Units in a Double Well System

Jonas Boym Flaten

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We want to analyse the one-dimensional two-electron system given (in position basis) by the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + V_L w_L[x_1] - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V_R w_R[x_2] + \frac{e^2}{4\pi\epsilon}\frac{1}{\sqrt{(x_1 - x_2)^2 + a^2}}, \tag{1}$$

where x_i is the position of electron i.

- Terms 1 and 3 are the kinetic terms for each particle; here m is the electron mass.
- Terms 2 and 4 are the potential terms for each particle; here $w_{\substack{L\\R}}$ are unitless well functions of depth 1 located at the left (L) and right (R) part of the system, so that $V_{\substack{L\\R}}$ (of dimension energy) are the respective depths of the left (L) and right (R) wells.
- Term 5 is the electric Coulomb interaction between the two particles; here e is the elementary charge, π is pi, ϵ is the vacuum permittivity and a is a shielding length necessary to avoid divergence problems in one dimension.

The Schrödinger equation governing the dynamics of this system is

$$\iota\hbar\frac{\partial}{\partial t}\Psi[t, x_1, x_2] = H\Psi[t, x_1, x_2], \tag{2}$$

where Ψ is the quantum state of the system (in position product basis), ι is the imaginary unit and $\hbar$ is the Dirac constant.

When writing a program to analyse the system above, we need to specify units for energy, time and length and use values consistent with these units throughout the code. We could in principle use standard SI units, however the values of the physical constants involved in (1) and (2) are all very small given in these units, with vastly different orders of magnitude. For example, the vacuum permittivity, in unit of farads per metre, is 10^{19} (ten quintillions) times the size of the electron mass in unit of kilograms! Such small numbers and huge differences are not suited for the floating point arithmetic of computers; multiplying or squaring them could lead to underflow and possibly severe numerical errors. Furthermore, the values of each constant are not even interesting on their own; only specific combinations dependent of <u>relative sizes</u> turn out to matter for the actual dynamics of the system. What are the typical energy quanta exchanged by the system, and what is the time scale at which something interesting happens to it? In order to answer these questions, we want to choose suitable units for energy, time and length so that the relative sizes of the terms in (1) and (2) become exposed. Such a choice of typical, or <u>natural</u>, units for the system will also make the involved numbers numerically feasible for our program to handle.

We introduce, then, an energy unit ε, a time unit τ and a length unit λ, and define <u>unitless quantities</u> (denoted with primes) by separating unit from value in all energy, length and time quantities:

$$H \equiv \varepsilon H', \qquad V_{\substack{L\\R}} \equiv \varepsilon V'_{\substack{L\\R}}, \tag{3}$$

$$t \equiv \tau t', \tag{4}$$

$$x_i \equiv \lambda x'_i, \qquad a \equiv \lambda a'. \tag{5}$$

Using these substitutions, we can rewrite the Hamiltonian (1) to

$$\varepsilon H' = -\frac{\hbar^2}{2m\lambda^2}\frac{\partial^2}{\partial x'^2_1} + \varepsilon V'_L w'_L[x'_1] - \frac{\hbar^2}{2m\lambda^2}\frac{\partial^2}{\partial x'^2_2} + \varepsilon V'_R w'_R[x'_2] + \frac{e^2}{4\pi\epsilon\lambda}\frac{1}{\sqrt{(x'_1 - x'_2)^2 + a'^2}}, \tag{6}$$

where we also substituted the well functions $w_{\substack{L\\R}}$ with the redefinitions

$$w'_{\substack{L\\R}}[x'] \equiv w_{\substack{L\\R}}[\lambda x'] \tag{7}$$

in order to make their arguments unitless. Equation (6) can then be divided by the energy unit ε to get the following expression for the <u>unitless Hamiltonian</u>:

$$H' = -\frac{\hbar^2}{2m\lambda^2\varepsilon}\frac{\partial^2}{\partial x'^2_1} + V'_L w'_L[x'_1] - \frac{\hbar^2}{2m\lambda^2\varepsilon}\frac{\partial^2}{\partial x'^2_2} + V'_R w'_R[x'_2] + \frac{e^2}{4\pi\epsilon\lambda\varepsilon}\frac{1}{\sqrt{(x'_1 - x'_2)^2 + a'^2}}. \tag{8}$$

In a similar fashion, we can rewrite the Schrödinger equation (2) to

$$\iota\frac{\hbar}{\tau}\frac{\partial}{\partial t'}\Psi'[t', x'_1, x'_2] = \varepsilon H'\Psi'[t', x'_1, x'_2], \tag{9}$$

(where we substituted the wavefunction Ψ with the redefinition

$$\Psi'[t', x'_1, x'_2] \equiv \Psi[\tau t', \lambda x'_1, \lambda x'_2], \tag{10}$$

in order to make its arguments unitless) which can again be divided by the energy unit to get the <u>unitless Schrödinger equation</u>

$$\iota\frac{\hbar}{\tau\varepsilon}\frac{\partial}{\partial t'}\Psi'[t', x'_1, x'_2] = H'\Psi'[t', x'_1, x'_2]. \tag{11}$$

Note that the equations (8) and (11) are perfectly equivalent to (1) and (2); we just separated the values from the units and divided by the energy unit to make both equations unitless. However, now comes the key point: We are still free to choose the units ε, τ and λ! By making smart choices we can simplify the equations so that they become both transparent and numerically feasible. There are several such choices, but a simple and common one is to choose the length unit such that $\frac{\hbar^2}{2m\lambda^2\varepsilon}$ in the unitless Hamiltonian becomes 1, which is the length unit

$$\lambda \equiv \frac{\hbar}{\sqrt{m\varepsilon}} \approx \sqrt{\frac{76.20\text{ meV}}{\varepsilon}}\text{ nm}, \tag{12}$$

or equivalently the energy unit

$$\varepsilon \equiv \frac{\hbar^2}{m\lambda^2} \approx \left(\frac{8.729\text{ nm}}{\lambda}\right)^2\text{ meV}, \tag{13}$$

as well as the time unit such that $\frac{\hbar}{\tau\varepsilon}$ in the unitless Schrödinger equation becomes 1, which is the time unit

$$\tau \equiv \frac{\hbar}{\varepsilon} \approx \frac{658.2\text{ meV}}{\varepsilon}\text{ fs}. \tag{14}$$

Then, the unitless Hamiltonian (8) simplifies to

$$H' = -\frac{1}{2}\frac{\partial^2}{\partial x'^2_1} + V'_L w'_L[x'_1] - \frac{1}{2}\frac{\partial^2}{\partial x'^2_2} + V'_R w'_R[x'_2] + \frac{\kappa}{\sqrt{(x'_1 - x'_2)^2 + a'^2}}, \tag{15}$$

where we introduced the unitless <u>Coulomb factor</u>

$$\kappa \equiv \frac{e^2}{4\pi\epsilon\lambda\varepsilon} = \frac{e^2}{4\pi\epsilon\hbar}\sqrt{\frac{m}{\varepsilon}} \approx \sqrt{\frac{27.21\text{ eV}}{\varepsilon}} \approx \frac{\lambda}{52.92\text{ pm}}. \tag{16}$$

Meanwhile, the unitless Schrödinger equation (11) simplifies to

$$\iota\frac{\partial}{\partial t'}\Psi'[t', x'_1, x'_2] = H'\Psi'[t', x'_1, x'_2]. \tag{17}$$

The unitless equations (15) and (17) are commonly used in programs, but one should always keep in mind the implicit choices (12) and (14) of length and time units, as well as the choice of energy unit, which

underlie them. We are actually still free to choose any energy unit ε, but note that this will then affect both the length unit λ and the time unit τ through (12) and (14). It will also determine the Coulomb factor ; κ which we must use in our calculations through (16). For example, if we input the well depths $V_{\substack{L\\R}}$ in unit of electronvolts, we have chosen $\varepsilon \equiv 1$ eV, which leads to $\lambda \approx 0.3$ nm and $\tau \approx 0.7$ fs, as well as the Coulomb factor $\kappa \approx 5$. On the other hand, if we use the specific Coulomb factor $\kappa \equiv 2326$, we have indirectly chosen $\varepsilon \approx 5.030$ µeV, which leads to $\lambda \approx 123.1$ nm and $\tau \approx 130.9$ ps. The chosen units ε, λ and τ should be reflected in all unitless quantities, such as the well depths $V'_{\substack{L\\R}}$, and they should also be provided (or multiplied back in) in all output from our program.
When analysing energy quanta of the system, that is, the energy differences between energy states, it is customary to express these in terms of the corresponding frequency of a photon emitted and absorbed during such a transition. A photon of energy ΔE would have a frequency f given by the relation

$$\Delta E = hf, \tag{18}$$

where h is the Planck constant, and by separating out the energy unit ε like above and dividing by h, we get the expression

$$f = \frac{\varepsilon}{h}\Delta E' \approx \frac{\varepsilon}{4.136 \text{ meV}}\Delta E' \text{ THz} \tag{19}$$

for the corresponding photonic frequency of any unitless energy quantum $\Delta E'$.

An energy unit of $\varepsilon \approx 5.024$ µeV, corresponding to the Coulomb factor of $\kappa = 2326$ and the length and time units $\lambda \approx 123.2$ nm and $\tau \approx 131.1$ ps introduced above, results in the following conversion formula from unitless energy quanta to the corresponding photonic frequency:

$$f \approx 1.216\Delta E' \text{ GHz}. \tag{20}$$