Dimensionless equations in non-relativistic quantum mechanics

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Abstract

We discuss the numerous advantages of using dimensionless equations in non-relativistic quantum mechanics. Dimensionless equations are considerably simpler and reveal the number of relevant parameters in the models. They are less prone to round-off errors when applying numerical methods because all the quantities are of the other of unity. A dimensionless equation facilitates the application of perturbation theory and provides a glimpse of the sort of solution we are going to obtain beforehand.

1 Introduction

Solving the Schrödinger equation in non-relativistic quantum mechanics is greatly facilitated if we first convert that equation into a dimensionless form. The reason is that fundamental constants like \( \hbar \) (Plank constant divided \( 2\pi \)) the electronic mass \( m_e \) and charge \( e \), as well as other model parameters, are removed leaving a much simpler equation [1]. The algebraic manipulation of the dimensionless

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equation is considerably less laborious and its numerical treatment, if it is not exactly solvable, exhibits less round-off errors after getting rid of such small numbers.

It is a common practice, though in our opinion quite undesirable, to state that “we choose units so that $\hbar = m = e = c = 1$” or similar expressions [2]. This is specially so in the case of pedagogical papers where one should teach the students to carry out the procedure of making dimensionless equations in detail [3]. For this reason, in this paper we show how to derive dimensionless equations and discuss the advantages of the approach as well as valuable information about the physical result we are looking for.

In section 2 we discuss several one-dimensional examples, in section 3 we focus on atoms and molecules, in section 4 we outline the utility of dimensionless equations in the application of perturbation theory and in section 5 we summarize the main results and draw conclusions.

## 2 One-dimensional models

In order to illustrate how to convert quantum-mechanical equations into dimensionless differential equations we begin with some simple one-dimensional models in non-relativistic quantum mechanics. For simplicity, we first focus on time-independent problems. The Hamiltonian operator for a particle of mass $m$ in a potential $V(x)$ in the coordinate representation is given by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x),$$  \hspace{1cm} (1)

where $-\infty < x < \infty$. The strategy is simple: we first define a dimensionless coordinate $\tilde{x} \equiv x/L$, where $L$ is a unit of length that we choose conveniently for each problem. If we take into account that $d/dx = (d\tilde{x}/dx) d/d\tilde{x} = L^{-1} d/d\tilde{x}$ we conclude that $d^2/dx^2 = L^{-2} d/d\tilde{x}^2$. Second, we define the dimensionless Hamiltonian operator $\tilde{H}$ as

$$\tilde{H} = \frac{mL^2}{\hbar^2} H = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{mL^2}{\hbar^2} V(L\tilde{x}).$$  \hspace{1cm} (2)
Therefore, if \( \psi \) is an eigenfunction of \( H \) with eigenvalue \( E \) (\( H \psi = E \psi \)) then the corresponding eigenvalue \( \tilde{E} \) of \( \tilde{H} \) is the dimensionless energy and both eigenvalues are related by

\[
E = \frac{\hbar^2}{mL^2} \tilde{E},
\]

where \( \hbar^2 / (mL^2) \) is the unit of energy.

As a first example we choose a particle of mass \( m \) in an impenetrable box of length \( L \)

\[
H \psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x),
\]

\[
\psi(0) = \psi(L) = 0.
\]

In this case the unit of length is given by the box length and we define \( \tilde{\psi}(\tilde{x}) \equiv \psi(L \tilde{x}) \) (the normalization factor is irrelevant for present discussion) that is a solution to

\[
-\frac{1}{2} \frac{d^2}{d\tilde{x}^2} \tilde{\psi}(\tilde{x}) = \tilde{E} \tilde{\psi}(\tilde{x}),
\]

and satisfies the boundary conditions \( \tilde{\psi}(0) = \tilde{\psi}(1) = 0 \). The eigenvalues of this equation are

\[
\tilde{E}_n = \frac{n^2 \pi^2}{2}, \quad n = 1, 2, \ldots,
\]

so that equations (6) and (3) yield the well known energies of the particle in a box [4]. It is clear that when we make the quantum-mechanical eigenvalue equation dimensionless we can predict the dependence of the energies on the model parameters and physical constants (\( \hbar, m \) and \( L \) in the present case) without solving the equation. Besides, equation (5) makes the statement “we choose units so that \( \hbar = m = L = 1 \)” self-evident (specially for pedagogical purposes). In addition to it, we also predict that the eigenfunctions for the particle in a box will depend on the variable \( \tilde{x} \equiv x/L \) and this is actually so as shown by [4]

\[
\psi_n = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right).
\]

It is always convenient to tell the students that the arguments of functions like \( \sin(z) \), \( \ln(z) \), \( \exp(z) \), etc should be dimensionless and that a result that does not
follow this rule is wrong. In our opinion, the dimensionless energy ˜\(E\) is more convenient than \(\epsilon \equiv 2mE/\hbar^2\) that exhibits units of length\(^{-2}\).

The example above may look unimpressive and we will discuss some others below. Another simple one is the harmonic oscillator with potential

\[ V(x) = \frac{k}{2} x^2, \quad (8) \]

where \(k > 0\) is the force constant. In this case we have

\[ \frac{mL^2}{\hbar^2} V(L\tilde{x}) = \frac{mL^4 k}{\hbar^2} \tilde{x}^2. \quad (9) \]

Therefore, if we choose

\[ L \equiv \left( \frac{\hbar^2}{mk} \right)^{1/4}, \quad (10) \]

then the dimensionless Hamiltonian operator will be

\[ \tilde{H} = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{1}{2} \tilde{x}^2, \quad (11) \]

and the unit of energy results to be

\[ \frac{\hbar^2}{mL^2} = \hbar \omega, \quad \omega = \sqrt{\frac{k}{m}}. \quad (12) \]

We realize that the energies of the harmonic oscillator are of the form \(E_n = \hbar \omega \tilde{E}_n\), where \(\tilde{E}_n\) is dimensionless. If we solve the eigenvalue equation we obtain the allowed energies \(E_n = \hbar \omega (n + 1/2),\ n = 0, 1, \ldots\) that agree with the previous equation because \(\tilde{E}_n = (n + 1/2)\) are the eigenvalues of the dimensionless Hamiltonian operator \((11)\). Once again, we realize the form of the energies in terms of the model parameters and physical constants \(\hbar, m\) and \(k\) without solving the eigenvalue equation. Besides, we also know that the states of the harmonic oscillator will be functions of \(\tilde{x}\). It is well known that in this case \(\psi_n(x) = N_n H_n(\tilde{x}) \exp \left(-\tilde{x}^2/2\right),\) where \(H_n(\tilde{x})\) is an Hermite polynomial and \(N_n\) a normalization factor \((4)\). Notice that the definition \((10)\) makes \(\frac{\hbar^2}{2mL^2}\) (which resembles the kinetic energy) equal to \(\frac{kL^2}{2}\) (which resembles the potential energy).
In some cases the potential-energy function is defined in terms of a length parameter, for example:

\[ V(x) = V_0 f \left( \frac{x}{a} \right) . \]  

(13)

In this case

\[ \frac{mL^2}{\hbar^2} V (L\tilde{x}) = \frac{mL^2}{\hbar^2} V_0 f \left( \frac{L\tilde{x}}{a} \right) , \]  

(14)

and we have two possibilities. If we choose \( L \equiv a \) we have

\[ \tilde{H} = \frac{ma^2}{\hbar^2} H = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \lambda f (\tilde{x}) , \quad \lambda = \frac{ma^2}{\hbar^2} V_0 , \]

\[ \frac{ma^2}{\hbar^2} E = \lambda \tilde{E} , \quad \tilde{E} = E \frac{V_0}{V_0} . \]  

(15)

If, on the other hand, we choose

\[ L \equiv \frac{\hbar}{\sqrt{mV_0}} , \]  

(16)

then

\[ \tilde{H} = \frac{1}{V_0} H = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + f \left( \frac{\tilde{x}}{\sqrt{\lambda}} \right) . \]  

(17)

Although the dimensionless Hamiltonians (15) and (17) are different and have different eigenvalues in both cases \( E = V_0 \tilde{E} (\lambda) \). The choice of \( L \) depends on what we are planning to do with the resulting dimensionless equation. The examples in section 4 will show the utility of this apparent arbitrariness.

Up to now we have been tacitly assuming that our interest was the calculation of the bound states supported by the potential. Suppose that we are interested in the calculation of the scattering states for the potential (13). In this case the present analysis tells us that the transmission \( T \) and reflection \( R \) coefficients can be expressed in terms of only two quantities: \( \lambda \) and \( \tilde{E} \). For instance, consider the textbook example given by the tunnel effect through the rectangular potential barrier

\[ V(x) = \begin{cases} 
0 & \text{for } x < 0 \\
V_0 & \text{for } 0 < x < a \\
0 & \text{for } x > a 
\end{cases} . \]  

(18)
This problem can be solved exactly and the result [4] rewritten as
\[
T \left( \tilde{E}, \lambda \right) = \begin{cases} 
\frac{4 \tilde{E}(1-\tilde{E})}{4E(1-\tilde{E}) + \sinh^2 \left( \sqrt{2\lambda(1-\tilde{E})} \right)} & 0 < \tilde{E} < 1 \\
\frac{2}{2 + \lambda} & \tilde{E} = 1 , \\
\frac{4E(E-1)}{4E(E-1) + \sin^2 \left( \sqrt{2\lambda(E-1)} \right)} & \tilde{E} > 1
\end{cases}
\] (19)

that confirms our prediction that \( T \) depends on only two dimensionless parameters when other strategies produce results in terms of more dimensional quantities [4].

Another interesting and well known example is the Morse oscillator with potential
\[
V(x) = D_e \left[ 1 - \exp (-ax) \right]^2,
\] (20)

where \( D_e, a > 0 \). In this case there are also two obvious possibilities and we choose \( L \equiv 1/a \) so that
\[
\tilde{H} = \frac{m}{\hbar^2 a^2} H = -\frac{1}{2} \frac{d^2}{dx^2} + \lambda \left[ 1 - \exp (-\tilde{x}) \right]^2 , \quad \lambda = \frac{mD_e}{\hbar^2 a^2} , \quad E = \frac{D_e}{\lambda} \tilde{E}(\lambda).
\] (21)
The bound-state energies of the Morse oscillator are known to be [5]
\[
E_n = \hbar c \left[ \omega_e (n + 1/2) - \chi_e \omega_e (n + 1/2)^2 \right],
\]
\[
\omega_e = \frac{a}{\pi c} \sqrt{\frac{2m}{2m}} , \quad \chi_e = \frac{\hbar c}{4D_e} \omega_e.
\] (22)

that can be easily rewritten as
\[
E_n = \frac{D_e}{\lambda} \left[ \sqrt{2\lambda} (n + 1/2) - \frac{1}{2} (n + 1/2)^2 \right],
\] (23)
in agreement with the prediction of present approach.

In a recent paper Ahmed et al [6] solved the Schrödinger equation with the potential
\[
V(x) = V_0 \left( 1 - e^{2|x|/a} \right), \quad V_0 > 0, \ a > 0,
\] (24)

that exhibits bound states in the continuum. In their figure 2 they state “Here, we take \( 2m/\hbar^2 = 1, V_0 = 50 \) and \( a = 1 \).” Obviously, these equalities are wrong because the left-hand sides have units and the right-hand ones do not. If we
apply the procedure outlined above we obtain an equation similar to \[ \text{(15)} \] with \( f(\tilde{x}) = 1 - e^{2|\tilde{x}|} \) and realize that the model depends on just one parameter \( \lambda \) that is dimensionless. Instead of searching for solutions for pairs of values of \( V_0 \) and \( a \) it is sufficient to obtain solutions for just one parameter \( \lambda \). If we calculate \( \tilde{E}(\lambda) \) then we have \( E = V_0 \tilde{E}(\lambda) \).

Just one more example from a paper published recently. Nguyen and Marsiglio \[ \cite{7} \] studied the Schrödinger equation with the potential \( V(x) = -\alpha/x^2 \) and proposed the alternative truncated potential

\[
V_\epsilon(x) = \begin{cases} 
-\frac{\alpha}{\epsilon} & \text{if } 0 < x < \epsilon \\
-\frac{\alpha}{x^2} & \text{if } \epsilon < x < \infty 
\end{cases}.
\]

(25)

If we carry out the change of variables discussed above with \( L^2 = \hbar^2 \epsilon^2/(2m\alpha) \) then we obtain the dimensionless Hamiltonian \( \text{(2)} \) with the potential

\[
\frac{2mL^2}{\hbar^2} V_\epsilon(L\tilde{x}) = \begin{cases} 
-1 & \text{if } 0 < \tilde{x} < \rho_0 \\
-\frac{2}{\rho_0^2} & \text{if } \rho_0 < \tilde{x} < \infty 
\end{cases} = \tilde{V}(\rho_0, \tilde{x}), \quad \frac{2mL^2}{\hbar^2} = \frac{\epsilon^2}{\alpha}, \quad \rho_0 = \frac{2m\alpha \hbar}{\epsilon^2}.
\]

(26)

Since the dimensionless potential-energy function \( \tilde{V}(\rho_0, \tilde{x}) \) depends on the parameters \( \alpha \) and \( \epsilon \) only through the parameter \( \rho_0 \) then the dimensionless energy will depend only on this parameter: \( \tilde{E}(\rho_0) \). Therefore, the actual energy will be of the form \( E = \frac{\alpha}{\epsilon^2} \tilde{E}(\rho_0) \). After solving the eigenvalue equation in terms of modified Bessel functions, the authors concluded that \( E = -\frac{2}{\rho_0^2} f(\rho_0^2) \). Once again, we have been able to predict a general feature of the quantum-mechanical energies without solving the Schrödinger equation.

In closing this section we briefly focus on the time-dependent Schrödinger equation

\[
i\hbar \frac{d}{dt} \psi = H\psi,
\]

(27)

and proceed as before with respect to the Hamiltonian operator. In addition to it we define the dimensionless time \( \tilde{t} \equiv \omega t \), where \( \omega \) is an arbitrary frequency. Upon choosing

\[
\hbar \omega \equiv \frac{\hbar^2}{mL^2},
\]

(28)
the Schrödinger equation becomes

\[ i \frac{d}{dt} \tilde{\psi} = \tilde{H} \tilde{\psi}. \]  

(29)

In the case of the harmonic oscillator, for example, it follows from equation (28) that \( \omega = \sqrt{k/m} \) is the oscillator frequency.

### 3 Atoms and molecules

The Hamiltonian operator for a system of \( K \) particles of masses \( m_i \), charges \( q_i \) at the positions \( \mathbf{r}_i, i = 1, 2, \ldots, K \) is given by \[ H = -\frac{\hbar^2}{2} \sum_{i=1}^{K} \frac{\nabla_i^2}{m_i} + \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \]  

(30)

where \( \epsilon_0 \) is the vacuum permittivity and \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) is obviously the distance between particles \( i \) and \( j \). In order to obtain a dimensionless Schrödinger equation we proceed as before and introduce a length unit \( L \) and the dimensionless positions \( \tilde{\mathbf{r}}_i \equiv \mathbf{r}_i / L \) so that \( \nabla_i^2 = L^{-2} \tilde{\nabla}_i^2 \). If \( m_e \) and \( -e \) denote the electronic mass and charge, respectively, then we define the dimensionless quantities \( \tilde{m}_i \equiv m_i / m_e \) and \( \tilde{q}_i \equiv q_i / e \) so that the dimensionless Hamiltonian operator \( \tilde{H} \) becomes

\[ \tilde{H} = \frac{mL^2}{\hbar^2} H = -\frac{1}{2} \sum_{i=1}^{K} \frac{\tilde{\nabla}_i^2}{\tilde{m}_i} + \frac{m_e L^2 e^2}{4\pi\epsilon_0 \hbar^2} \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \frac{\tilde{q}_i \tilde{q}_j}{\tilde{r}_{ij}}. \]  

(31)

Therefore, if we choose \( L \equiv \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \),

(32)

the dimensionless Hamiltonian becomes

\[ \tilde{H} = -\frac{1}{2} \sum_{i=1}^{K} \frac{\tilde{\nabla}_i^2}{\tilde{m}_i} + \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \frac{\tilde{q}_i \tilde{q}_j}{\tilde{r}_{ij}}. \]  

(33)

It is worth noticing that \( L \equiv a_0 \) is the well known atomic unit of length and

\[ \frac{\hbar^2}{m_e a_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0}, \]  

(34)

is the atomic unit of energy. This equation also shows that \( a_0 \) makes a term that looks as a kinetic energy (left) equal to other term that looks like a potential
(right). As argued above, one of the most noticeable advantages of this procedure is that we get rid of small numbers like $\hbar, e, m_{e}, \epsilon_{0}, \text{ etc.}$ It is equivalent to setting these quantities equal to unity. Such small numbers may increase the round-off errors in a numerical calculation of atomic and molecular properties and for this reason atomic units are used throughout [5][8].

The potential-energy function of this system of particles is invariant under space translations and, consequently, we should remove the free motion of the center of mass before applying any approximate method to the Schrödinger equation [9][10] (and references therein). However, this issue is not relevant to present discussion because we do not solve any equation here.

As an example, consider the Hamiltonian operator for the hydrogen atom [5][8]

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r},$$

(35)

where $m \equiv m_{e}m_{n}/(m_{e} + m_{n})$ is the reduced mass of the system, $m_{n}$ the nuclear mass and $r$ the distance between the nucleus and the electron. The reduced mass appears when we remove the motion of the center of mass as mentioned above.

In atomic units the Hamiltonian (35) becomes

$$\tilde{H} = -\frac{1}{2\tilde{m}} \tilde{\nabla}^2 - \frac{1}{\tilde{r}}, \quad \tilde{m} = \frac{m_{n}}{m_{n} + m_{e}}.$$

(36)

If instead of the unit of length (32) we choose

$$L \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2},$$

(37)

the Hamiltonian operator for hydrogen takes an even simpler form

$$\tilde{H} = -\frac{1}{2} \tilde{\nabla}^2 - \frac{1}{\tilde{r}}.$$

(38)

In the case of atoms it is common usage to resort to the so-called clamped-nucleus approximation, which for hydrogen can be expressed as follows:

$$\lim_{m_{n} \to \infty} \tilde{m} = 1.$$

(39)

Within this approximation it is not necessary to remove the motion of the center of mass because it is located at the nucleus that remains fixed at origin [5][8].

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However, in the case of highly accurate calculations (which may also include relativistic effects) the mass-polarization terms due to the nuclear motion should be taken into consideration.

4 Perturbation theory

In this section we show that suitable dimensionless Schrödinger equations may facilitate the application of perturbation theory \[1\]. Since, as already pointed out above, we do not solve the Schrödinger equation in this paper we will not be concerned with the convergence properties of the perturbation series.

The first example is the widely discussed quartic anharmonic oscillator that we write in the following way

\[
H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad V(x) = \frac{k_2}{2} x^2 + k_4 x^4, \quad k_2, k_4 > 0. \tag{40}
\]

On applying the strategy outlined in section 2 we have

\[
\frac{mL^2}{\hbar^2} V(L\tilde{x}) = \frac{mk_2 L^4}{2\hbar^2} \tilde{x}^2 + \frac{mk_4 L^6}{\hbar^2} \tilde{x}^4. \tag{41}
\]

In this case we can try two choices of the length unit \(L\), the first one is the harmonic oscillator length \(L \equiv \left[\frac{\hbar^2}{m k_2}\right]^{1/4}\) that leads to

\[
\tilde{H} = \frac{H}{\hbar \omega} = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{\tilde{x}^2}{2} + \lambda \tilde{x}^4,
\]

\[
\omega = \sqrt{\frac{k_2}{m}}, \quad \lambda = \frac{\hbar k_4}{(mk_2)^{1/2}} = \frac{\hbar k_4}{m^2 \omega^3},
\]

\[
\tilde{E}(\lambda) = \frac{E}{\hbar \omega}. \tag{42}
\]

If we apply perturbation theory we obtain the \(\lambda\)-power series

\[
E = \hbar \omega \sum_{j=0}^{\infty} \tilde{E}^{(j)} \lambda^j, \tag{43}
\]

that is suitable for sufficiently small values of \(\lambda\). There are several efficient methods for the calculation of the coefficients \(\tilde{E}^{(j)}\) in exact analytical form to any desired order \(j\) \[1\].
A second choice is
\[ L \equiv \left( \frac{\hbar}{\sqrt{mk_4}} \right)^{1/3} = \left( \frac{\hbar}{m\omega \lambda^{1/3}} \right)^{1/2}, \] (44)
that leads to
\[ \tilde{H} = \frac{H}{\hbar \omega \lambda^{1/3}} = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{\tilde{x}^2}{2\lambda^{2/3}} + \tilde{x}^4, \]
\[ \tilde{E}(\lambda) = \frac{E}{\hbar \omega \lambda^{1/3}}. \] (45)

This equation suggests that we can expand the energies as
\[ E = \hbar \omega \lambda^{1/3} \sum_{j=0}^{\infty} \tilde{e}^{(j)} \lambda^{-2j/3}. \] (46)

In this case we cannot obtain the expansion coefficients \( \tilde{e}^{(j)} \) exactly but the mere knowledge of the existence of this series is useful in the application of some resummation methods [1]. It is worth pointing out that a calculation for a single value of \( \lambda \) is equivalent to an infinite number of calculations based on variations of \( m, k_2 \) and \( k_4 \) such that \( k_4 / (mk_2^3)^{1/2} \) is constant. This fact is an obviously useful advantage of resorting to a dimensionless equation.

Let us now consider a one-dimensional Hamiltonian operator with the potential (13), where \( V_0 > 0 \) and \( f(q) \) exhibits a minimum at \( q = 0 \) such that \( f(0) = 0 \). We assume that \( f(q) \) can be expanded in a Taylor series
\[ f(q) = \sum_{j=2}^{\infty} \frac{f_j}{j!} q^j. \] (47)

The dimensionless Hamiltonian reads
\[ \tilde{H} = \frac{mL^2}{\hbar^2} H = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{mL^4V_0f_2^2}{2\hbar^2a^2} \tilde{x}^2 + \sum_{j=3}^{\infty} \frac{mV_0L^{j+2}}{j!\hbar^2a^j} f_j \tilde{x}^j. \] (48)

If we choose
\[ L \equiv \left( \frac{\hbar^2a^2}{mf_2^2V_0} \right)^{1/4}, \] (49)
then the dimensionless Hamiltonian becomes
\[ \tilde{H} = -\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{1}{2} \tilde{x}^2 + \sum_{j=3}^{\infty} \frac{f_j^{j+2}}{f_2} \lambda^{j+2} \tilde{x}^j, \quad \lambda \equiv \frac{L}{a} = \left( \frac{\hbar^2}{ma^2f_2V_0} \right)^{1/4}, \] (50)
which shows that the energies can be expanded as

\[ E = \hbar \sqrt{ \frac{V_0 f_2}{ma^2}} \sum_{j=0}^{\infty} \tilde{E}^{(j)} Z^j. \] (51)

There are efficient approaches for the exact analytical calculation of the coefficients \( \tilde{E}^{(j)} \). [1]

The last example is the Hamiltonian operator for an atom with \( N \) electrons and nuclear charge \( Z e \) in the clamped-nucleus approximation

\[ H = H_0 + H', \]

\[ H_0 = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{4\pi\varepsilon_0 r_i}, \]

\[ H' = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}, \] (52)

where \( r_i \) is the distance between the electron \( i \) and the nucleus and \( r_{ij} \) the distance between a pair of electrons. Since the Schrödinger equation for \( H_0 \) is exactly solvable we can apply perturbation theory where \( H' \) is the perturbation. In what follows we show that the dimensionless equation gives us valuable information about the solution derived from perturbation theory.

As in the previous examples, the dimensionless Hamiltonian is

\[ \tilde{H} = \frac{m_e L^2}{\hbar^2} H = \frac{1}{2} \sum_{i=1}^{N} \hat{\nabla}_i^2 - \sum_{i=1}^{N} \frac{m_e LZe^2}{4\pi\varepsilon_0 \hbar^2 \tilde{r}_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{m_e L e^2}{4\pi\varepsilon_0 \hbar^2 \tilde{r}_{ij}}. \] (53)

In this case we choose

\[ L = \frac{4\pi\varepsilon_0 \hbar^2}{m_e Ze^2} = \frac{a_0}{Z}, \] (54)

and obtain

\[ \tilde{H} = -\frac{1}{2} \sum_{i=1}^{N} \hat{\nabla}_i^2 - \sum_{i=1}^{N} \frac{1}{\tilde{r}_i} + \frac{1}{Z} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{\tilde{r}_{ij}}. \] (55)

It is clear that the result of the application of perturbation theory as indicated above will be a series of the form

\[ E = \frac{\hbar^2 Z^2}{m_e a_0^2} \sum_{j=0}^{\infty} \tilde{E}^{(j)} Z^{-j}. \] (56)
Since the perturbation coefficients $\tilde{E}^{(j)}$ only depend on $N$, then if the number of electrons remains constant we conclude that the rate of convergence of this perturbation series will improve with $Z$.

5 Conclusions

This paper shows the advantages of using dimensionless equations in non-relativistic quantum mechanics. The dimensionless Schrödinger equation is simpler than the original one which facilitates the process of obtaining the desired solutions. If one has to resort to a numerical method the dimensionless equation (with all its quantities of the order of unity) is considerably less prone to round-off errors. When we derive a dimensionless equation we realize which are the relevant parameters that should appear in the solution beforehand. In the case of perturbation theory we can predict the general form of the solution and obtain a suitable perturbation parameter. It is also important to realize that the proper scaling of the variables is by no means guesswork. A suitable definition for $L$ is dictated by the form of the equation for the physical problem. We believe that it is worthwhile to teach this approach in undergraduate as well as graduate courses on quantum mechanics. It is worth adding that dimensionless equations are also useful in other areas of physics, such as, for example, classical physics [11, 12].

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