
The reflection and transmission coefficient is plotted as a function of $N$ and $k$. The values for the potential depth are taken from $N \in \{1, 3\}$ and the energy interval is $k \in [0.05, 0.75]$. We observe that the reflection coefficient decreases as the energy increases. On the other hand, the transmission coefficient increases with the increase in energy.

A collection of functions examining the anharmonic Pöschel-Teller potential is contained in the package `AnharmonicOscillator`. Useful
functions in examining the anharmonic model are PoeschelTeller[], AsymptoticPT[] and PlotPT[] (compare the complete listing in Section 5.8.3).

5.6 Motion in the Central Force Field

The stationary states of a particle in a spherically symmetric potential are determined by the Schrödinger equation with the Hamiltonian operator

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r), \]  

(5.6.70)

where \( r = \sqrt{x^2 + y^2 + z^2} \) measures the distance of the particle from the origin of the potential. Using the spherical symmetry of the problem, we can rewrite the Schrödinger equation in spherical coordinates

\[
\left[-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\hbar^2}{2mr^2} \left( \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \phi^2} \right) + V(r) - E \right] \psi(r, \vartheta, \phi) = 0, \]

(5.6.71)

or, in a more compact form,

\[
\left(-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2}{2mr^2} \hat{L}^2 + V(r) - E \right) \psi = 0, \]

(5.6.72)

where \( \hat{L}^2 \) is the square of the angular momentum operator. Problems which can be identified by such a Hamiltonian operator are very common in physics such as follows:

1. The H-atom
2. An ion with one electron
3. The three-dimensional harmonic oscillator
4. The three-dimensional potential well, quantum dot
5. The Yukawa particle (a shielded Coulomb potential)
6. The free particle.

In close analogy to classical motion in a central field, we find in quantum mechanics that the angular momentum is conserved. The angular momentum is defined by
\[ \mathbf{L} = \mathbf{r} \times \mathbf{p}. \]  
(5.6.73)

Other constants of motion are the Hamiltonian, the square of the angular momentum, and the \( z \)-component of the angular momentum. The related operators \( \hat{H}, \hat{L}^2, \) and \( \hat{L}_z \) create a complete system of commuting operators. The solutions of the related eigenvalue problems completely determine the properties of the system. As in classical mechanics, we can take advantage of the conservation of angular momentum to reduce a three-dimensional problem to a one-dimensional one. Similarly, we can use the conservation of the angular momentum to separate the coordinates \( r, \theta, \) and \( \phi \) in the Schrödinger equation (5.6.72).

The dependence of the wave function \( \psi \) on the angles \( \theta \) and \( \phi \) is determined by the operators \( \hat{L}^2 \) and \( \hat{L}_z \). In spherical coordinates, we can express the \( z \) component of the angular momentum by \( \hat{L}_z = -i \hbar \frac{\partial}{\partial \phi}. \) The eigenvalues of \( \hat{L}_z \), are found by solving the equation

\[
\frac{\hbar}{i} \frac{\partial \psi(\phi)}{\partial \phi} = L_z \psi(\phi),
\]
(5.6.74)

where \( 0 \leq \phi \leq 2 \pi \). The solutions of Eq. (5.6.74) are

\[
\psi(\phi) = A e^{\frac{im}{\hbar} \phi}. \tag{5.6.75}
\]

Since the solution (5.6.75) must be uniquely defined, it has to satisfy the condition

\[
\psi(\phi) = \psi(\phi + 2 \pi). \tag{5.6.76}
\]

The eigenvalues \( L_z / \hbar = m \) where \( m = 0, \pm 1, \pm 2, \ldots \) satisfy condition (5.6.76). The eigenvalues of the operator \( \hat{L}_z \) are thus discrete and represented by

\[
L_z = \hbar m, \text{ where } m = 0, \pm 1, \pm 2, \ldots \tag{5.6.77}
\]

Since we require normalized eigenfunctions (i.e., \( \int_0^{2\pi} \psi^*_m \psi_m d\phi = 1 \)), the normalized solutions are

\[
\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{5.6.78}
\]

A similar treatment yields the eigenvalues and eigenfunctions of the square of the angular momentum \( \hat{L}^2 \) from the differential equation

\[
\hat{L}^2 \psi = L^2 \psi. \tag{5.6.79}
\]
In spherical coordinates, the operator $\hat{L}^2$ is represented by

$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \quad (5.6.80)$$

Inserting expression (5.6.80) into Eq. (5.6.79), we get

$$\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{L^2}{\hbar^2} \right) \psi(\theta, \phi) = 0. \quad (5.6.81)$$

Equation (5.6.81) is the defining equation of the spherical harmonics $Y_{l,m}$ if the eigenvalues satisfy $L^2 = \hbar^2 l (l + 1)$ with $l = 0, 1, 2, \ldots$:

$$\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + l (l + 1) \right) Y_{l,m}(\theta, \phi) = 0. \quad (5.6.82)$$

The eigenvalues of $\hat{L}^2$ are determined by the quantum numbers $l = 0, 1, 2, \ldots$. Their related eigenfunctions are the spherical harmonics $Y_{l,m}$ of order $l$. Comparing the structure of the eigenfunctions of the harmonic oscillator to that of the eigenfunctions of the angular momentum $\hat{L}^2$, we observe that in the case of $\hat{L}^2$ with eigenvalues $L^2 = \hbar^2 l (l + 1)$, there are $2l + 1$ eigenfunctions $Y_{l,m}$. The eigenfunctions $Y_{l,m}$, however, are different in the second quantum number $m$, which is known as the magnetic quantum number. For a fixed value of $L^2$, $m$ counts the different projections on the $z$-axis. If we determine $l$, we find different values for $m$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \quad (5.6.83)$$

and limited to the range $-l \leq m \leq l$. For the proof of the above relations, we refer the reader to the book by Cohen-Tannoudji et al. [5.6].

The complete representation of the spherical harmonics for positive $m$ is

$$Y_{l,m}(\theta, \phi) = \frac{(-1)^m}{\sqrt{2\pi}} e^{i m \phi} \sqrt{\frac{(2l + 1)(l - m)!}{2(l + m)!}} \sin^m \theta P^m_l(\cos \theta). \quad (5.6.84)$$

$P^m_l(x)$ denotes the $m$th associated Legendre function of order $l$. In case of negative quantum numbers $m$, we use the relation

$$Y_{l,-m}(\theta, \phi) = (-1)^m Y_{l,m}^\ast(\theta, \phi). \quad (5.6.85)$$

If we use the representation of the spherical harmonics given by relation (5.6.84), it is easy to show that the $Y_{l,m}$ are also eigenfunctions of the operator $\hat{L}_z$. By a simple calculation, we find

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} Y_{l,m}(\theta, \phi) = \hbar m Y_{l,m}(\theta, \phi). \quad (5.6.86)$$
We now can state that the spherical harmonics are eigenfunctions of both the $z$-component of the angular momentum operator and the square of the angular momentum operator. The corresponding eigenvalues are

\[ L^2 = \hbar^2 l (l + 1) \quad \text{and} \quad L_z = \hbar m. \quad (5.6.87) \]

The spherical harmonics are accessed in Mathematica by the function SphericalHarmonicY[] available in the package CentralField` in Section 5.8.4. The Legendre polynomials are available using LegendreP[].

So far, we have determined the eigenfunctions depending on $J$ and $f$. Separating the angular terms from the radial part of the wave function, we get the representation

\[ \psi(r, \vartheta, \phi) = h(r) Y_{l,m}(\vartheta, \phi). \quad (5.6.88) \]

Relation (5.6.88) used with Eq. (5.6.72) allows the derivation of a determining equation for the radial part $h(r)$ of the wave function $\psi$. The wave function separates because the coordinate system of our problem is separable. The radial function $h(r)$ is dependent on the energy $E$, the quantum number $l$, and the potential energy $V(r)$. Consequently, the radial part of the wave function is independent of $m$: In a spherical potential, there are no distinguishing directions breaking the symmetry.

Inserting relation (5.6.88) into the Schrödinger equation (5.6.72) and using our above results for the angular momentum, we get, after substituting $u(r) = r h(r)$, the eigenvalue problem for the radial part of the wave function

\[ \left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right) u(r) = E u(r). \quad (5.6.89) \]

$u(r) = r h(r)$ is substituted since for $r \to 0$, the function $h(r)$ has to be finite (i.e., $u(r) \to 0$ for $r \to 0$). Note that in Eq. (5.6.89), all parameters are known except for potential $V(r)$. For the following discussion, we assume that the potential $V(r)$ represents a Coulomb interaction of the two particles,

\[ V(r) = -\frac{Ze^2}{r}. \quad (5.6.90) \]

This type of potential applies to the hydrogen and hydrogenlike atoms where $Z = 1$ as well as to ionized atoms like He$^+$, Li$^{2+}$, and so forth.
The stationary states of an electron in a Coulomb potential result from the eigenvalue equation

\[
\left( \frac{d^2}{dr^2} + \frac{2mE}{h^2} + \frac{2mZe^2}{h^2r} - \frac{l(l+1)}{r^2} \right) u(r) = 0. \tag{5.6.91}
\]

To carry out our calculation, it is convenient to introduce scaled variables

\[
\rho = \frac{r}{a} \quad \text{and} \quad \epsilon = \frac{E}{E_0},
\]

where \( a = \hbar^2/(me^2) \approx 5.29 \times 10^{-11} \) m is Bohr’s radius and \( E_0 = e^2/(2a) = me^4/\hbar^2 \approx 13.5 \) eV, the ionization energy of the hydrogen atom. The Schrödinger equation (5.6.91) is thus represented by

\[
\left( \frac{d^2}{d\rho^2} + \epsilon + \frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2} \right) u(\rho) = 0, \tag{5.6.93}
\]

which allows a representation as

\[
\text{radialEVProblem} = \partial_{\rho,\rho} u[\rho] + \left( \epsilon + \frac{2Z}{\rho} - \frac{1}{\rho^2} \right) u[\rho] = 0
\]

\[
\left( - \frac{l(l+1)}{\rho^2} + \epsilon + \frac{2Z}{\rho} \right) u(\rho) + u''(\rho) = 0
\]

We restrict our calculations to the case of bound states characterized by negative energy values. To find appropriate representations of a solution ansatz for \( u(r) \), we examine the limits \( r \to 0 \) and \( r \to \infty \). The function \( u(\rho) \) is either given by a polynomial in \( \rho \) \( u_0(\rho) = \rho^\alpha \) or by an exponential relation \( u_0 = A e^{-\gamma \rho} + B e^{\gamma \rho} \), where \( \gamma^2 = -\epsilon \). The results of these expressions are conditions for the parameters \( \alpha \) and \( B \) which satisfy \( \alpha = l + 1, B = 0 \). Using these results both expressions are reducible to

\[
u_0(\rho) = \rho^{l+1} e^{-\gamma \rho} f(\rho)
\]

or, in a manageable form,

\[
\text{tr1} = u \to \text{Function}[\rho, \rho^{l+1} e^{-\gamma \rho} f[\rho]]
\]

\[
u \to \text{Function}[\rho, \rho^{l+1} e^{-\gamma \rho} f(\rho)]
\]
Substituting expressions (5.6.94) into Eq. (5.6.93) and using \( x = 2 \gamma \rho \), we get the standard form of Kummer's differential equation:

\[
x f'' + (2 (l + 1) - x) f' - \left( l + 1 - \frac{Z}{\gamma} \right) f = 0,
\]

(5.6.95)

where primes denote differentiation with respect to \( x \). The Mathematica version of this transformation using original variables is gained by

\[
gl = \text{radialEVProblem} /\!\!/ \text{tr1} /\!\!/ \text{Simplify}
\]

\[
e^{-\gamma \rho} \rho^l
\]

\[
((\rho \gamma^2 - 2 (l + 1) \gamma + 2 Z + \epsilon \rho) f(\rho) + 2 (l - \gamma \rho + 1) f'(\rho) + \rho f''(\rho)) = 0
\]

The solution can be directly derived from

\[
solution = \text{DSolve}[\text{gl}, f, \rho] /\!\!/ \text{Flatten}
\]

\[
\{f \to \text{Function}[\{\rho\}, e^{(\gamma - i \sqrt{\epsilon}) \rho} c_1 U\left(-\frac{-\sqrt{\epsilon} l - i Z - \sqrt{\epsilon}}{\sqrt{\epsilon}}, 2 l + 2, 2 i \sqrt{\epsilon} \rho\right) + e^{(\gamma - i \sqrt{\epsilon}) \rho} c_2 L^{{l+1}}_e^{-l+2;2} \left(2 i \sqrt{\epsilon} \rho\right)\}
\]

which simplifies if we assume that the energies \( \epsilon \) are negative:

\[
f[\rho] /\!\!/ \text{solution} /\!\!/ \epsilon \to -\epsilon /\!\!/ \text{PowerExpand} /\!\!/ \text{Simplify}
\]

\[
e^{(\gamma + \sqrt{\epsilon}) \rho} \left\{ c_1 U\left(1 + \frac{Z}{\sqrt{\epsilon}} + 1, 2 l + 2, -2 \sqrt{\epsilon} \rho\right) + c_2 L^{{l+1}}_{-\frac{Z}{{\sqrt{\epsilon}}}}(-2 \sqrt{\epsilon} \rho)\right\}
\]

The solutions of Eq. (5.6.95) are, in general, confluent hypergeometric functions \( \left(_1 F_1\right) \)

\[
f_1(\rho) = c \left(_1 F_1\right)\left(l + 1 - \frac{Z}{\gamma}, 2 l + 2; 2 \gamma \rho\right)
\]

(5.6.96)

reducing to Laguerre's and Kummer's function. To satisfy the normalization condition, series (5.6.96) must terminate at a finite order.
This restriction excludes Kummer’s function \( H_{1} = 0 \) and induces the quantization of the energy values by
\[
l + 1 - \frac{Z}{\gamma} = -n_r, \quad \text{with} \quad n_r = 0, 1, 2, \ldots \tag{5.6.97}
\]
The solution of Eq. (5.6.97) with respect to \( g \) delivers
\[
g = \frac{Z}{n_r + l + 1}, \tag{5.6.98}
\]
or, by replacing \( g^2 = -\varepsilon \), yields energy values \( \varepsilon = -Z^2 / (n_r + l + 1)^2 \) to be
\[
E = -\frac{Z^2}{(n_r + l + 1)^2} E_0 = -\frac{Z^2}{n^2} E_0. \tag{5.6.99}
\]
The quantum number \( n \) is the principal quantum number determined by the radial quantum number \( n_r \) \( (n_r = 0, 1, 2, \ldots) \) and the angular quantum number \( l \) \( (l = 0, 1, 2, \ldots) \). The wave function of the electron in the Coulomb potential is given by
\[
\psi_{n,l,m}(\rho, \vartheta, \phi) = N_{n,l} \rho^{Z/n} \, _1F_1 \left( l + 1 - n, 2 \, l + 2; \frac{2Z}{n} \rho \right) Y_{l,m}(\vartheta, \phi), \tag{5.6.100}
\]
where \( N_{n,l} \) is the normalization constant
\[
N_{n,l} = \frac{1}{(2l+1)!} \sqrt{\frac{(n+l)!}{2n(n-l-1)!}} \left( \frac{2Z}{n} \right)^{(l+3)/2}. \tag{5.6.101}
\]
The radial part of the wave function \( h(\rho) \) consists of
\[
h_{n,l}(\rho) = N_{n,l} \rho^l e^{-Z\rho/n} \, _1F_1 \left( l + 1 - n, 2 \, l + 2; \frac{2Z}{n} \rho \right). \tag{5.6.102}
\]
Since the first argument in the hypergeometric function is a negative integer, the function \( _1F_1 \) in the radial part reduces to a polynomial known as a Laguerre polynomial. In Mathematica, the Laguerre polynomials are denoted by \texttt{LaguerreL[]}\(^\text{\textregistered}\). One useful parameter of the radial wave function is \( n_r = n - l - 1 \). This parameter counts the nodes of the eigenfunction along the horizontal axis. This behavior is shown in Figure 5.6.18 for \( n = 3 \) and \( l = 0, 1, 2 \). Figure 5.6.18 is created by

```mathematica
Plot[
{Radial[r, 3, 0, 1], Radial[r, 3, 1, 1],
Radial[r, 3, 2, 1]}, {r, 0, 25},
AxesLabel -> {"r", "h"}, Prolog -> Thickness[0.001]]
```
The function `Radial[]` used in the `Plot[]` function is part of the package `CentralField`. This package also contains `Angle[]` for the angular part of the wave function. The definition of `Angle[]` is, in some ways, redundant since `Mathematica` accounts for the angular part of the wave function under the name `SphericalHarmonicY[]`. However, we separately define the angular part of the wave function to show how relations (5.6.84) and (5.6.85) are expressed in terms of `Mathematica`.

The above wave function is applied to representations of orbitals of an atom or a molecule. Chemists, for example, work with molecular orbital theory to describe the binding of atoms. This theory makes extensive use of the angular wave functions $Y_{l,m}$. In order to describe the binding of a molecule, it is necessary to use a linear combination of the angular parts of the wave function. We create such a superposition of the $Y_{l,m}$’s by the function `Orbital[]`, which is part of the package `CentralField`. `Orbital[]` creates sums and differences of the spherical harmonics in the form

$$w(\theta, \phi) = (| Y \rangle_{l,m} \pm Y_{l,-m} |)^2. \quad (5.6.103)$$

Relation (5.6.103) represents the probability of finding an electron within a certain domain of the angular part of the space. In Figures 5.6.19-22, we have plotted some particular examples for orbitals.
Figure 5.6.19. Angular part of the wave function for $l = 2$ and $m = 0$. 

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Figure 5.6.20. Orbital for the quantum numbers \( l = 2 \) and \( m = \pm 1 \) formed from the difference \( |Y_{2,1} - Y_{2,-1}|^2 \).

Figure 5.6.21. A plot of the sum of the wave functions with quantum numbers \( l = 2 \) and \( m = \pm 2 \).
Figures 5.6.19-22 show an inner view of the orbitals for a certain range of $\phi$. Similar pictures for other quantum numbers are created by the superposition of the angular wave functions $Y_{l,m}$ with the help of `Angle[]`. The figures of the orbitals are created by the function sequence
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\textbf{AnglePlot[Orbital[l,m,\theta,\phi,\text{"plus"}],\theta,\phi].} An example of the application of this function is given below.

\texttt{AnglePlot[Orbital[\theta, \phi, 4, 2, \text{"minus"}], \theta, \phi];}

---

\section*{5.7 Second Virial Coefficient and Its Quantum Corrections}

Nearly 100 years ago, Kannerligh Onnes described the thermodynamic behavior of a gas in form of an equation which should become as virial equation of state one of the most successful theories for the link between the microscopic physics of molecular interactions and macroscopic thermodynamic properties:

\[
\frac{P V}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots, \tag{5.7.104}
\]
where \( B(T) \), \( C(T) \), and \( D(T) \) are the second, third, and fourth virial coefficients of increasing complexity, \( R \) is the gas constant, \( V \) is the volume, and \( T \) is the absolute temperature in the virial equation.

Immediately after the introduction of the virial equation, Ornstein calculated the second virial coefficient (SVC) using Gibb's statistical calculation techniques

\[
B(T) = -2 \pi N_A \int_0^\infty \left( \frac{e^{-U(r)/k_B T}}{k_B T} - 1 \right) r^2 \, dr
\]

(5.7.105)

where \( N_A \) is Avogadro's constant, \( U(r) \) is the intermolecular potential, and \( k_B \) is the Boltzmann constant. The exciting history of the virial equation and its relation to the phenomenological van der Waals equation as well as the history of the calculation of \( B(T) \) for various molecular potentials is covered in an excellent article by Rowlinson [5.7]. He discusses the van der Waals equation and its implications to the development of the real gas and the liquid. In spite of the strong influence of the van der Waals equation on the study of molecular interactions, it could not describe accurately the behavior of any substance. Rowlinson points out how an empirical proposal of Onnes was combined with the theoretical development of Gibbs and Ornstein to produce the viral equation of state, one of the most useful theories of any state of matter.

Before the theory was worked out completely and before the quantum theory of the intermolecular potential was developed, the second virial coefficient (SVC) was investigated by interaction potentials of the kind

\[
U(r) = \left( \frac{A}{r^m} - \frac{B}{r^n} \right)
\]

(5.7.106)

mostly associated with Lennard-Jones [5.8]. After the derivation of the dispersion forces proportional to \( r^{-6} \) by London [5.9], the \((12 - 6)\)-potential has become very popular. Theory and numerical results of this and related potential are discussed in detail in the classical monographs by Hirschfelder et al. [5.10] on the molecular theory of gases and liquids and by Mason and Spurling [5.11] on the viral equation of state. As will be pointed out subsequently, the SVC is an integral over a function of \( U(r) \).

In teaching statistical thermodynamics, however, one wants to give a final result not as an integral but as an explicit function of the temperature and
molecular parameters. Especially for the \((m-n)\)-Lennard-Jones potential (abbreviated by \((m,n)\)-LJ) analytical results in terms of series expansions with the \(\Gamma\) function have been given in [5.12]. It was pointed out, however, by several authors, also in recent textbooks that for the potential, especially the \(12-6\), no closed solution exists. That this statement is not correct will be shown subsequently in the sketch on analytical approaches to the SVC. What is lacking, however, is a consistent derivation of the SVC, its quantum corrections, and its temperature derivatives from one integral. The present section aims at such a unified derivation. Also, other results in the literature will be reduced to these results.

### 5.7.1 The SVC and Its Relation to Thermodynamic Properties

The necessary formulas for the SVC and its quantum corrections are collected to show the importance for thermodynamic functions. The virial equation of state was given in Eq. (5.7.104). A knowledge of the virial coefficients and their temperature dependence describes the \(pVT\) behavior of the gas completely, if one assumes the convergence of the series. For the classical part \(B_c\) of the \(B(T)\), one derives

\[
B_c(T) = 2\pi N_A \int_0^\infty (e^{-\beta U(r)} - 1) r^2 dr
\]

\[
= -\frac{2\pi N_A \beta}{3} \int_0^\infty e^{-\beta U(r)} \left( \frac{dU}{dr} \right) r^3 dr
\]  

(5.7.107)

after partial integration. \(N_A\) is Avogadro's number, \(\beta = (k_B T)^{-1}\), \(k_B\) is the Boltzmann constant, and \(U(r)\) is the interatomic or intermolecular potential. The index \(c\) on \(B\) denotes the purely classical part of our considerations. For low temperatures and light atoms and molecules like He, Ne, and \(H_2\), one has to take quantum mechanics into account. It was shown with the \((12-6)\) potential for He that at very low temperatures, the full quantum mechanical calculation has to be performed, but for temperatures above 5K, the semiclassical expansion without the symmetry term is sufficient:

\[
B = B_c + \frac{\hbar^2}{m} B_{q_1} + \left( \frac{\hbar^2}{m} \right)^2 B_{q_2} + \ldots
\]

(5.7.108)

with

\[
B_{q_1} = \frac{\pi N_A \beta^3}{6} \int_0^\infty e^{-\beta U} U^2 r^2 dr
\]

(5.7.109)
The SVC is important for the correct calculation of thermodynamic functions at high temperatures, as it includes not only the bound states usually only taken into account in the calculation of partition functions but also meta-stable and continuum states. This was shown explicitly for a Rydberg diatomic potential by Sinanoglu and Pitzer [5.13]; a more recent discussion on the splitting of the phase space of the SVC was given by Friend [5.14].

The thermodynamic functions related to the SVC, $B$, and its temperature derivatives $B_n = T^n (d^n B / dT^n)$ are given by the internal energy

$$\frac{\tilde{U} - \tilde{U}^0}{RT} = -\left( \frac{B_1}{V} + \ldots \right),$$

the enthalpy

$$\frac{\tilde{H} - \tilde{H}^0}{RT} = \frac{B - B_1}{V} + \ldots,$$

the entropy

$$\frac{\tilde{S} - \tilde{S}^0}{R} = -\left\{ \ln p + \frac{B_1}{V} + \frac{B^2}{2V} + \ldots \right\},$$

and the specific heat

$$\frac{\tilde{C}_p - \tilde{C}_p^0}{RT} = -\left\{ \frac{B_2}{V} - \frac{(B-B_1)^2}{V} + \ldots \right\}$$

$$\mu_T C_p^0 = -[B - T B'] +$$

$$\frac{1}{V} [2B^2 - 2TB'B' - \frac{RT^2}{C_p^0} (B - T B') B'' + \ldots] + \ldots.$$

Thermodynamic functions give the extent of the values from the value of a perfect gas in its normal state denoted by a superscript ($^o$); the tilde ($\sim$) represents molar quantities. From these formulas follows that for a complete analytical theory of the SVC and for thermodynamic functions with two-body interactions, one has to calculate
\[ B(T) = B_c(T) + B_{q_1}(T) + B_{q_2}(T) + \ldots \]  
(5.7.116)

### 5.7.2 Calculation of the Classical SVC \( B_c(T) \) for the \((2n - n)\)-Potential

A useful method of evaluating the thermodynamic properties of gases at high temperatures is to treat the entire gas as a monoatomic assembly with gas imperfections given by

\[ \frac{P}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots, \]  
(5.7.117)

where \( B(T) \), \( C(T) \), and \( D(T) \) denote the second, third, and fourth virial coefficients, respectively. Our interest here is the second virial coefficient \( B_c(T) \) (SVC) and its quantum mechanical corrections up to second order. All of the thermodynamic properties of the gas are then obtained directly from the equation of state as represented by Eq. (5.7.117).

In the following calculations, we will examine the two-parameter Lennard-Jones potential (LJ):

\[
\text{LJ} = 2 \left( \frac{n \epsilon}{n-m} \right)^{m} \left( \frac{\sigma^n}{r} - \left( \frac{\sigma^n}{r} \right)^{m} \right) 
\]

\[
2 \left( \frac{n \epsilon}{n-m} \right)^{m} \left( - \left( \frac{\sigma^n}{r} \right)^{m} + \left( \frac{\sigma^n}{r} \right)^{n} \right) 
\]

where \( \epsilon \) is the well depth and \( \sigma \) is the internuclear distance. Our interest is mainly concerned with the case when \( m = n \) and \( n \) is replaced by an even number of \( m \). As a two-parameter potential with \( \epsilon, \sigma \), the \((m - n)\)-potential, is simple but not very flexible. An additional parameter is introduced in the spherical Kihara hard-core potential [5.15]:

\[
\text{Kihara} = 2 n \left( \frac{n}{m} \right)^{m} \epsilon \left( \frac{\sigma - 2a}{r - 2a} \right)^{n} - \left( \frac{\sigma - 2a}{r - 2a} \right)^{m} 
\]

\[
2 n \left( \frac{n}{m} \right)^{m} \epsilon \left( - \left( \frac{\sigma - 2a + \sigma}{-2a + r} \right)^{m} + \left( \frac{\sigma - 2a + \sigma}{-2a + r} \right)^{n} \right) 
\]

\[-m + n \]
The Kihara potential is $\infty$ for $r < 2a$ and is connected with the LJ potential if we replace the radial coordinate $r$, the potential depth $\epsilon$, and intermolecular distance by

$$\text{transforms} = \{ r \rightarrow 2a + r, \epsilon \rightarrow \frac{(n - m) \left( \frac{m \epsilon}{n-m} \right)^{\frac{m}{n-m}}}{n}, \sigma \rightarrow 2a + \sigma \};$$

Applying these transformations to the Kihara potential, we find

$$tK = \text{Simplify}[\text{Kihara} /. \text{transforms}]$$

$$2 \left( \frac{n}{m} \right)^{\frac{m}{n-m}} \left( \frac{m \epsilon}{n-m} \right)^{\frac{m}{n-m}} \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^m$$

Comparing the LJ potential with the transformed Kihara potential, we observe their equivalence:

$$\text{PowerExpand}[tK == \text{LJ}]$$

True

meaning that both potentials are identical. Thus, we can unify the calculations for one type of potential. We therefore restrict our considerations to the LJ potential. We note that the following results are also valid in case of the Kihara potential. Our main interest is concerned with a subclass of LJ potentials where the exponents $n, m$, are given by an even integer and the integer itself. For such a combination, the LJ potential reduces to a $(2n - n)$-potential, which is given by

$$U(r) = \text{LJ} /. \{ n \rightarrow 2n, m \rightarrow n \}$$

$$4 \epsilon \left( \left( \frac{\sigma}{r} \right)^{2n} - \left( \frac{\sigma}{r} \right)^{n} \right)$$
The first derivative, the intermolecular force, needed to evaluate (5.7.107) follows from the potential by differentiating $U(r)$ with respect to $r$:

$$\text{Force} = \text{Simplify}\left[-\frac{\partial U(r)}{\partial r}\right]$$

$$4n\epsilon\left(\frac{\sigma}{r}\right)^n\left(2\left(\frac{\sigma}{r}\right)^n - 1\right) \frac{1}{r}$$

Inserting the potential $U(r)$ and the force into Eq. (5.7.107), we find

$$B_c = \frac{1}{3} (2\pi N_A \beta) \int_0^\infty e^{-\beta U(r)} \text{Force} r^3 \, dr$$

Integrate::gener : Unable to check convergence. More…

$$\frac{2}{3} \pi \beta \left(\int_0^\infty 4 e^{-4\beta\epsilon\left(\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{\epsilon}\right)^n\right)} n r^2 \epsilon\left(\frac{\sigma}{r}\right)^n \left(2\left(\frac{\sigma}{r}\right)^n - 1\right) \, dr\right) N_A$$

At first glance, the result is disappointing because Mathematica does not evaluate the integral. However, it returns the integral containing the explicit expressions for the potential $U$ and its first derivative. A second examination of the integral reveals that we found a Laplace transform of the first derivative of $U$, the negative force. To recognize that the above integral represents a Laplace transform, let us introduce the following substitutions:

$$\text{substitution} = \{r \rightarrow \sigma t^{-1/n}, \text{DifferentialD}(r) \rightarrow \frac{\partial (\sigma t^{-1/n})}{\partial t} \text{DifferentialD}(t)\};$$

Applying this substitution to the integrand $B_c$, we are able to reduce (5.7.107) to a Laplace integral. The integrand of this integral is calculated by the transformation
The integrand is given by

\[ \frac{1}{3} ((-2 \pi N_A \beta)) e^{-\beta U(r)} \text{Force} r^3 \text{DifferentialD}(r) \] / substitution /. \text{DifferentialD}(t) \rightarrow 1 \]

\[ \frac{8}{3} e^{-(r^2-\beta \epsilon)} \pi^{3/2} (2 \epsilon - 1) \beta \epsilon \sigma^3 N_A \]

Inserting the new integrand into the classical part of the SVC, we find

\[ B_c = \int_0^\infty \text{integrand} \, dt \]

Integrate::gener : Unable to check convergence. More…

The result shows that under the conditions \( \text{Re}(\frac{1}{n}) < \frac{1}{3} \) and \( \text{Re}(\beta \epsilon) > 0 \), the integral exists and the SVC is represented by hypergeometric functions \(_1 F_1\) depending on the potential parameter \( n \), the inverse temperature \( \beta \), and the potential depth \( \epsilon \). If the conditions on \( n \) and \( \beta \epsilon \) are not satisfied, we observe that the integral cannot be evaluated. A more usable representation of the result for our further calculations is generated if we suppress the conditions under which the integral is solvable. We select
The result is that the classical SVC for \((2n-n)\) potentials can be represented by hypergeometric functions. A graphical representation of the SVC in a scaled representation follows:

\[
\frac{1}{3} 2^{n+1} \pi (\beta \epsilon)^{3/2} \sigma^3 \\
\left( \Gamma \left(1 - \frac{3}{2n}\right) \right) \left( \binom{1}{F_1} \left(1 - \frac{3}{2n}; \frac{1}{2}; \beta \epsilon \right) - 2 \beta \epsilon \binom{1}{F_1} \left(1 - \frac{3}{2n}; \frac{3}{2}; \beta \epsilon \right) \right) + \\
\sqrt{\beta \epsilon} \left( 2 \Gamma \left(\frac{3(n-1)}{2n}\right) \binom{1}{F_1} \left(\frac{3(n-1)}{2n}; \frac{3}{2}; \beta \epsilon \right) - \right) \left( \Gamma \left(\frac{n-3}{2n}\right) \binom{1}{F_1} \left(\frac{n-3}{2n}; \frac{1}{2}; \beta \epsilon \right) \right) \Lambda
\]

The plot shows that the classical SVC possesses a single maximum in the variable \(\beta \epsilon\). In addition to the graphical representation of the SVC, the analytical result allows us to apply the result to thermodynamic quantities as given in Eqs. (5.7.111-5.7.115). This opens the way to access thermodynamic quantities like the internal energy. The internal energy for example is defined in terms of the SVC by
\[ \frac{U - U^0}{RT} = -\left( \frac{B_1}{V} + \ldots \right) \quad B_n = T^n \frac{d^n B}{dT^n}, \]  

which becomes
5.7 Second Virial Coefficient

\[
\text{InternalEnergy} = -\frac{T \frac{\delta (\text{Be}/\beta \rightarrow \frac{1}{2} \pi \alpha^3)}{\delta T}}{V}
\]

\[
= -\frac{1}{V} \left( \frac{1}{3} 2^{\frac{n-3}{2}} \pi \alpha^3 \right)
\]

\[
\left( - \left( \varepsilon \left( 2 \Gamma \left( \frac{3(n-1)}{2n} \right) \right)_1 F_1 \left( \frac{3(n-1)}{2n}; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) - \Gamma \left( \frac{n-3}{2n} \right) \right) \right) / \left( 2 T^2 \left( \frac{\varepsilon}{T k_B} k_B \right) \right) + \\
\Gamma \left( 1 - \frac{3}{2n} \right) \left( \frac{4 (1 - \frac{3}{2n}) \Gamma \left( \frac{3(n-1)}{2n} \right) \Gamma \left( \frac{n-3}{2n} + 1; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) \varepsilon^2}{3 T^3 k_B^3} \right) + \\
\frac{2 \varepsilon T^2 k_B \left( 1 - \frac{3}{2n} \right) \Gamma \left( \frac{3(n-1)}{2n} \right) \varepsilon}{T^2 k_B} - \\
\frac{2 (1 - \frac{3}{2n}) \Gamma \left( \frac{3(n-1)}{2n} \right) \left( \frac{3(n-1)}{2n} + 1; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) \varepsilon^2}{n T^2 k_B} - \\
\frac{2 (n-1) \varepsilon \Gamma \left( \frac{n-3}{2n} \right) \left( \frac{n-3}{2n} + 1; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right)}{n T^2 k_B} \\
\sqrt{\frac{\varepsilon}{T k_B}} \left( \frac{\varepsilon}{T k_B} \right)^{\frac{3}{2n}} N_A - \frac{1}{n T^2 k_B} \\
\left( 2^{\frac{n+1}{2n}} \pi \varepsilon \alpha^3 \right) \left( \sqrt{\frac{\varepsilon}{T k_B}} \left( 2 \Gamma \left( \frac{3(n-1)}{2n} \right) \right)_1 F_1 \left( \frac{3(n-1)}{2n}; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) - \Gamma \left( \frac{n-3}{2n} \right) \left( \frac{n-3}{2n}; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) \right) + \\
\Gamma \left( 1 - \frac{3}{2n} \right) \left( \frac{3(n-1)}{2n}; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right) - \\
\frac{2 \varepsilon T^2 k_B \left( 1 - \frac{3}{2n} \right) \Gamma \left( \frac{3(n-1)}{2n}; \frac{3}{2}; \frac{\varepsilon}{T k_B} \right)}{T k_B} \left( \frac{\varepsilon}{T k_B} \right)^{\frac{3}{2n}-1} N_A \right) \\
\right)
\]

In the above line, we used relation (5.7.111) to represent the internal energy. Since the SVC in our calculations does not depend explicitly on
the temperature $T$, we replaced the reduced temperature $\beta$ by $1/(k_B T)$. After this replacement in $B_c$, we differentiate the resulting expression with respect to $T$. A multiplication of the result by $T$ and a normalization with the volume $V$ delivers the final result. All of these steps are contained in the above input line. The result is a general analytic expression for the internal energy allowing the choice of the temperature $T$, the potential depth $\epsilon$, the radius $\sigma$, and the exponent of the potential $n$. To describe a specific gas, we have to insert numeric values for the parameters into the result. For example, we find for $\epsilon = 1$, $n = 6$, $\sigma = 1$, $N_A = 1$, $k_B = 1$, $T = 200$, and $V = 1$ an internal energy of

```
<<Miscellaneous`PhysicalConstants`

InternalEnergy /. {\epsilon \to 10^{-20} \text{ Joule}, n \to 6, \sigma \to 10^{-8}, N_A \to \text{AvogadroConstant}, k_B \to \text{BoltzmannConstant}, T \to 200 \text{ Kelvin}, V \to 1}

- \frac{132.423}{\text{Mole}}
```

By inserting the model parameters $\epsilon$, $n$, $\sigma$, and the other thermodynamic parameters $N_A$, $k_B$, and $V$, we have access to the numerical values of the internal energy as well. If we vary the temperature $T$, these values show the dependence of the internal energy on $T$. If we are interested in the temperature dependence of the internal energy, we can generate a plot by...
If we change, in addition to $T$, the exponent $n$ in the potential, we get the following figure.
The reader can determine other thermodynamic quantities of his interest, such as enthalpy, entropy, heat capacity at constant pressure, or the Joule–Thomson coefficient.

5.7.3 Quantum Mechanical Corrections $B_{q_1}(T)$ and $B_{q_2}(T)$ of the SVC

Up to the present considerations, we only know the classical behavior of the gas for high temperatures. The following discussion includes two quantum mechanical corrections allowing us to discuss all thermodynamic quantities in cases where quantum corrections are necessary.

The quantum mechanical corrections $B_{q_1}$ and $B_{q_2}$ in Eq. (5.7.109) and (5.7.110) are realized by the same substitution as demonstrated in the
classical calculation. The integrand of the first quantum correction is transformed by

\[
\text{integrandQc1} =
\]

\[
\text{Simplify}\left[\frac{2 \pi N_A \beta^3 e^{-\beta U(r)} r^2 \left(\frac{\partial U(r)}{\partial r}\right)^2 \text{DifferentialD}(r)}{48 \pi^2} / \text{substitution} / \right].
\]

\[
\quad - 2 e^{-\frac{1}{2} \left(\frac{1}{t^n}\right)^n \left(\frac{1}{t^n}\right)^{-1}} \beta \epsilon n t^{-\frac{n+1}{n}} \left(\frac{1}{t^n}\right)^{2n} \left(1 - 2 \left(\frac{1}{t^n}\right)^n \right)^2 \beta^3 \epsilon^2 \sigma N_A
\]

The related integral follows by inserting the integrand into the integral:

\[
\text{Bq1} = \int_0^\infty \text{integrandQc1} \, dt
\]

If \(\text{Re}(\beta \epsilon) > 0\),

\[
-\frac{1}{3 \pi} \left(2 \frac{1}{n} - 2 \right) n \beta^3 \epsilon^2 \left(\beta \epsilon \right)^{\frac{1}{n} - 5} \left(\Gamma\left(1 - \frac{1}{2} n \right)\right) \frac{n}{1} F_1 \left(1 - \frac{1}{2} n ; \frac{1}{2} ; \beta \epsilon \right) \left(\beta \epsilon \right)^{3/2} +
\]

\[
\Gamma\left(2 - \frac{1}{2} n \right) \left(1 F_1 \left(2 - \frac{1}{2} n ; \frac{1}{2} ; \beta \epsilon \right) - 4 \beta \epsilon \left(2 - \frac{1}{2} n ; \frac{3}{2} ; \beta \epsilon \right)\right)
\]

\[
\sqrt{\beta \epsilon} + 2 \beta \epsilon \left(\frac{3}{2} - \frac{1}{2} n \right)
\]

\[
\left(\beta \epsilon \left(1 F_1 \left(\frac{3}{2} - \frac{1}{2} n ; \frac{3}{2} ; \beta \epsilon \right) - 1 F_1 \left(3 - \frac{1}{2} n ; \frac{1}{2} ; \beta \epsilon \right)\right) +
\]

\[
\Gamma\left(\frac{5}{2} - \frac{1}{2} n \right) \left(1 F_1 \left(\frac{5}{2} - \frac{1}{2} n ; \frac{3}{2} ; \beta \epsilon \right)\right) N_A\right).
\]

Integrate\[
-\frac{2 e^{-\frac{1}{2} \left(\frac{1}{t^n}\right)^n \left(\frac{1}{t^n}\right)^{-1}} \beta \epsilon n t^{-\frac{n+1}{n}} \beta^3 \epsilon^2 \sigma N_A \left(\frac{1}{t^n}\right)^{2n}}{3 \pi} +
\]

\[
8 e^{-\frac{1}{2} \left(\frac{1}{t^n}\right)^n \left(\frac{1}{t^n}\right)^{-1}} \beta \epsilon n t^{-\frac{n+1}{n}} \beta^3 \epsilon^2 \sigma N_A \left(\frac{1}{t^n}\right)^{3n}
\]

\[
8 e^{-\frac{1}{2} \left(\frac{1}{t^n}\right)^n \left(\frac{1}{t^n}\right)^{-1}} \beta \epsilon n t^{-\frac{n+1}{n}} \beta^3 \epsilon^2 \sigma N_A \left(\frac{1}{t^n}\right)^{4n}
\]

\[
\left(t, 0, \infty\right), \text{Assumptions} \to \text{Re}(\beta \epsilon) \leq 0\]]
Again, we find an analytic representation of the first quantum mechanical correction of the SVC by means of hypergeometric functions $_1 F_1$. The integrand for the second quantum correction $B_{q2}$ follows by

\[
\text{integrandQc2 = Simplify}
\left[
\text{PowerExpand}\left[-\frac{1}{1920 \pi^4} \left(2 \pi N_A \beta^4 e^{-\beta U(r)} \left(-\frac{1}{36} 5 \beta^2 \left(\frac{\partial U(r)}{\partial r}\right)^4 + \right.ight.ight.
\right.
\]

\[
\left.
\left.
\left.
\frac{10 \beta}{9 r} \left(\frac{\partial U(r)}{\partial r}\right)^3 + \right.
\left.
\left.
\left.
\frac{2}{r} \left(\frac{\partial U(r)}{\partial r}\right)^2 + \left(\frac{\partial^2 U(r)}{\partial r \partial r}\right)^2 \right) r^2
\right.
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\r
\[ 
Bq_2 = \int_0^{\infty} \text{integrandQc2} \, dt 
\]

Integrate::gener : Unable to check convergence. More…

\[- \frac{1}{540 \pi^3 \alpha} \left( n \beta^4 \epsilon^2 \right) \text{If} \left( \text{Re} \left( \frac{1}{n} \right) > -2 \wedge \text{Re} (\epsilon) > 0, \right. \\

\left. \frac{52^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{\beta} + \frac{1}{2n}; \frac{1}{2}; \frac{1}{\beta} \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} + \\

\frac{92^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \frac{1}{\beta} \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^2 \epsilon^2} + \\

\frac{92^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \frac{1}{\beta} \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^2 \epsilon^2} + \\

\frac{272^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^2 \epsilon^2} - \\

\frac{92^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} - \\

\frac{92^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} - \\

\frac{92^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 3 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{3}{2} + \frac{1}{2n}; \frac{1}{\beta} \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} - \\

\frac{52^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} - \\

\frac{52^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta \epsilon} - \\

\frac{152^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 \epsilon^3} + \\

\frac{152^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^2 \epsilon^2} - \\

\frac{92^{-2 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 \epsilon^3} - \\

\frac{92^{-1 - \frac{1}{n}} \Gamma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{F1} \left( \frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon \right) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 \epsilon^3} - 
\]
\[
\begin{align*}
9^2 & \frac{2^{-1/n} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta^3 \epsilon^3} \frac{1}{\Gamma(\frac{1}{2} (7 + \frac{1}{n}) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}} - \\
5^2 & \frac{2^{-1 - \frac{1}{n}} n^2 \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta^4 \epsilon^4} \frac{1}{\Gamma(\frac{1}{2} (7 + \frac{1}{n}) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}} + \\
15^2 & \frac{2^{-1 - \frac{1}{n}} n^2 \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta^3 \epsilon^3} \frac{1}{\Gamma(\frac{1}{2} (7 + \frac{1}{n}) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}} + \\
5^2 & \frac{2^{-1/n} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta^3 \epsilon^3} \frac{1}{\Gamma(\frac{1}{2} (7 + \frac{1}{n}) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}} + \\
5^2 & \frac{2^{-1/n} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta^3 \epsilon^3} \frac{1}{\Gamma(\frac{1}{2} (7 + \frac{1}{n}) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{\frac{3}{2} - \frac{1}{2n}}} - \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
9^2 & \frac{2^{-4 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
5^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
15^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
5^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
5^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
5^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} - \\
9^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
27^2 & \frac{2^{-3 - \frac{1}{n}} \Gamma(\frac{1}{2} (7 + \frac{1}{n})) \frac{1}{1 + \frac{1}{2n}}; \frac{1}{2}; \beta \epsilon}{\beta \epsilon} (\beta \epsilon)^{-\frac{1}{2n}} + \\
\end{align*}
\]
\[
15 2^{-2-\frac{1}{n}} n^2 \Gamma(3 + \frac{1}{2n}) I_1(3 + \frac{1}{2n}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} + \\
5 2^{-1-\frac{1}{n}} n^2 \Gamma(3 + \frac{1}{2n}) I_1(3 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} \\
5 2^{-1/n} n^2 \Gamma(3 + \frac{1}{2n}) I_1(3 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} - \\
15 2^{-1/n} n^2 \Gamma(3 + \frac{1}{2n}) I_1(3 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} + \\
5 2^{-3-\frac{1}{n}} n^2 \Gamma(4 + \frac{1}{2n}) I_1(4 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} - \\
5 2^{-1/n} n^2 \Gamma(4 + \frac{1}{2n}) I_1(4 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon) (\beta \epsilon)^{-\frac{1}{2n}} \\
27 \epsilon^\beta \sqrt{\pi} (\frac{2 \beta \epsilon}{3} + 1) \sigma (\beta \epsilon)^{3/2} - \\
\frac{9 \epsilon^\beta \epsilon}{4 \beta^3 \epsilon^3} \sqrt{\pi} (2 \beta \epsilon + 1) \sigma (\beta \epsilon)^{3/2} - \frac{9 \epsilon^\beta \epsilon}{4 \beta^2 \epsilon^3} \sqrt{\pi} \sigma (\beta \epsilon)^{3/2} + \\
\frac{9 \epsilon^\beta \epsilon \sigma (2 \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \epsilon})) - \frac{3 \epsilon^\beta \epsilon}{\sqrt{\beta \epsilon}} - 2 \sqrt{\pi}) \sqrt{\beta \epsilon}}{8 \beta \epsilon} \\
\frac{1}{2 \beta \epsilon} \left( \begin{array}{c} 9 \sigma \\
\frac{e^\beta \epsilon (\sqrt{\pi} - \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \epsilon})))}{2 \sqrt{\beta \epsilon}} \end{array} \right) + \\
\frac{1}{8 \beta^2 \epsilon^2} \left( \begin{array}{c} 9 \sigma \\
\frac{-e^\beta \epsilon (2 \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \epsilon})) - \frac{2 e^{-\beta \epsilon}}{\sqrt{\beta \epsilon}} - 2 \sqrt{\pi})}{\sqrt{\beta \epsilon} - 1} \end{array} \right),
\]

Integrate \( e^{-4(0-1)/\beta \epsilon} t (4 (18 n^2 + (27 - 10 \beta \epsilon) n + 9) t^{2+\frac{1}{n}} + \) \\
\( 4 ((5 \beta^2 \epsilon^2 - 36) n^2 + 12 (5 \beta \epsilon - 3) n - 9) t^{2+\frac{1}{n}} - \) \\
\( 160 n \beta \epsilon (n \beta \epsilon + 3) t^{2+\frac{1}{n}} + 160 n \beta \epsilon (3 n \beta \epsilon + 2) t^{2+\frac{1}{n}} - \) \\
\( 640 n^2 \beta^2 \epsilon^2 t^{2+\frac{1}{n}} + 320 n^2 \beta^2 \epsilon^2 \beta e^{3/2} + \) \\
\( 9 (n + 1)^2 t^{2+\frac{1}{n}} - 72 \sigma t^2 + 72 \sigma t - 18 \sigma \), \( \{t, 0, \infty\} \),

Assumptions: \( \left( \text{Re} \left( \frac{1}{n} \right) > -2 \wedge \text{Re}(\beta \epsilon) > 0 \right) \} \left( N_A \right) \).
\[
Bq2 = Bq2 / a_\_ \ If[b_\_, e_\_, d___] → a \_ c
\]

\[
- \frac{1}{540 \pi^3 \sigma} \left( n \beta^4 e^2 \left( -\frac{5 \beta^2}{\epsilon^2} + \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (3 + \frac{1}{n})) F_1(\frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} + \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (3 + \frac{1}{n})) F_1(\frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right) \right.
\]

\[
+ \frac{27 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (3 + \frac{1}{n})) F_1(\frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
+ \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (3 + \frac{1}{n})) F_1(\frac{3}{2} + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
+ \frac{5 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
+ \frac{15 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
+ \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
+ \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
- \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
- \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]

\[
- \frac{9 \beta^2}{\epsilon^2} \Gamma(\frac{1}{2} (5 + \frac{1}{n})) F_1(\frac{5}{2} + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon (\beta \epsilon)^{\frac{1}{2} - \frac{1}{2n}} \right)
\]
\[
\frac{52^{-1 - \frac{1}{n}} n^2 \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{7}{2}; \frac{1}{2}; -\beta \epsilon; \beta \epsilon\right) e^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 e^4} + \\
\frac{152^{-1 - \frac{1}{n}} n^2 \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{7}{2}; \frac{1}{2}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 e^4} + \\
\frac{52^{-1/n} n \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{7}{2}; \frac{1}{2}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{\frac{3}{2} - \frac{1}{2n}}}{\beta^3 e^4} + \\
\frac{52^{-2 - \frac{1}{n}} n^2 \Gamma\left(\frac{1}{2} \left(9 + \frac{1}{n}\right)\right) F_1\left(\frac{9}{2}; \frac{1}{2}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{\frac{3}{2} - \frac{1}{2n}}}{\beta^5 e^3} - \\
\frac{92^{-3 - \frac{1}{n}} \Gamma\left(1 + \frac{1}{2n}\right) F_1\left(1 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} - \\
\frac{92^{-3 - \frac{1}{n}} \Gamma\left(\frac{1}{2n}\right) F_1\left(1 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{52^{-3 - \frac{1}{n}} n^2 \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{152^{-1 - \frac{1}{n}} n \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} - \\
\frac{92^{-3 - \frac{1}{n}} \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} - \\
\frac{92^{-1 - \frac{1}{n}} n^2 \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} - \\
\frac{92^{-1 - \frac{1}{n}} n \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} - \\
\frac{52^{-1/n} n \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{92^{-1 - \frac{1}{n}} \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{92^{-1/n} n \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{272^{-1 - \frac{1}{n}} n \Gamma\left(2 + \frac{1}{2n}\right) F_1\left(2 + \frac{1}{2n}; \frac{3}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + \\
\frac{152^{-2 - \frac{1}{n}} n^2 \Gamma\left(3 + \frac{1}{2n}\right) F_1\left(3 + \frac{1}{2n}; \frac{1}{2}; \beta \epsilon; \beta \epsilon\right) e^{-\frac{1}{2n}}}{\beta e} + 
\]
Using $\varepsilon/k_B$ and $\frac{2}{3} \pi N_A \sigma^3$ in a scaling transformation for the temperature in the SVC, we get $B^*(T)$ tabulated in books like Hirschfelder et al [5.10]. These authors introduce a scaled representation of the SVC by $B_c^* = B_c / (\frac{2}{3} \pi N_A \sigma^3)$ with a reduced temperature of $T^* = k_B T / \varepsilon$. 

\[
\begin{align*}
52^{-1-\frac{1}{n}} & n \Gamma(3 + \frac{1}{2n})_1 F_1(3 + \frac{1}{2n}; \frac{1}{2}; \beta \varepsilon) (\beta \varepsilon)^{-\frac{1}{2n}} \frac{1}{\beta^2 e^2} \\
52^{-1/n} n^2 & \Gamma(3 + \frac{1}{2n})_1 F_1(3 + \frac{1}{2n}; \frac{3}{2}; \beta \varepsilon) (\beta \varepsilon)^{-\frac{1}{2n}} \\
152^{-1/n} n & \Gamma(3 + \frac{1}{2n})_1 F_1(3 + \frac{1}{2n}; \frac{3}{2}; \beta \varepsilon) (\beta \varepsilon)^{-\frac{1}{2n}} \\
52^{-3-\frac{1}{n}} & n^2 \Gamma(4 + \frac{1}{2n})_1 F_1(4 + \frac{1}{2n}; \frac{1}{2}; \beta \varepsilon) (\beta \varepsilon)^{-\frac{1}{2n}} \\
& \frac{1}{\beta^2 e^2} \\
27 e^{\beta \varepsilon} & \sqrt{\pi} (\frac{2 \beta \varepsilon}{3} + 1) \sigma (\beta \varepsilon)^{3/2} \\
& \frac{9 e^{\beta \varepsilon} \sqrt{\pi} (2 \beta \varepsilon + 1) \sigma (\beta \varepsilon)^{3/2}}{4 \beta^2 e^3} \\
& \frac{9 e^{\beta \varepsilon} \sigma (2 \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \varepsilon})) - \frac{2 e^{-\beta \varepsilon}}{\sqrt{\beta \varepsilon}} - 2 \sqrt{\pi}) \sqrt{\beta \varepsilon}}{8 \beta \varepsilon} \\
& \frac{1}{2 \beta \varepsilon} \left( 9 \sigma \left( e^{\beta \varepsilon} \sqrt{\beta \varepsilon} (\sqrt{\pi} - \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \varepsilon}))) + \frac{e^{\beta \varepsilon} (\sqrt{\pi} - \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \varepsilon}))) + 1}{2 \sqrt{\beta \varepsilon}} \right) - \frac{1}{8 \beta^2 e^2} \right) \\
& \left( 9 \sigma \left( -e^{\beta \varepsilon} \left( 2 \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \varepsilon})) - \frac{2 e^{-\beta \varepsilon}}{\sqrt{\beta \varepsilon}} - 2 \sqrt{\pi} \right) (\beta \varepsilon)^{3/2} - \frac{3}{2} e^{\beta \varepsilon} \left( 2 \sqrt{\pi} (1 - \text{erf}(\sqrt{\beta \varepsilon})) - \frac{2 e^{-\beta \varepsilon}}{\sqrt{\beta \varepsilon}} - 2 \sqrt{\pi} \right) \sqrt{\beta \varepsilon} - 1 \right) \right) \left| N_A \right|
\end{align*}
\]
\[
\text{BStar} = \text{Simplify}\left[ \frac{\text{Bq2} \left( \frac{n^2}{m} \right)^2 + \frac{\text{Bq1} n^2}{m} + \text{Bc}}{\frac{2}{3} \pi N_A \sigma^3} \right] / / \left( \epsilon \to \frac{1}{\beta T} \right) \Rightarrow \lambda \to \Lambda \sigma \sqrt{m \epsilon}
\]

\[
\frac{1}{45 \pi^4} \left( 2^{-7 - \frac{1}{n}} \left( \frac{1}{T} \right)^{4 - \frac{1}{n}} \right)
\]

\[
9 \left( 2^{2 + \frac{1}{n}} n \Lambda^4 \sigma \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{2}{2} n} \right) + 9 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{3}{3} n} \right)
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{3}{3} n} \right) -
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{5}{5} n} \right) -
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{3}{3} n} \right) -
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{5}{5} n} \right) -
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{3}{3} n} \right) +
\]

\[
45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{5}{5} n} \right) + 45 \left( 2^{1 + \frac{1}{n}} e^\frac{1}{T} n \sqrt{\pi} \Lambda^4 \sigma \text{erf} \left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{n} - \frac{3}{3} n} \right)
\]

\[
\frac{1}{T}^{\frac{1}{n} - \frac{3}{3} n} - 20 n^3 \Lambda^4 \sigma \left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \text{erf} \left( \frac{1}{T} \left( 5 + \frac{1}{n} \right) \right) \left( \frac{3}{2} \left( \frac{1}{2} \right) \sqrt{\frac{1}{T}} \right) +
\]

\[
18 n T \Lambda^4 \sigma \left( 1 + \frac{1}{2 n} \right) \text{erf} \left( \frac{1}{T} + \frac{1}{2 n} \right) +
\]

\[
9 n^2 T \Lambda^4 \sigma \left( \frac{1}{2 n} \right) \text{erf} \left( \frac{1}{T} + \frac{1}{2 n} \right) +
\]

\[
18 n T \Lambda^4 \sigma \left( \frac{1}{2 n} \right) \text{erf} \left( \frac{1}{T} + \frac{1}{2 n} \right) -
\]
10 n^3 \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
72 n^3 T^2 \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
72 n^2 T^2 \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
18 n^2 T \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) - \\
120 n^2 T \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
80 n^2 \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) - \\
144 n^3 T \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) - \\
216 n^2 T \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) - \\
72 n T \Lambda^4 \Gamma(2 + \frac{1}{2 n})_1 F_1(2 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) - \\
40 n^2 T^2 \Lambda^4 \Gamma(3 + \frac{1}{2 n})_1 F_1(3 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) - \\
60 n^3 \Lambda^4 \Gamma(3 + \frac{1}{2 n})_1 F_1(3 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
80 n^3 \Lambda^4 \Gamma(3 + \frac{1}{2 n})_1 F_1(3 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) + \\
240 n^2 T \Lambda^4 \Gamma(3 + \frac{1}{2 n})_1 F_1(3 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) - \\
10 n^3 T^2 \Lambda^4 \Gamma(4 + \frac{1}{2 n})_1 F_1(4 + \frac{1}{2 n}; \frac{1}{2}; \frac{1}{T}) + \\
80 n^3 T \Lambda^4 \Gamma(4 + \frac{1}{2 n})_1 F_1(4 + \frac{1}{2 n}; \frac{3}{2}; \frac{1}{T}) + \\
40 n^2 \Lambda^4 \Gamma(\frac{1}{2} (3 + \frac{1 n}{n}))_1 F_1(\frac{1}{2} (3 + \frac{1 n}{n}); \frac{1}{2}; \frac{1}{T}) + \\
\frac{1}{T}\sqrt{1} \\
36 n^3 \Lambda^4 \Gamma(\frac{1}{2} (3 + \frac{1 n}{n}))_1 F_1(\frac{1}{2} (3 + \frac{1 n}{n}); \frac{3}{2}; \frac{1}{T}) + \\
\frac{1}{T}\sqrt{1} \\
72 n^2 \Lambda^4 \Gamma(\frac{1}{2} (3 + \frac{1 n}{n}))_1 F_1(\frac{1}{2} (3 + \frac{1 n}{n}); \frac{3}{2}; \frac{1}{T}) + \\
\frac{1}{T}\sqrt{1} \\
36 n \Lambda^4 \Gamma(\frac{1}{2} (3 + \frac{1 n}{n}))_1 F_1(\frac{1}{2} (3 + \frac{1 n}{n}); \frac{3}{2}; \frac{1}{T}) + \\
\frac{1}{T}\sqrt{1} \\
40 n^3 \Lambda^4 \Gamma(\frac{1}{2} (5 + \frac{1 n}{n}))_1 F_1(\frac{1}{2} (5 + \frac{1 n}{n}); \frac{1}{2}; \frac{1}{T}) - \\
\frac{1}{T}\sqrt{1}
where $\Lambda = \hbar / (\sigma m^{1/2})$ is the reduced de Broglie wavelength of relative motion. $B^*$ is an even polynomial of fourth order in $\Lambda$. It contains the classical, first, and second quantum corrections as zeroth-, second-, and fourth-order coefficients, respectively. We extract the reduced representation of the second quantum correction by

$$
\begin{align*}
&\frac{240 n^2 \Lambda^4 \Gamma\left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(5 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\sqrt{\frac{1}{T}}} \\
&\frac{120 n^3 \Lambda^4 \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(7 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\sqrt{\frac{1}{T}}} \\
&\frac{72 n^3 \Lambda^4 \Gamma\left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(3 + \frac{1}{n}\right); \frac{1}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} \\
&\frac{108 n^2 \Lambda^4 \Gamma\left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(3 + \frac{1}{n}\right); \frac{1}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} \\
&\frac{36 n \Lambda^4 \Gamma\left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(3 + \frac{1}{n}\right); \frac{1}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} + \\
&\frac{120 n^2 \Lambda^4 \Gamma\left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(5 + \frac{1}{n}\right); \frac{1}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} + \\
&\frac{144 n^3 \Lambda^4 \Gamma\left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(5 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} + \\
&\frac{144 n^2 \Lambda^4 \Gamma\left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(5 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} + \\
&\frac{36 n \Lambda^4 \Gamma\left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(5 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} + \\
&\frac{40 n^3 \Lambda^4 \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(7 + \frac{1}{n}\right); \frac{1}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} - \\
&\frac{80 n^2 \Lambda^4 \Gamma\left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(7 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}} - \\
&\frac{20 n^3 \Lambda^4 \Gamma\left(\frac{1}{2} \left(9 + \frac{1}{n}\right)\right) F_1\left(\frac{1}{2} \left(9 + \frac{1}{n}\right); \frac{3}{2}; \frac{1}{T}\right)}{\left(\frac{1}{T}\right)^{3/2}}
\end{align*}
$$
5. Quantum Mechanics

\[ bq2 = \text{Coefficient}[BStar, \Lambda, 4] \]

General::spell1 : Possible spelling error: new

symbol name "bq2" is similar to existing symbol "Bq2". More...

\[
\frac{1}{45 \pi^4} \left( 2^{-7-\frac{1}{n}} \left( \frac{1}{T} \right)^{4-\frac{1}{2n}} \left( 9 2^{2+\frac{1}{n}} n \sigma \left( \frac{1}{T} \right)^{\frac{1}{2n}} - 9 2^{1+\frac{1}{n}} e^\frac{1}{n} n \sqrt{n} \sigma \left( \frac{1}{T} \right)^{\frac{1}{2}} \right) + 9 2^{1+\frac{1}{n}} e^\frac{1}{n} n \sqrt{n} \sigma \left( \frac{1}{T} \right)^{\frac{1}{2}} \right) + \right.
\]

\[
20 n^3 \Gamma\left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) \right) \, \text{; } F_1\left( \frac{1}{2} \left( 5 + \frac{1}{n} \right) ; \frac{3}{2} ; \frac{1}{T} \right) \sqrt{\frac{1}{T}} + \\
18 n T \Gamma\left( 1 + \frac{1}{2n} \right) \, \text{; } \text{erf}\left( \sqrt{\frac{1}{T}} \right) \left( \frac{1}{T} \right)^{\frac{1}{2}} \left( \frac{1}{2} \right) + 9 n^2 T \Gamma\left( 1 \right)\right]
\]

\[
F_1\left( 1 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + 18 n T \Gamma\left( \frac{1}{2n} \right) \, F_1\left( 1 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) - \\
10 n^3 \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + 72 n^2 T^2 \Gamma\left( 2 + \frac{1}{2n} \right)\right]
\]

\[
F_1\left( 2 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) - 120 n^2 T \Gamma\left( 2 + \frac{1}{2n} \right)\right]
\]

\[
18 n T^2 \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + 18 n^2 T^2 \Gamma\left( 2 + \frac{1}{2n} \right)\right]
\]

\[
F_1\left( 2 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + 80 n^2 \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) - \\
144 n^3 T \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) - \\
216 n^2 T \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) - \\
72 n T \Gamma\left( 2 + \frac{1}{2n} \right) \, F_1\left( 2 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) - \\
40 n^2 T^2 \Gamma\left( 3 + \frac{1}{2n} \right) \, F_1\left( 3 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) - \\
60 n^3 T \Gamma\left( 3 + \frac{1}{2n} \right) \, F_1\left( 3 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + \\
80 n^3 \Gamma\left( 3 + \frac{1}{2n} \right) \, F_1\left( 3 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) + \\
240 n^2 T \Gamma\left( 3 + \frac{1}{2n} \right) \, F_1\left( 3 + \frac{1}{2n} ; \frac{3}{2} ; \frac{1}{T} \right) - \\
10 n^3 T^2 \Gamma\left( 4 + \frac{1}{2n} \right) \, F_1\left( 4 + \frac{1}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) + \\]
\[
\begin{align*}
&80 n^3 T \Gamma \left(4 + \frac{1}{2n}\right) \frac{1}{\Gamma} \left(4 + \frac{1}{2n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&40 n^2 \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&36 n^3 \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&72 n^2 \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&36 n \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&40 n^3 \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) - \\
&240 n^2 \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) - \\
&120 n^3 \Gamma \left(\frac{1}{2} \left(7 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(7 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) - \\
&72 n^2 \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) - \\
&108 n^2 \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) - \\
&36 n \Gamma \left(\frac{1}{2} \left(3 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(3 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&120 n^2 \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&144 n^3 \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&144 n^2 \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
&36 n \Gamma \left(\frac{1}{2} \left(5 + \frac{1}{n}\right)\right) \frac{1}{\Gamma} \left(\frac{1}{2} \left(5 + \frac{1}{n}; \frac{3}{2}; \frac{1}{T}\right) + \\
\end{align*}
\]
And the classical SVC in reduced variables is

\[
\begin{aligned}
\frac{40 n^3 \Gamma\left(\frac{1}{2} (7 + \frac{1}{n})\right) i F_1\left(\frac{1}{2} (7 + \frac{1}{n}); \frac{3}{2}; \frac{1}{T}\right)}{(\frac{1}{T})^{3/2}} \\
\frac{80 n^2 \Gamma\left(\frac{1}{2} (7 + \frac{1}{n})\right) i F_1\left(\frac{1}{2} (7 + \frac{1}{n}); \frac{3}{2}; \frac{1}{T}\right)}{(\frac{1}{T})^{3/2}} \\
\frac{20 n^3 \Gamma\left(\frac{1}{2} (9 + \frac{1}{n})\right) i F_1\left(\frac{1}{2} (9 + \frac{1}{n}); \frac{3}{2}; \frac{1}{T}\right)}{(\frac{1}{T})^{3/2}}
\end{aligned}
\]

The first quantum mechanical correction is extracted by

\[
bq1 = \text{Coefficient}[\text{BStar}, \Lambda, 2]
\]

General::spell1 : Possible spelling error: new
symbol name "bq1" is similar to existing symbol "Bq1". More…

\[
\frac{1}{45 \pi^4} \left( 2^{-7 - \frac{1}{2n}} \left( \frac{1}{T} \right)^{\frac{1}{2n}} \left( -45 2^{4+\frac{2}{n}} n \pi^2 \Gamma\left( 2 - \frac{1}{2n} \right) F_1\left( 2 - \frac{1}{2n}; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-3} + 
\right.
\]

\[
45 2^{5+\frac{2}{n}} n \pi^2 \Gamma\left( \frac{3}{2} - \frac{1}{2n} \right) F_1\left( \frac{3}{2} - \frac{1}{2n}; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-\frac{5}{2}} - 
\]

\[
45 2^{5+\frac{2}{n}} n \pi^2 \Gamma\left( \frac{5}{2} - \frac{1}{2n} \right) F_1\left( \frac{5}{2} - \frac{1}{2n}; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-\frac{5}{2}} - 
\]

\[
45 2^{4+\frac{2}{n}} n \pi^2 \Gamma\left( 1 - \frac{1}{2n} \right) F_1\left( 1 - \frac{1}{2n}; \frac{1}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-2} + 
\]

\[
45 2^{6+\frac{2}{n}} n \pi^2 \Gamma\left( 2 - \frac{1}{2n} \right) F_1\left( 2 - \frac{1}{2n}; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-2} - 
\]

\[
45 2^{4+\frac{2}{n}} n \pi^2 \Gamma\left( \frac{3}{2} - \frac{1}{2n} \right) F_1\left( \frac{3}{2} - \frac{1}{2n}; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{n}-\frac{3}{2}} \right)
\]

And the classical SVC in reduced variables is
The derived results are analytic expressions in terms of hypergeometric functions \( _1F_1 \) allowing a graphical and analytical treatment of the SVC, including quantum corrections. The representation of the second virial coefficient up to second-order quantum corrections is thus given by

\[
\text{bc} = \text{Coefficient}[\text{BStar, } \Lambda, 0] = \frac{1}{45 \pi^4} \left(2^{-\frac{7}{6}-\frac{1}{n}} \left(\frac{1}{T}\right)^{\frac{4}{2n}} - 45 2^{\frac{7}{6}+\frac{3}{n}} \pi^4 \Gamma\left(n-\frac{3}{2n}\right) _1F_1\left(n-\frac{3}{2n}; \frac{3}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2n}} + \right.
\]

\[
 45 2^{\frac{7}{6}+\frac{3}{n}} \pi^4 \Gamma\left(1 - \frac{3}{2n}\right) \left( T_1F_1\left(1 - \frac{3}{2n}; \frac{3}{2}; \frac{1}{T}\right) - 2 _1F_1\left(1 - \frac{3}{2n}; \frac{3}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2n}} - 2 \right) + \left.
\]

The derived results are analytic expressions in terms of hypergeometric functions \( _1F_1 \) allowing a graphical and analytical treatment of the SVC, including quantum corrections. The representation of the second virial coefficient up to second-order quantum corrections is thus given by

\[
b_{\text{star}} = \text{bc} + \Lambda^2 \text{bq1} + \Lambda^4 \text{bq2};
\]

To demonstrate the influence of the quantum mechanical corrections, let us graphically examine the classical SVC, the two quantum corrections, and the total representation of the SVC. We plot the reduced quantities depending on the variable \( T^* = T \). Figure 5.7.23 shows the influence of the first and second quantum correction on the SVC.
Figure 5.7.23. The figure contains the classical SVC (blue), the first quantum mechanical correction (red), the second quantum correction of SVC (green), and the sum of the three parts (black). We note that the second quantum corrections contains terms linear in $\sigma$. Therefore, in addition to $\Lambda$ and $n$ we have to specify the value of $\sigma$.

For practical applications, it is sometimes necessary to have the numerical values of the SVC and its first and second temperature derivatives available. The numerical values of these quantities are tabulated in the book by Hirschfelder et al. for the (12-6)-LJ potential. The first and second derivative of $B_c^*$ with respect to $T*$ then follows by
\[ b_1 = T \frac{\partial \text{bc}}{\partial T} \]

\[
T \left( \frac{1}{45 \pi^4} \left( 2 - \frac{7}{n} \right) \left( \frac{1}{T} \right)^{4 - \frac{1}{n}} \left( 45 2^{7 + \frac{4}{n}} \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right) \right) \right. \\
\left. \left( \phantom{\text{bc}} \right) \right) \\
\frac{1}{T^2} \left( 1 - \frac{3}{2n} ; \frac{1}{2} ; \frac{1}{T} \right) - \frac{2 (1 - \frac{3}{2n}) \text{bc}(2 - \frac{3}{2n} ; \frac{3}{2} ; \frac{1}{T})}{T} + \\
4 (1 - \frac{3}{2n}) \text{bc}(2 - \frac{3}{2n} ; \frac{5}{2} ; \frac{1}{T}) \right) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{3}{2}} + \\
45 2^{7 + \frac{4}{n}} \left( \frac{2}{n} - \frac{7}{2} \right) \pi^4 \Gamma (\frac{n - 3}{2n}) \text{bc}(\frac{n - 3}{2n} ; \frac{1}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{5}{2}} - \\
45 2^{8 + \frac{4}{n}} \left( \frac{2}{n} - \frac{7}{2} \right) \pi^4 \Gamma (\frac{3(n - 1)}{2n}) \text{bc}(\frac{3(n - 1)}{2n} ; \frac{3}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{5}{2}} \\
\left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{3}{2}} - 45 2^{7 + \frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma (1 - \frac{3}{2n}) \\
\left( T \text{bc}(1 - \frac{3}{2n} ; \frac{1}{2} ; \frac{1}{T}) - 2 \text{bc}(1 - \frac{3}{2n} ; \frac{3}{2} ; \frac{1}{T}) \right) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{7}{2}} + \\
45 2^{7 + \frac{4}{n}} (n - 3) \pi^4 \Gamma (\frac{n - 3}{2n}) \text{bc}(\frac{n - 3}{2n} + 1 ; \frac{3}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{-\frac{3}{2} - \frac{3}{2}} \\
\frac{1}{n} \left( 45 2^{8 + \frac{4}{n}} (n - 1) \pi^4 \Gamma (\frac{3(n - 1)}{2n}) \right. \\
\left. \text{bc}(\frac{3(n - 1)}{2n} + 1 ; \frac{5}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{5}{2}} \right) \right) - \\
\frac{1}{45 \pi^4} \left( 2 - \frac{7}{n} \right) \left( 4 - \frac{1}{2n} \right) \left( \frac{1}{T} \right)^{5 - \frac{1}{n}} \left( -45 2^{7 + \frac{4}{n}} \pi^4 \Gamma (\frac{n - 3}{2n}) \right. \\
\text{bc}(\frac{n - 3}{2n} ; \frac{1}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{7}{2}} + 45 2^{8 + \frac{4}{n}} \pi^4 \Gamma (\frac{3(n - 1)}{2n}) \\
\text{bc}(\frac{3(n - 1)}{2n} ; \frac{3}{2} ; \frac{1}{T}) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{7}{2}} + 45 2^{7 + \frac{4}{n}} \pi^4 \Gamma (1 - \frac{3}{2n}) \\
\left( T \text{bc}(1 - \frac{3}{2n} ; \frac{1}{2} ; \frac{1}{T}) - 2 \text{bc}(1 - \frac{3}{2n} ; \frac{3}{2} ; \frac{1}{T}) \right) \left( \frac{1}{T} \right)^{\frac{2}{n} - \frac{7}{2}} \right) \]
\[
b_2 = T^2 \frac{\partial^2 bc}{\partial T \partial T} \]

\[
T^2 \left( \frac{1}{45 \pi^4} \left\{ 452^{7+\frac{4}{n}} \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right) \left( 8 \left( 1 - \frac{3}{2n} \right) \frac{1}{T} \right) + \right. \right. \\
\left. \left. \frac{4 \left( 1 - \frac{3}{2n} \right) (2 - \frac{3}{2n}) \frac{1}{T} \right) - \frac{8 \left( 1 - \frac{3}{2n} \right) (2 - \frac{3}{2n}) \frac{1}{T}}{3 T^3} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} - 90 2^{7+\frac{1}{2}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} - 4 \left( 1 - \frac{3}{2n} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-3} + \frac{4 \left( 1 - \frac{3}{2n} \right) \frac{1}{T}}{3 T^2} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-2} \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} + 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 7 \right) \left( \frac{2}{n} - \frac{5}{2} \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \frac{1}{T} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} + 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \left( \frac{2}{n} - 2 \right) \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right) \\
\left( T \frac{1}{T} \right)^{\frac{2}{n}-3} - 2 \left( \frac{1}{T} \right)^{\frac{2}{n}-3} + \frac{1}{n} \left( 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 7 \right) \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} - \frac{1}{n} \left( 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} + \frac{1}{n} \left( 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} \right) \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} + \frac{1}{n} \left( 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} \right) \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} + \frac{1}{n} \left( 452^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \\
\left( \frac{1}{T} \right)^{\frac{2}{n}-3} \right) \right) \]
\[
\frac{1}{n} \left( 45 2^{8+\frac{4}{n}} \left( \frac{2}{n} - \frac{7}{2} \right) (n-1) \pi^4 \Gamma \left( \frac{3(n-1)}{2n} \right) \right)
\]

\[
{}_1F_1 \left( \frac{3(n-1)}{2n} + 1; \frac{5}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-\frac{1}{2}} +
\]

\[
\frac{1}{n} \left( 45 2^{8+\frac{4}{n}} \left( \frac{2}{n} - \frac{3}{2} \right) (n-1) \pi^4 \Gamma \left( \frac{3(n-1)}{2n} \right) \right)
\]

\[
{}_1F_1 \left( \frac{3(n-1)}{2n} + 1; \frac{5}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-\frac{1}{2}} \right) -
\]

\[
\frac{1}{n} \left( 15 2^{8+\frac{4}{n}} \left( \frac{n-3}{2n} + 1 \right) (n-3) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) \right)
\]

\[
{}_1F_1 \left( \frac{n-3}{2n} + 2; \frac{5}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{2}+\frac{1}{2n}} \right)
\]

\[
\frac{1}{n} \left( 9 2^{8+\frac{4}{n}} \left( \frac{3(n-1)}{2n} + 1 \right) (n-1) \pi^4 \Gamma \left( \frac{3(n-1)}{2n} \right) \right)
\]

\[
{}_1F_1 \left( \frac{3(n-1)}{2n} + 2; \frac{7}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{1}{2}+\frac{2}{2n}} \right) \right) \left( \frac{1}{T} \right)^{4-\frac{1}{2n}} -
\]

\[
\frac{1}{45 \pi^4} \left( 2^{-7-\frac{1}{2}} \left( 4 - \frac{1}{2n} \right) \left( 45 2^{7+\frac{4}{n}} \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right) \right) \right)
\]

\[
\left( {}_1F_1 \left( 1 - \frac{3}{2n} + 1; \frac{1}{2}; \frac{1}{T} \right) \right) - \frac{2 \left( 1 - \frac{3}{2n} \right) {}_1F_1 \left( 2 - \frac{3}{2n} + \frac{3}{2}; \frac{1}{2}; \frac{1}{T} \right)}{3 T^2} +
\]

\[
\frac{4 \left( 1 - \frac{3}{2n} \right) {}_1F_1 \left( 2 - \frac{3}{2n} + \frac{5}{2}; \frac{1}{2}; \frac{1}{T} \right)}{3 T^2} \left( \frac{1}{T} \right)^{\frac{2}{n}-3} +
\]

\[
45 2^{7+\frac{4}{n}} \left( \frac{2}{n} - \frac{7}{2} \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) {}_1F_1 \left( \frac{n-3}{2n} + \frac{1}{2}; \frac{1}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}+\frac{3}{2}} -
\]

\[
45 2^{8+\frac{4}{n}} \left( \frac{2}{n} - \frac{3}{2} \right) \pi^4 \Gamma \left( \frac{3(n-1)}{2n} \right) {}_1F_1 \left( \frac{3(n-1)}{2n} + \frac{3}{2}; \frac{1}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-\frac{1}{2}} - 45 2^{7+\frac{4}{n}} \left( \frac{2}{n} - 3 \right) \pi^4 \Gamma \left( 1 - \frac{3}{2n} \right)
\]

\[
\left( T {}_1F_1 \left( 1 - \frac{3}{2n} + \frac{1}{2}; \frac{1}{2}; \frac{1}{T} \right) - 2 {}_1F_1 \left( 1 - \frac{3}{2n} + \frac{3}{2}; \frac{1}{2}; \frac{1}{T} \right) \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-\frac{3}{2}} +
\]

\[
45 2^{7+\frac{4}{n}} \left( n-3 \right) \pi^4 \Gamma \left( \frac{n-3}{2n} \right) {}_1F_1 \left( \frac{n-3}{2n} + 1; \frac{3}{2}; \frac{1}{T} \right) \left( \frac{1}{T} \right)^{\frac{2}{n}-\frac{3}{2}}
\]
\[
\frac{1}{n} \left( 45 2^{8+\frac{4}{n}} (n-1) \pi^4 \Gamma\left(\frac{3(n-1)}{2n}\right) \right.
\]
\[
\left. \quad _1F_1\left(\frac{3(n-1)}{2n} + 1; \frac{5}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2} - \frac{7}{2}} \right)
\]
\[
\left(\frac{1}{T}\right)^{\frac{5}{2} - \frac{1}{2n}} + \frac{1}{45 \pi^4} \left(2^{-7-\frac{1}{n}} \left(4 - \frac{1}{2n}\right)\left(5 - \frac{1}{2n}\right)\right)
\]
\[
\left(-45 2^{7+\frac{4}{n}} \pi^4 \Gamma\left(\frac{n-3}{2n}\right) \right) \left._1F_1\left(\frac{n-3}{2n}; \frac{1}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2} - \frac{7}{2}} \right) +
\]
\[
45 2^{8+\frac{4}{n}} \pi^4 \Gamma\left(\frac{3(n-1)}{2n}\right) \left._1F_1\left(\frac{3(n-1)}{2n}; \frac{3}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2} - \frac{7}{2}} \right) +
\]
\[
45 2^{7+\frac{4}{n}} \pi^4 \Gamma\left(1 - \frac{3}{2n}\right) \left(T \left._1F_1\left(1 - \frac{3}{2n}; \frac{1}{2}; \frac{1}{T}\right) \right) -
\]
\[
2 \left._1F_1\left(1 - \frac{3}{2n}; \frac{3}{2}; \frac{1}{T}\right) \left(\frac{1}{T}\right)^{\frac{3}{2} - \frac{3}{2}} \right) \left(\frac{1}{T}\right)^{6-\frac{1}{2n}} \right)
\]

The first few lines of table I-B contained in the appendix of Hirschfelder et al. then follows by
Comparing the calculated figures with Hirschfelder's result demonstrates excellent agreement. The analytical results derived in the calculations above are not restricted to the (12-6)-LJ potential but allow any choice of the exponent $n > 3$. For example, we can determine the SVC for a (16-8)-potential by

$$t1 = \text{Table}[N[(T, bc, b1, b2, b1 - bc) /. n \to 6, 9], \{T, .3, 1, .05\}];$$

PrependTo[t1, {"T", "Bc", "b1", "b2", "b1-Bc"}];

TableForm[Map[Map[PaddedForm[#, {5, 2}] &, #] &, t1]]
We also can represent the data graphically:
Knowing the analytical expressions of the SVC, we are able to calculate either numerical values of of the classical SVC and its derivatives or represent the data graphically. We are not only restricted to classical values but can incorporate the quantum mechanical corrections. The first and second temperature derivatives for $B_q^*$ are

\[ bqq1 = T \partial_T b_{\text{star}}; \]

\[ bqq2 = T^2 \partial_{TT} b_{\text{star}}; \]

A table containing the SVC with quantum corrections and the two derivatives is generated by
\text{t3} = \text{Table[} \\
N[\{T, \text{bstar, bqq1, bqq2, bqq1 - bstar}\}/\{\pi \to 8, \sigma \to 1, \Lambda \to 1\}, 9], \\
\{T, 1, 2, .05\}]; \text{PrependTo[t3, \{"T", "B\*", "B1\*", "B2\*", "B1\*-B\*"\}];} \\
\text{TableForm[Map[Map[PaddedForm[\#, \{5, 4\}] \&, \#] \&, t3]]} \\

\begin{tabular}{|c|c|c|c|c|} 
\hline 
T & B\* & B1\* & B2\* & B1\*-B\* \\
\hline 
1.0000 & -1.3947 & 3.1190 & -7.8531 & 4.5137 \\
1.0500 & -1.2481 & 2.8954 & -7.3252 & 4.1435 \\
1.1000 & -1.1181 & 2.6961 & -6.8361 & 3.8141 \\
1.1500 & -1.0022 & 2.5181 & -6.3879 & 3.5203 \\
1.2000 & -0.8985 & 2.3587 & -5.9797 & 3.2572 \\
1.2500 & -0.8051 & 2.2156 & -5.6087 & 3.0207 \\
1.3000 & -0.7208 & 2.0866 & -5.2718 & 2.8074 \\
1.3500 & -0.6443 & 1.9700 & -4.9658 & 2.6143 \\
1.4000 & -0.5746 & 1.8643 & -4.6874 & 2.4388 \\
1.4500 & -0.5108 & 1.7680 & -4.4338 & 2.2788 \\
1.5000 & -0.4524 & 1.6801 & -4.2022 & 2.1325 \\
1.5500 & -0.3987 & 1.5995 & -3.9903 & 1.9982 \\
1.6000 & -0.3491 & 1.5256 & -3.7959 & 1.8746 \\
1.6500 & -0.3032 & 1.4574 & -3.6173 & 1.7606 \\
1.7000 & -0.2606 & 1.3945 & -3.4527 & 1.6551 \\
1.7500 & -0.2210 & 1.3362 & -3.3007 & 1.5572 \\
1.8000 & -0.1842 & 1.2821 & -3.1600 & 1.4662 \\
1.8500 & -0.1497 & 1.2317 & -3.0296 & 1.3814 \\
1.9000 & -0.1175 & 1.1848 & -2.9084 & 1.3023 \\
1.9500 & -0.0873 & 1.1409 & -2.7955 & 1.2282 \\
2.0000 & -0.0590 & 1.0998 & -2.6902 & 1.1588 \\
\hline 
\end{tabular}

These values are graphically represented by

5. Quantum Mechanics
5.7 Second Virial Coefficient

Stogryn and Hirschfelder [5.16] showed that the SVC can be separated into a bound state, a meta-stable state, and a continuum state contribution. For the (12-6)-LJ potential, they gave the temperature dependence of these contributions in tabular form.

At low temperatures, the average energies of the colliding molecules are of the order of the energy of the well depth. The molecule spends much time in the bound region of the molecular potential. Mutual attraction of the molecules results in a decrease of pressure, and the SVC is negative.
At high temperatures, corresponding to high energies compared to the well depth, the main contribution comes from the repulsive branch of the potential. Repulsion increases the pressure and SVS becomes negative.

From the above-mentioned investigation of the SVC for the (12-6)-LJ potential follows that the SVC for the bound states and the meta-stable states remains positive, whereas the contribution by the continuum states becomes negative and equals the bound state and metastable state contribution at the Boyle temperature leading to $B(T) = 0$. The shape dependence of the SVC on the exponent $n$ is shown in Figure 5.7.24.

The Boyle temperatures are calculated by solving the defining equation $B(T_B) = 0$. The solution is carried out by the function FindRoot[]:

\[
\text{ns} = \{4.0, 4.5, 5, 5.5, 6, 6.5, 7, 7.5\};
\]

\[
\text{Plot}\left[\text{Evaluate}\left[\text{Map}\left[\text{bc} / . n \rightarrow \# & , \text{ns}\right]\right],
\{T, 1, 300\}, \text{AxesLabel} \rightarrow \{"T^*", "B_{q0}^*"\},
\text{PlotStyle} \rightarrow \text{RGBColor}[0, 0, 0.996109],
\text{TextStyle} \rightarrow \{\text{FontFamily} \rightarrow \text{"Arial"},
\text{FontSize} \rightarrow 15, \text{FontWeight} \rightarrow \text{"Bold"}\},
\text{AxesStyle} \rightarrow \{\text{Thickness}[0.005]\},
\text{Prolog} \rightarrow \{\text{Text}["n=4.0", \{161.363, 0.171682\}],
\text{Text}["n=7.5", \{161.363, 0.6\}]\}\right];
\]
The following table collects the Boyle-temperatures for different values of \( n \):

\[
\text{tabBoyle} = \{(\text{Table}[i, \{i, 3.1, 7.5, .1]\}) \cdot \text{BoyleT}\};
\]

\[
\text{tb} = \text{Prepend}[\text{tabBoyle}, \{"n", "T_B"\}];
\]

A graphical representation of these numerical values is given in the following plot:

\[
\text{ListPlot}[\text{tabBoyle}, \text{AxesLabel} \rightarrow \{"n", "T_B"\}, \\
\text{PlotStyle} \rightarrow \text{RGBColor}[0.996109, 0, 0]];
\]

The result is that the Boyle tempearaure is a decreasing function which has a singularity at \( n = 3 \). For \( n \) values much larger than 3, the Boyle temperature approaches zero.

At often unphysically high temperatures, the molecules collide with such high energies that they interpenetrate each other. They behave as if they had a smaller volume so that B(T) goes through a maximum. This is shown in Figure 5.7.24. To determine the change of this maximum by altering the potential order, we determine the coresponding temperature values by
\[ T_{\text{max}} = \left( \text{FindRoot}[\#1 == 0, \{T, 20\}] \& /@ \right. \\
\left. \left( \partial_T \text{bc} /\!. n \rightarrow \#1 \& \right) /@ \text{Table}[i, \{i, 3.2, 7.5, .1\}] \right); \]

FindRoot::lstol:
The line search decreased the step size to within tolerance specified by AccuracyGoal and PrecisionGoal but was unable to find a sufficient decrease in the merit function. You may need more than MachinePrecision digits of working precision to meet these tolerances. More…

FindRoot::lstol:
The line search decreased the step size to within tolerance specified by AccuracyGoal and PrecisionGoal but was unable to find a sufficient decrease in the merit function. You may need more than MachinePrecision digits of working precision to meet these tolerances. More…

These maximum temperatures are collected in the following table. For He, this maximum was observed experimentally near 200 K.

\[
\text{tabTmax} = \\
\text{Transpose}[\{\text{Table}[i, \{i, 3.2, 7.5, .1\}], T /. \text{Tmax}\}]; \\
\text{tT} = \text{Prepend}[\text{tabTmax}, \{"n", "T_{\text{max}}"\}];
\]

The graphical representation of these data is given in the following plot:

\[
\text{ListPlot}[\text{tabTmax}, \text{AxesLabel} \rightarrow \{"n", "T_{\text{max}}"\}, \\
\text{PlotStyle} \rightarrow \text{RGBColor}[0.996109, 0, 0], \\
\text{PlotRange} \rightarrow \{[3, 7.7], [0, 220]\}];
\]
5.7.5 The High-Temperature Partition Function for Diatomic Molecules

The partition function of a diatomic molecule is important for many applications from astrophysics to reaction kinetics. In courses on physical chemistry, it is treated in the harmonic oscillator approximation – rigid rotator approximation, and anharmonicity and rotation – vibration interactions are included in the spirit of the JANAF tables.

It is known from high-temperature chemistry that for accurate thermodynamic functions, bound states from the solution of the rotation–vibration Schrödinger equation of the molecule

\[
\frac{\partial^2 \psi_{vJ}}{\partial r^2} - \left( U(r) + \frac{J(J+1)\hbar^2}{2\mu r^2} - E_{vJ} \right) \psi_{vJ} = 0
\]  

(5.7.119)

where \( \psi_{vJ} \) are rotation–vibration eigenfunctions, \( v \) and \( J \) are vibrational and rotational quantum numbers, respectively, \( \mu \) represents the reduced mass, and \( E_{vJ} \), the rotation–vibration eigenvalues, must be calculated. The meta-stable states behind the rotational barrier must be included.

Mies and Julienne [5.18] investigated the statistical thermodynamic of the diatomic molecule using numerical techniques for the exact scattering theory of the SVC.

For the equilibrium reaction

\[ X_2 \rightleftharpoons 2 X \]

as an example, they showed that the concentration equilibrium constant \( K_c \) can be expressed by the SVC

\[ B(T) = -K_c \]

(5.7.120)

As for real molecules and atoms excited, often degenerate electronic states must be included, they defined a generalized SVC by

\[ \langle B \rangle = (\sum_i B_i(t) g_i(x_2) e^{-E_{ij}/(k_B T)}) (\sum_j g_j(x) e^{-E_{ij}/(k_B T)}), \]

where \( B_i \) is the SVC for a molecular state \( i \), \( g \) is the electronic degeneracy \( E_{ij} \) is the excitation energy, \( g_j \) is the electronic degeneracy of the atomic
state \( j \) and \( E_j \) is its excitation energy. Phair, Birlsi and Holland [5.17] derived the partition function from

\[ K_p = \frac{K_c}{RT} = \frac{1}{k_B T} \frac{q(X)}{V} \left( \frac{q(X)}{V} \right)^2, \]

with \( K_p \) the pressure equilibrium constant, \( V \) the volume of the system, \( q(X) \) the monomer partition function, and \( q(X_2) \) the dimer partition function.

As \( q(X) \) depends only on mass, temperature, volume, and electronic degeneracy \( g \), the diatomic partition function for the bound state can be written

\[ q(X_2) = -B(T) \left( \frac{2 \pi m_e k_B T}{\hbar^2} \right)^3 \frac{V}{N_A} g_0(X) e^{-D_0/(k_B T)}, \quad (5.7.121) \]

where \( D_0 \) is the spectroscopic dissociation energy of the ground electronic state of the molecule \( X_2 \), if the energy zero is taken as the lowest vibrational state (one can take as well \( D_e \) as energy zero). If we insert the analytical results for \( B(T) \) for the \((2n-n)\)-potential derived above a closed-form representation of a realistic partition function including rotation–vibration coupling, anharmonicity up the dissociation limit, meta-stable states behind the rotational barrier, and the continuum or scattering states.

From the diatomic partition function, the molecular thermodynamic functions can be calculated by standard methods. Phais et al. [5.17] gave explicite formulas for

\[ H^0_T - H^0_0 = RT \left( 4 + \frac{B_1^c}{B^c} + \ldots \right), \quad (5.7.122) \]
\[ C_p^0 = R \left( 4 + 2 \frac{B_1^c}{B^c} + \frac{B_2^c}{B^c} - \left( \frac{B_1^c}{B^c} \right)^2 \right). \quad (5.7.123) \]

Equation (5.7.122) scaled by \( R \) reads

\[ C_p = -\left( \frac{b_1}{bc} \right)^2 + \frac{2 b_1}{bc} + \frac{b_2}{bc} + 4; \]

A graphical representation of this function for different values of \( n \) is given next.
Phair et al. used a five-parameter Hulburt–Hirschfelder potential in their numerical calculations for $B_{q0}$. The following set of data is taken from their article representing the scaled $C_p$ values [5.17].

\[
data = \{\{0.0174, 4.5\}, \{0.0384, 4.57\}, \{0.0522, 4.69\}, \\
0.0696, 4.75\}, \{0.0869, 5.035\}, \{0.1043, 5.52\}, \\
0.1217, 5.99\}, \{0.1304, 6.14\}, \{0.139, 6.20\}, \\
0.147, 6.19\}, \{0.156, 6.09\}, \{0.174, 5.75\}, \\
0.191, 5.28\}, \{0.208, 4.83\}, \{0.217, 4.62\}\};
\]

A combination of our symbolic calculations and their numerical results demonstrates a qualitative agreement. The results are shown in the Figure 5.7.25.
5.8 Exercises

1. Examine the spectrum of the eigenvalues for a potential well with different depths. Give a graphical representation of the eigenvalues depending on different depths.

2. Determine the wave functions for different eigenvalues for the potential well by using the methods discussed in Section 5.3.

3. Check the relation $|a|^2 + |b|^2 = 1$ for the anharmonic oscillator.

4. Reexamine the Pöschel–Teller problem and study the expectation values $\langle x^n \rangle$ given by

$$\langle x^n \rangle = \int \psi^* x^n \psi \, dx$$

for different values of $n$.

5. Plot the radial part of the wave function of the hydrogen atom for different quantum numbers $n$ and $l$. Examine the influence of the charge $Z$. 

Shape dependence of the “dissociation” maximum of the heat capacity $C_p$. The points denoted by dots are for $N_2$ taken from Phair et al, using the five parameter Hulburt–Hirschfelder potential in the numerical calculation of $B_{00}$ and its temperature derivatives.

Figure 5.7.25.
6. Create a graphical representation of the $f$ orbital for the europium atom.

## 5.9 Packages and Programs

### 5.9.1 Package QuantumWell

This package serves to examine a one-dimensional quantum dot.

```mathematica
BeginPackage["QuantumWell"];

Clear[PsiSym, PsiASym, Spectrum];

PsiSym::usage = "PsiSym[x_,k_,a_] determines the symmetric
eigenfunction for a potential well of depth $V_0$. The input parameter $k$ fixes the energy and
$2a$ the width of the well. PsiSym is useful for
a numerical representation of eigenfunctions.";

PsiASym::usage = "PsiASym[x_,k_,a_] determines the antisymmetric
eigenfunction for a potential well of depth $V_0$. The input parameter $k$ fixes the energy and
$2a$ the width of the well. PsiASym is useful for
a numerical representation of eigenfunctions.";

Spectrum::usage = "Spectrum[V0_,a_] calculates the negative
eigenvalues in a potential well. $V_0$ is the
potential depth and $2a$ the width of the well. The eigenvalues are returend as a list
and are available in the variables lsym and
lasym as replacement rules. The corresponding
plots of eigenfunctions are stored in the
variables Plsym and Plasym. The determining
equation for the eigenvalues is plotted.";
```
(*---define global variables---*)

Plsym::usage = "Variables containing the symmetric plots of the eigenfunctions."
Plasym::usage = "Variables containing the antisymmetric plots of the eigenfunctions."
lsym::usage = "List of symmetric eigenvalues."
lasym::usage = "List of antisymmetric eigenvalues."
k::usage = "Eigenvalue."

Begin["`Private`"];

(*---symmetric eigenfunctions---*)
Psisy[x_, k_, a_] := Block[{},
  (*---define the three domains of solution---*)
  Which[-Infinity < x && x < -a,
    1/Sqrt[a Exp[-2 a k Tan[k a]] (1 + 1/(k Tan[k a]) a) + k Tan[k a]/(k^2 a) + (k Tan[k a])^2/k^2)]
    Exp[k Tan[k a] x], -a <= x && x <= a,
    1/Sqrt[a Exp[-2 a k Tan[k a]] (1 + 1/(k Tan[k a]) a) + k Tan[k a]/(k^2 a) + (k Tan[k a])^2/k^2)]
    Exp[-k Tan[k a] a] Cos[k x] / Cos[k a],
    a < x && x < Infinity, 1/Sqrt[a Exp[-2 a k Tan[k a]]
    (1 + 1/(k Tan[k a]) a) + k Tan[k a]/(k^2 a) + (k Tan[k a])^2/k^2)] Exp[-k Tan[k a] x]];  

(*---antisymmetric eigenfunctions---*)
Psias[x_, k_, a_] := Block[{},
  (*---define the three domains of solution---*)
  Which[-Infinity < x && x < -a,
    -1/Sqrt[a Exp[-2 a (-k Cot[k a])]
    (1 + 1/(-k Cot[k a]) a) + (-k Cot[k a])^2/k^2)]
    Exp[(-k Cot[k a]) x], -a <= x && x <= a,
    1/Sqrt[a Exp[-2 a (-k Cot[k a])]
    (1 + 1/(-k Cot[k a]) a) + (-k Cot[k a])^2/k^2)]
    Exp[-(-k Cot[k a]) a] Sin[k x] / Sin[k a],
    a < x && x < Infinity,
    1/Sqrt[a Exp[-2 a (-k Cot[k a])]
    (1 + 1/(-k Cot[k a]) a) + (-k Cot[k a])^2/k^2)]
\[ \exp \left( -(k \cot(k a)) x \right) \]

(*---determination of the eigenvalues; plot of the eigenfunctions---*)
Spectrum[V0_, a_] :=
Block[{
hbar = 1, m = 1, ymax, C2, rhs, lhssym, lhasym, equatsym, equatasym, kmax, nsym, nasym, resultsym, resultasym},
(*---define constants and the eigenvalue equation---*)
C2 = 2 m V0 a^2 / (hbar^2);
rhs = Tan[k a];
lhssym = Sqrt[C2 - (k a)^2] / (k a);
lhasym = -k a / Sqrt[C2 - (k a)^2];
equatsym = Sqrt[C2 - (k a)^2] / (k a) - Tan[k a];
equatasym = -k a / Sqrt[C2 - (k a)^2] - Tan[k a];
(*---location of the singularity in k---*)
kmax = Sqrt[C2 / a^2];
(*---number of symmetric eigenvalues---*)
nsym = Floor[N[kmax / (Pi / a)] + 1;
(*---number of antisymmetric eigenvalues---*)
nasymp = Floor[N[(kmax - Pi / (2 a)) / (Pi / a)] + 1;
(*---initialize the lists for the eigenvalues---*)
lsym = {};
lasymp = {};
(*---calculate the symmetric eigenvalues---*)
Do[resultsym = Chop[FindRoot[
equatsym == 0, \{k, 0.1 + (Pi / a) (i - 1)\}]]; 
AppendTo[lsym, resultsym], \{i, 1, nsym\}];
(*---Chop[] replaces small numbers \(<10^{-10})\) by 0---*)
(*---calculate the antisymmetric eigenvalues---*)
Do[resultasym = Chop[FindRoot[equatasym == 0, 
\{k, Pi / (2 a) + 0.1 + (Pi / a) (i - 1)\}]]; 
AppendTo[lasymp, resultasym], \{i, 1, nasym\}];
(*---plot the eigenvalue equation---*)
ymax = lhssym 1.5 /. lsym[[1]];
Off[Plot::plnr];
Plot[\{rhs, lhssym, lhasym\}, 
\{k, 0.01, 3 kmax / 2\}, PlotRange \rightarrow \{-ymax, ymax\},
Prolog \rightarrow Thickness[0.001],
PlotStyle \rightarrow \{RGBColor[1, 0, 0], Dashing[\{\}]\],
Dashing[{1/60}], AxesLabel -> {"k", " "}];
On[Plot::plnr];

(*---plot the symmetric eigenfunctions---*)
Do[k1 = k /. lsym[[i]]];
Plsym[i] = Plot[Psisym[x, k1, a], {x, -2 a, 2 a},
AxesLabel -> {"x", "\!(\psi^\prime s)\)\n"}, PlotLabel ->
" \!(\langle k\_i\rangle) = " <> ToString[k1],
Frame -> True, PlotRange -> All,
Prolog -> Thickness[0.001], PlotStyle ->
{Dashing[{1/(i 20).exist}], {i, 1, nsym}};

(*---plot the antisymmetric eigenfunctions---*)
Do[k1 = k /. lasym[[i]]];
Plasym[i] = Plot[Psiasym[x, k1, a], {x, -2 a, 2 a},
AxesLabel -> {"x", "\!(\psi^\prime a)\)\n"},
PlotLabel -> " \!(\langle k\_i\rangle) = " <> ToString[k1],
Frame -> True, PlotRange -> All,
Prolog -> Thickness[0.001], PlotStyle ->
{Dashing[{1/(i 20).exist}], {i, 1, nasym}};

(*---print the eigenvalues---*)
Print[" ";
Print[" ---- eigenvalues ---- ";
Print[" "];
Do[k1 = k /. lsym[[i]]];
If[i <= nasym, k2 = k /. lasym[[i]], k2 = "----"];
Print[" sym eigenvalue k",
i, " = ", k1, " asym eigenvalue k",
i, " = ", k2], {i, 1, nsym}]];

End[];
EndPackage[];

Set::patset : Warning: k : usage in assignment
k : usage = Eigenvalue. represents a named pattern;
use symbol::tag to represent a message name. More…

Here are some tests of the symmetric and antisymmetric wave function.
\begin{verbatim}
Plot[{PsiSym[x, 1.30183, 1],
      PsiSym[x, 3.818578969739773`, 1]}, {x, -2., 2},
   Frame -> True, FrameLabel -> {"x", "\(\psi^s\)"},
   PlotStyle -> {RGBColor[1, 0, 0], RGBColor[0, 0, 1]},
   Prolog -> {{RGBColor[1, 0, 0], Text["k_1=1.3018",
      {1., -0.220252}]}, {RGBColor[0, 0, 1],
      Text["k_2=3.8185", {1., -0.420252}]}}];
\end{verbatim}
5. Quantum Mechanics

5.9.2 Package HarmonicOscillator

The package HarmonicOscillator provides functions to represent eigenfunctions of the harmonic oscillator.

BeginPackage["HarmonicOscillator\~"];

Clear[a, across, Psi, wcl, wqm];

Psi::usage = "Psi[xi_,n_] represents the eigenfunction of the harmonic oscillator. The first argument xi is the spatial coordinate. The second argument n fixes the eigenstate."

wcl::usage = "wcl[xi_,n_] calculates the classical probability"
of locating the particle in the harmonic potential. The first argument \( \xi \) is the spatial coordinate while \( n \) determines the energy given as eigenvalue."

\[
\text{wqm}::\text{usage} =
\text{"wqm}[\xi_, n_] \text{ calculates the quantum mechanical probability for an eigenvalue state } n. \text{ The first argument represents the spatial coordinate.";}
\]

\[
\text{a}::\text{usage} = \text{"a}[\psi_, \xi_:x] \text{ annihilation operator for eigenfunction } \psi. \text{ The second argument specifies the independent variable of the function } \psi."; \]

\[
\text{across}::\text{usage} =
\text{"across}[\psi_, \xi_:x] \text{ creation operator for eigenfunction } \psi. \text{ The second argument specifies the independent variable of } \psi."; \]

\[
\text{x}::\text{usage}; \]

\[
\text{Begin["`Private`"]}; \]

(*---eigenfunctions of the harmonic oscillator---*)
\[
\Psi[\xi_, n_] :=
\text{HermiteH}[n, \xi] \text{ Exp}[-\xi^2 / 2] / \text{Sqrt}[n! 2^n \text{Sqrt}[\pi]]; \]

\[
\Psi[\xi, n] := \text{HermiteH}[n, \xi] \text{ Exp}[-\xi^2 / 2] / \text{Sqrt}[n! 2^n \text{Sqrt}[\pi]]; \]

(*---classical probability distribution of the harmonic oscillator---*)
\[
\text{wcl}[\xi_, n_] := 1 / (\text{Sqrt}[2 n + 1] \text{Sqrt}[1 - (\xi / \text{Sqrt}[2 n + 1])^2] 2 \pi); \]

(*---quantummechanical probability distribution of the harmonic oscillator---*)
\[
\text{wqm}[\xi_, n_] := \Psi[\xi, n]^2; \]

(*---annihilation operator---*)
\[
\text{a}[\psi_, \xi_:x] := (\xi \psi + D[\psi, \xi]) / \text{Sqrt}[2]; \]

(*---creation operator---*)
across[ψ_, xi_: x] := (x ψ - D[ψ, xi]) / Sqrt[2];
End[];
EndPackage[];

5.9.3 Package AnharmonicOscillator

The package AnharmonicOscillator serves to determine the properties of
the Pöschel–Teller problem.

BeginPackage["AnharmonicOscillator"];
Clear[AsymptoticPT, PlotPT, PoeschelTeller];
PoeschelTeller::usage = "PoeschelTeller[x_, n_, indexN_] calculates the
eigenfunction of the Pöschel Teller potential
for discrete eigenvalues. N determines the
depth of the potential V0 Sech[x] by V0=N(N+1).
n fixes the state where 0 < n <= N."];

w1a::usage = "The variable contains the
analytic expression for the asymptotic
approximation for x -> -Infinity.";

w2a::usage = "The variable contains the
analytic expression for the asymptotic
approximation for x -> Infinity.";

Transmission::usage = "Variable containing the expression
for the transmission coefficient. The
independent variables are N and k.";

Reflection::usage = "Variable containing the reflection coefficient.
The independent variables are N and k.";

AsymptoticPT::usage = "AsymptoticPT[indexN_,kin_] determines the
asymptotic approximation for |x|->Infinity
for the continuous case of eigenvalues in"
a Poeschel Teller potential. The function yields an analytic expression for $|b(k)|^2$. The variables Transmission and Reflection contain the expressions for the transmission and the reflection coefficients. $w1a$ and $w2a$ contain the approximations for $x\to -\infty$ and $x\to \infty$, respectively.

PlotPT::usage = "PlotPT[kini_, kend_, type_] gives a graphical representation of the reflection or transmission coefficient depending on the value of the variable type. If type is set to the string r the reflection coefficient is plotted. If type is set to the transmission coefficient is represented. This function creates 5 different curves.";

Begin["`Private`"];

(*---define the eigenfunctions---*)
PoeschelTeller[x_, n_Integer, indexN_Integer] :=
  Block[{norm, integrand, xi},
    If[n <= indexN && n > 0, (*---eigenfunctions are the associated Legendre polynomials---*)
      integrand = LegendreP[indexN, n, xi];
      (*---calculate the normalization constant---*)
      norm = Integrate[integrand^2/(1 - xi^2), {xi, -1, 1}];
      ((*---normalize and simplify the functions---*)
       integrand = integrand/Sqrt[norm] /. xi -> Tanh[x];
       Simplify[integrand],
      (*---error conditions---*)
      If[indexN < n,
        Print["--- wrong argument! use n > N"]];
      If[n < 0, Print["--- wrong argument! use n < 0"]]]];

(*---asymptotic expansion---*)
AsymptoticPT[indexN_, kin_] :=
  Block[{
    k, rule1, rule2, wavefkt1, wavefkt2, asympt1, w1, asynt2, w2, akh, bkh, ak},

(*---replacement rules for the parameters---*)
rule1 = {a -> 1/2 - I k + (1/4 + V0)^(1/2),
        b -> 1/2 - I k - (1/4 + V0)^(1/2), c -> 1 - I k};
rule2 = {V0 -> indexN (1 + indexN)};
wavefkt1 = a k ((1 - xi^2)/4) (-I k/2);
wavefkt2 = Hypergeometric2F1[a, b, c, (1 + xi)/2];
(*---asymptotic expansion for x→-Infinity,
equation 5.5.63---*)
asymt1 = Series[wavefkt1, {xi, -1, 0}];
w1 = wavefkt1 Normal[asymt1] /. rule1;
w1 = w1 /. rule2;
w1 = w1 /. xi → Tanh[x];
w1 = Simplify[w1];
w1 = w1 /. Sech[x] → 2 Exp[-x];
w1a = PowerExpand[w1];
(*---asymptotic expansion for x→
   Infinity by equation 5.5.65-5.5.68---*)
asymt2 = Series[wavefkt2, {xi, 1, 1}];
(*---invert substitution---*)
w2 = wavefkt1 Normal[asymt2] /. xi → Tanh[x];
(*---eliminate higher terms---*)
w2 = Expand[Simplify[w2] /. -1 + Tanh[x] → 0];
(*---asymptotic
   behavior for Sech[] and Tanh[]---*)
w2 = w2 /. {Sech[x] → Exp[-x],
            1 - Tanh[x] → Exp[-2 x]};
w2 = w2 /. rule1;
w2 = w2 /. rule2;
w2a = PowerExpand[w2];
(*---determine the
coefficients a[k] and b[k]---*)
akh = Coefficient[w2a, Exp[-I k x]] /. ak → 1;
bkh = Coefficient[w2a, Exp[I k x]] /. ak → 1/akh;
(*---calculate the transmission and
reflection coefficient---*)
Transmission = 1/(akh Conjugate[akh]) /. k → kin;
Reflection = bkh Conjugate[bkh] /. k → kin;
{Transmission, Reflection};

(*---graphical representation of the
reflection and transmission coefficient---*)
PlotPT[kini_, kend_, type_]:=
Block[{k0 = kini, ke = kend, p, t1, label},
  t1 = Transpose[Table[AsymptoticPT[indexxN, kk],
    {kk, k0, ke, (ke - k0) / 5}]];
  If[type == "r", p = t1[[2]];
    label = "|b|\(^2\)",
    p = t1[[1]];
    label = "|a|\(^2\)";
    Plot[Chop[p], {indexxN, 1, 2}, AxesLabel ->
      {"N", label}, Prolog -> Thickness[0.001]];
  ]]
End[];
EndPackage[];

5.9.4 Package CentralField

CentralField is a package allowing you to represent the eigenfunctions for
problems with a central field.

BeginPackage["CentralField`"];
Clear[Radial, Angle, AnglePlot, Orbital];

Radial::usage = "Radial[ro_, n_, l_, Z_] calculates the radial representation
of the eigenfunctions for an electron in
the Coulomb potential. The numbers
n and l are the quantum numbers for the
energy and the angular momentum
operator. Z specifies the number of
charges in the nucleus. The radial
distance between the center and the
electron is given by ro."

Angle::usage = "Angle[theta_, phi_,
  l_, m_] calculates the angular part of
the wave function for an electron in the
Coulomb potential. The numbers L
and m denote the quantum numbers for the
angular momentum operator. Theta
and phi are the angles in the spherical
coordinate system.";
Orbital::usage = "Orbital[\theta_, \\
    \phi_, l_, m_, type_String] calculates the \\
superposition of two wave functions for \\
the quantum numbers \( m \pm l = \pm m \) and \\
\( m \pm l = -m \). The variable type allows the \\
creation of the sum or the difference \\
of the wave functions. The string values \\
of type are either plus or minus.";

AnglePlot::usage = 
"AnglePlot[pl_, \theta_, \phi_] gives a graphical 
representation of the function contained 
in pl. The range of representation 
is \( \pi \leq \phi < 5\pi/2 \) and \( 0 < \theta < \pi \). 
Theta is measured with 
respect to the vertical axis. This function 
is useful for plotting the orbitals 
and the angular part of the eigenfunction.";

(*---define global variables---*)

theta::usage;
phi::usage;
ro::usage;
n::usage;
l::usage;
m::usage;

Begin["\`Private\"];

(*---radial part of the eigenfunctions 
in the Coulomb potential---*)

Radial[ro_, n_, l_, Z_] := Block[{norm, hnl}, 
    (*---normalization---*)
    norm = (Sqrt[(n + 1)! / (2 n (n - l - 1)!)]) 
        ((2 Z) / n)^(l + 3/2) / (2 l + 1) !;
    (*---definition of the wave function---*)
    hnl = norm ro^l Exp[-((Z ro) / n)] 
        Hypergeometric1F1[l + 1 - n, 2 l + 2, (2 Z ro) / n]];
(*---angular part of the eigenfunctions in the Coulomb field---*)

\[\text{Angle}[\theta_, \phi_, l_, m_] := \text{Block[}
\{\text{norm, legendre, x, angle, ml, result}\}, \text{ml} = \text{Abs}[m];
(*---normalization---*)
\text{norm} = (-1)^\text{ml}\sqrt{\left((2l+1)(1-\text{ml}!) / (2(l+\text{ml}!)\right) / \text{Sqrt}[2\pi];}
(*---eigenfunctions---*)
\text{legendre} = \text{Sin}[\theta]^\text{ml}\text{D}[\text{LegendreP}[l, x], \{x, \text{ml}\}];
\text{legendre} = \text{legendre} /. x \rightarrow \text{Cos}[\theta];
(*---consider the cases } m>0 \text{ and } m<0---*)
\text{If}[m \geq 0, \text{angle} = \text{Exp}[\text{Im}\phi],
\text{angle} = (-1)^\text{ml}\text{Exp}[-(\text{Im}\text{ml}\phi)];
(*---normalized eigenfunction---*)
\text{result} = \text{norm}\text{legendre}\text{angle};

(*---create orbitals---*)

\text{Orbital}[\theta_, \phi_, l_, m_, \text{type}_\text{String}] := \text{Block[}\{\text{norm, ml, rule, wave, wave2}\},
\text{ml} = \text{Abs}[m];
(*---replacement rule for the exponential function---*)
\text{rule} = \{E^\text{(Complex}[0, \text{a_}] (x_)) \rightarrow
\text{Cos}[x\text{Abs}[\text{a}]] + I\text{Sign}[\text{a}\text{Sin}[x\text{Abs}[\text{a}]])\};
(*---distinguish different cases---*)
\text{If}[\text{ml} \geq 1,
\text{If}[\text{type} = \"plus\",
(*---sum of the wave functions for a fixed } m---*)
\text{wave} = \text{Expand}[\text{Angle}[\theta, \phi, l, \text{ml}] +
\text{Angle}[\theta, \phi, l, -\text{ml}] /. \text{rule}],
(*---difference of the wave function for a fixed } m---*)
\text{wave} = \text{Expand}[\text{Angle}[\theta, \phi, l, \text{ml}] -
\text{Angle}[\theta, \phi, l, -\text{ml}] /. \text{rule}];
\text{wave2} = \text{wave}^2;
(*---normalization of the superposition---*)
\text{norm} = \text{Integrate[wave2, \{phi, 0, 2\pi\}, \{theta, 0, \pi\}]};
\[
\text{wave2} = \text{Expand}[\text{wave2}/\text{Abs}[\text{norm}]], \\
\text{wave} = \text{Angle}[\theta, \phi, l, m_l]^2];
\]

(*---graphical representation of the angular part---*)

\[
\text{AnglePlot}[pl_, \theta_, \phi_] := \text{Block}[],
\]

(*---\theta is measured with respect to the vertical axis---*)\[
\text{ParametricPlot3D}[
\{-pl \sin[\theta] \cos[\phi], -pl \sin[\theta] \sin[\phi], \\
pl \cos[\theta]\}, \{\theta, 0, \pi\}, \{\phi, \pi, 5 \pi/2\}, \text{PlotRange} \to \text{All}, \text{PlotPoints} \to \{40, 40\}];
\]

End[];

EndPackage[];