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An exactly solvable model of laser-molecule interaction

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[**Introduction**] Analytical solutions to the time-dependent Schrödinger equation are in general rare. Therefore, to study time-dependent problems such as the interaction of a molecule with a laser pulse, numerical techniques are indispensable. In particular in the case when the strength of the laser field becomes comparable to the binding forces within a molecule, so that perturbation theory cannot be used, direct numerical integration of the Schrödinger equation is often the only way of obtaining information about the wave function. However, for systems with several electrons and nuclei, grid methods become impractical, and approximate schemes [1] must be employed instead. One difficulty with such methods is that it may be difficult to estimate the numerical error made compared to the exact solution. Solutions to model problems may here provide a way to test approximate numerical schemes.

In the present contribution, we derive an exact solution to a model problem with two electrons and two protons, coupled to an external driving field. The solution is found for arbitrary strength, pulse shape and frequency of the applied light field. For certain parameters, observables such as the electron density may be written down in closed, analytic form. In the general case, finding the complete, 12-dimensional, time-dependent wave function is reduced to the solution of a combination of one-dimensional, static problems. Similar model problems have been considered before [2,3], although not for laser-induced coupled electron and proton motion.

[**Theoretical model**] The model system consists of two pairs of particles: two electrons, interacting via the Coulomb potential, and two protons, also with Coulombic interaction. The electron-proton potential is modeled as a harmonic potential, and both electrons and protons are externally confined by an additional harmonic potential. The light-matter coupling with the laser field $\boldsymbol{E}(t)$ is included in the standard dipole form. The Hamiltonian, with electron coordinates $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ and proton coordinates $\boldsymbol{R}_1$, $\boldsymbol{R}_2$, reads (in atomic units)

$$\begin{aligned} H = &-\frac{\nabla^2_{\boldsymbol{R}_1}}{2M} - \frac{\nabla^2_{\boldsymbol{R}_2}}{2M} + \frac{1}{|\boldsymbol{R}_1 - \boldsymbol{R}_2|} - \frac{\nabla^2_{\boldsymbol{r}_1}}{2} - \frac{\nabla^2_{\boldsymbol{r}_2}}{2} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \\ &+ \frac{\omega^2}{2}\left[(\boldsymbol{R}_1 - \boldsymbol{r}_1)^2 + (\boldsymbol{R}_1 - \boldsymbol{r}_2)^2\right] + \frac{\omega^2}{2}\left[(\boldsymbol{R}_2 - \boldsymbol{r}_1)^2 + (\boldsymbol{R}_2 - \boldsymbol{r}_2)^2\right] \\ &+ \frac{M\Omega^2}{2}\left(\boldsymbol{R}_1^2 + \boldsymbol{R}_2^2\right) + \frac{\Omega^2}{2}\left(\boldsymbol{r}_1^2 + \boldsymbol{r}_2^2\right) + \boldsymbol{E}(t)\cdot(\boldsymbol{r}_1 + \boldsymbol{r}_2 - \boldsymbol{R}_1 - \boldsymbol{R}_2)\,. \end{aligned} \tag{1}$$

By going to the new coordinates $\boldsymbol{r}_+ = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$, $\boldsymbol{r}_- = \boldsymbol{r}_1 - \boldsymbol{r}_2$, $\boldsymbol{R}_+ = (\boldsymbol{R}_1 + \boldsymbol{R}_2)/2$, $\boldsymbol{R}_- = \boldsymbol{R}_1 - \boldsymbol{R}_2$, $\boldsymbol{r} = (M\boldsymbol{R}_+ + \boldsymbol{r}_+)/(1+M)$, and $\boldsymbol{q} = \boldsymbol{R}_+ - \boldsymbol{r}_+$, the Hamiltonian (1) separates. The complete, time-dependent wave function may thus be written in product form,

$$\Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{r}_1, \boldsymbol{r}_2, t) = \zeta(\boldsymbol{r})e^{-iE_{\boldsymbol{r}}t}\chi(\boldsymbol{R}_-)e^{-iE_{\boldsymbol{R}_-}t}\psi(\boldsymbol{r}_-)e^{-iE_{\boldsymbol{r}_-}t}\phi(\boldsymbol{q}, t). \tag{2}$$

[**Discussion**] The solutions $\zeta(\boldsymbol{r})$, $\chi(\boldsymbol{R}_-)$, $\psi(\boldsymbol{r}_-)$, and $\phi(\boldsymbol{q}, t)$ have all been discussed in the literature [2,3]. In particular, the time-dependent function $\phi(\boldsymbol{q}, t)$ is the solution to

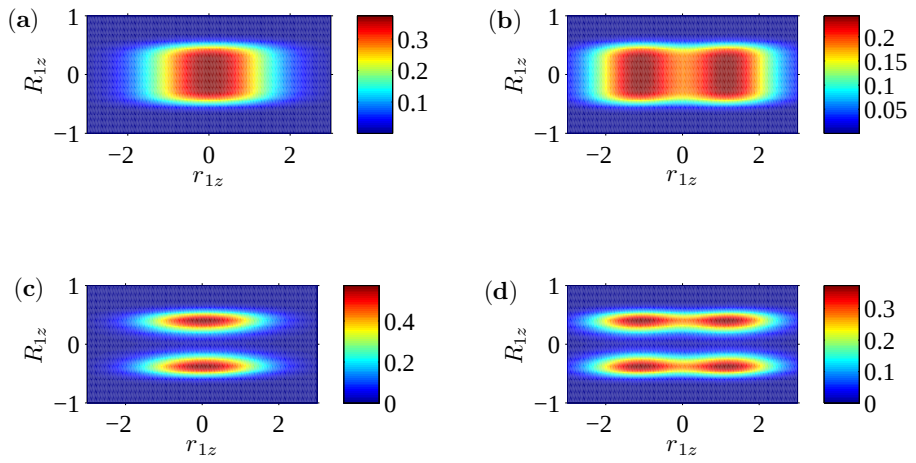

Figure 1: The electron-proton density $\rho_{ep}(R_{1z}, r_{1z}, t)$ at $t = 0$, for different angular momentum quantum numbers l_e, l_p of the electrons and protons. In (a), $(l_e, l_p) = (0, 0)$, in (b), $(l_e, l_p) = (1, 0)$, in (c), $(l_e, l_p) = (0, 1)$, and in (d), $(l_e, l_p) = (1, 1)$.

the quantum harmonic oscillator driven by an external field, and may be written in closed form for reasonable choices of the laser field $\boldsymbol{E}(t)$. Finding the functions $\chi(\boldsymbol{R}_-)$ and $\psi(\boldsymbol{r}_-)$ may be reduced to finding the eigenfunctions of a static, one-dimensional problem with potential $V(x) = \omega^2 x^2 + 1/x$.

From the wave function Ψ, we calculate a few observables of interest. For a particular choice of parameters $\omega^2 + \Omega^2/2 = 1/8$, the electron density ρ_{2e} in the direction of the applied field (z-direction) may be written in closed, analytic form. Another interesting observable that is easily computed is the time-dependent electron-proton density,

$$\rho_{ep}(R_{1z}, r_{1z}, t) = \int dR_{1x} dR_{1y} dr_{1x} dr_{1y} d^3R_2 d^3r_2 |\Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{r}_1, \boldsymbol{r}_2, t)|^2, \tag{3}$$

an example of which is shown in Fig. 1.

We have also used the exact wave function Ψ to study the accuracy of the Born-Oppenheimer approximation (BOA) applied to this model. We find that the BOA is in most cases very good, except if the system is driven resonantly, that is, if the carrier laser frequency equals the eigenfrequency of the system. In this case, the system absorbs energy, which results in that the expectation value of the dipole moment continues to oscillate after the laser pulse has passed. Use of the BOA to calculate the dipole moment predicts a too low frequency for this oscillation.

[References]

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