Weisskopf–Wigner model for wavepacket excitation

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Abstract. We consider a laser-induced molecular excitation process as a decay of a single energy state into a continuum. The analytic results based on the Weisskopf–Wigner approach and perturbation calculations are compared with numerical wavepacket results. We find that the decay model describes the excitation process well within the expected parameter region.

1. Introduction

It has been known for a long time that when an isolated bound state is interacting with a continuum of quantum states, the occupation of the bound state experiences exponential decay; the first proper treatment was given by Weisskopf and Wigner in 1930 [1]. A simple example of such a situation is a two-state atom coupled to the electromagnetic modes of the vacuum, which leads to spontaneous emission (see e.g. [2, 3]). The general model has been described in detail within the formalism of scattering theory in [4], but this approach provides only a steady state treatment. In a recent paper [5] we considered this problem in a genuine time-dependent setting and discussed the decay process as a method to prepare a moving wavepacket on a molecular electronic state in accordance with our earlier treatment of coupled-channel molecular wavepacket dynamics (for a review see [6]). We now proceed to study the validity of this exponential decay description of laser-induced wavepacket excitation in molecules.

The prototype model for the Weisskopf–Wigner decay is shown in figure 1(a): the discrete state embedded in a continuum acquires a Lorentzian lineshape, which corresponds to exponential decay of its occupation. The theoretical description leading to exponential decay is based on an approximation which represents the continuum spectral density by a single dominating pole [7, 8]. In the general case this is only an approximation, which is expected to hold in the perturbative limit of weak coupling between the discrete state and the continuum, in which case the result of time-dependent perturbation theory agrees with the Weisskopf–Wigner result. When we go beyond this limit, the result is non-exponential decay [4] or a continuous transition of the decay into a periodic oscillating behaviour of Rabi type as discussed in [9]. Thus we need to establish for molecular excitation the parameter regions where (i) the perturbation approach is applicable and (ii) where the excitation process can be described as exponential decay into the continuum.

In this paper we develop further the decay model introduced in [5] and featured in figure 1(b). The lowest vibrational level of the molecular electronic ground state corresponds to the discrete state; it can be described adequately by the harmonic potential $U_1$. The
molecular counterpart of the continuum is an excited electronic state which can be adequately described by the linear potential $U_2$ near the molecular equilibrium position. Usually state 2 is a dissociating one, but it could also represent a bound state in an energy region where the vibrational states have a very small separation (quasi-continuum). These potentials are a good basis for the molecular processes within the Born–Oppenheimer approximation. If we also apply the dipole and rotating-wave approximations to the laser–molecule interaction, we can shift the excited state potential down by one laser photon, which then leads to the elimination of the rapidly oscillating field term from the coupling between the states 1 and 2 (for more details see [6]).

If the parameters of our model are chosen such that the vibrational excited states of the harmonic potential remain mostly unoccupied during the interaction, the decay of the oscillator ground state can be taken to be a model of the level scheme in figure 1. The couplings between the oscillator state and the eigenstates of the slope are not constant; the Condon factors describing the overlap between the ground and excited state wavefunctions have an energy dependence which complicates the model. Thus for simplicity (one less parameter to consider) we arrange the sloping potential $U_2$ so that a Franck–Condon transition at the origin of the coordinate system gives the maximum overlap between the wavefunctions. Then we expect the Condon factor to depend only slowly on energy around $E_0$ and the model will simulate the behaviour of the Weisskopf–Wigner situation.

This paper is organized as follows. Section 2 presents the basic model. In section 3 we give the results of our numerical computations and discuss the occurrence of exponential decay. It is found that this can be observed in a parameter range where the decay rate is less than a definite value. This indicates that the exponential behaviour can indeed be achieved only in a perturbative regime as expected. We also find that the occupation of state 2 emerges in the form of a localized wavepacket even beyond this perturbative parameter regime. In section 4 we discuss the analytic result for the decay and compare this with our results obtained from numerical integration of our wavepacket model. Finally, we summarize and discuss our results in section 5.

2. The model

We consider a one-dimensional system, with spatial coordinate $x$ and two internal states $\{ |1\rangle, |2\rangle \}$. The Hamiltonian of the system is written as

$$H = [T_x + U_1(x)] |1\rangle \langle 1| + [T_x + U_2(x)] |2\rangle \langle 2| + V [ |2\rangle \langle 1| + |1\rangle \langle 2|]$$

(1)
where the coupling $V$ is chosen to be real. We define (in suitably chosen dimensionless units, cf [5, 6])

$$T_x = -\frac{\partial^2}{\partial x^2}$$

$$U_1(x) = \frac{1}{2}x^2$$

$$U_2(x) = \frac{1}{\sqrt{2}} - \alpha x .$$

The Hamiltonian (1) describes our chosen model as shown in figure 1(b). Since in our scaling the energy of the lowest level of the harmonic potential is

$$E_0 = \frac{1}{2} \omega = \frac{1}{\sqrt{2}}$$

the energy of the linear potential resonates with the ground state at $x = 0$ (see figure 1).

The eigenfunction of the ground state of the harmonic oscillator is

$$\phi_0(x) = \frac{1}{(2\pi)^{1/8}} \exp \left(-\frac{x^2}{2^{3/2}}\right)$$

with the energy eigenvalue (3). In the domain we are investigating, the higher eigenfunctions are not supposed to play any role and consequently they are not needed, as already mentioned in section 1.

The eigenvalues of the linear state $U_2$ form a continuum $[-\infty, \infty]$ with the corresponding eigenfunctions easily obtained by a Fourier transform

$$\tilde{\psi}_E(k) \equiv \int dx \ e^{-ikx} \psi_E(x).$$

The functional form is that of the Airy function and a suitable normalization is given by

$$\psi_E(x) = \int \frac{dk}{2\pi \sqrt{\alpha}} \exp \left[i \left(x + \frac{E}{\alpha}\right) k - \frac{k^3}{3\alpha}\right]$$

where the energy parameter is

$$E = E - \frac{1}{\sqrt{2}}.$$

It is easy to prove the energy normalization

$$\int \psi_E^*(x) \psi_E(x) \ dx = \delta(E - E')$$

and the completeness

$$\int \psi_E^*(x') \psi_E(x) \ dE = \delta(x - x').$$

With these relations we see that the density of states is unity.

We assume that the system is prepared in the initial state

$$|i\rangle = \phi_0(x) |1\rangle$$

which is then coupled to the continuum by the parameter $V$. Using the result of the time-dependent perturbation theory (Fermi golden rule) the leakage into state $|2\rangle$, i.e. into our final state $|f\rangle$, is expected to occur at the rate

$$\Gamma = 2\pi \ |\langle i | H | f \rangle|^2 = 2\pi V^2 \ |\langle \phi_0 | \psi_{E_0} \rangle|^2$$
where the continuum function is evaluated at the energy (3) and the parameter dependence is almost entirely in the Condon factor \( \langle \phi_0 | \psi_{E_0} \rangle \).

From the normalization of equation (6) we expect the decay rate to scale as

\[ \Gamma \propto 2\pi \frac{V^2}{\alpha} \equiv \Gamma_0 \]  

where we have defined an effective decay parameter \( \Gamma_0 \). When \( \Gamma_0 \) is below some limiting value, we expect that equation (11) gives a reasonable approximation to the decay rate of the initial state (10). The result is modified by the Condon factor which will be discussed below.

3. Numerical calculations

We have used the numerical approach described in section 2.3.3 of [6] to propagate the initial state wavepacket (10) on the coupled energy surfaces of equation (1). However, instead of switching the coupling on suddenly we have used the coupling term

\[ V(t) = \begin{cases} V_0 \text{sech}\left[\left(t - t_0\right)/T\right] & t \leq t_0 \\ V_0 & t > t_0 \end{cases} \]  

where \( t_0 \) indicates, in practice, the beginning of the excitation process and we have set \( T = 0.05 \) in our scaled units.

In particular, we have looked into the possible occurrence of exponential decay and the emergence of an outgoing wavepacket on state \( |2\rangle \) in our model. Some typical results of our calculations are shown in figures 2 and 3. They present the logarithm of the occupation \( P_1 \) of the state \( |1\rangle \) as a function of time. Both figures show descending curves which indicate exponential decay. For very large values of \( \Gamma_0 \) the initial state occupation \( P_1 \) becomes clearly oscillatory as demonstrated in figure 4.

| \( \alpha \) | \( \Gamma_0 \) |
|---|---|
| 1 | 1.6 |
| 2 | 0.8 |
| 3 | 0.5 |

![Figure 2](image_url)  
Figure 2. The occupation \( P_1(t) \) for \( V_0 = 0.5 \). Note the logarithmic scale on the vertical axis.
various parameter combinations, however, indicates that monotonic exponential decay is observed for values of $V_0^2$ smaller than a constant times $\alpha$, thus indicating that the parameter (12) plays a decisive role in the phenomenon. In figure 5 we show the data points that correspond to exponential and non-exponential decay in the $(\alpha, V_0^2)$ plane. The exponential decay points fall into a region for which we have roughly

$$\Gamma_0 < 2 - 2.5$$

which is thus taken to be the limit of validity of the simple pole approximation for decay.
Typically the non-exponential behaviour appears in $P_1$ and $P_2$ as oscillations and the exponential behaviour as a steady change (this is demonstrated in figure 6).

We have also studied how the emerging probability on level $|2\rangle$ forms a wavepacket. For the case $V_0 = 0.7, \alpha = 2$ ($\Gamma_0 \approx 1.5$) we observe a clear wave crest emerging in figure 7. This is followed by a long, slowly diminishing tail representing the final leakage out of state $|1\rangle$. We have, however, observed that the formation of a wavepacket is not conditioned on the occurrence of exponential decay. In figure 8 we still see a well developed
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Figure 7. The excited state wavepacket $P_2(x, t)$ for $V = 0.7$ and $\alpha = 2$. This is in the exponential decay regime since $\Gamma_0 = 1.5$. Here $t_0 = 1.0$.

Figure 8. The excited state wavepacket $P_2(x, t)$ for $V_0 = 1.5$ and $\alpha = 3$. This is in the non-exponential decay regime since $\Gamma_0 = 4.7$.

wavepacket for the parameters $V_0 = 1.5$ and $\alpha = 3$ ($\Gamma_0 \sim 4.7$) far exceeding that for which perturbation theory would be expected to work.
We have not carried out a systematic investigation of the occurrence of a well formed wavepacket. This is as subjective a phenomenon as the exponential decay. Because we initially find no probability on state $|2\rangle$ and ultimately there is no longer any probability leaking out of state $|1\rangle$, there must be a localized wavepacket emerging out of the system. However, a few words connecting the results of this paper to our previous work [10–13] are appropriate here.

In both figures 7 and 8 we see a clear, peaked wave crest wavepacket. On the other hand, figures 2 and 3 show that for all parameter values the ground state occupation behaviour is not exponential when $t \simeq t_0$. This is because initially the excitation process follows the well known area theorem, which for two resonant levels and a coupling $V_0$ states that $P_1 = 1 - P_2 = \cos^2[V_0(t - t_0)] \simeq 1 - V_0^2(t - t_0)^2 + O[(t - t_0)^4]$ for $t \geq t_0$. This is the origin of Rabi oscillations (if the levels are off resonance, then the oscillation frequency and amplitude are modified). For more details see e.g. [6]. These oscillations simply indicate that both states are ‘equal’, i.e. transitions can also take place back from state $|2\rangle$ to state $|1\rangle$.

In the Weisskopf–Wigner regime the second state acts like a reservoir and population can move only from state $|1\rangle$ to state $|2\rangle$. This is the point where the dynamics of the wavepacket on state $|2\rangle$ comes to the rescue. In our earlier studies we have given special attention to cases where the dynamics inhibits the Rabi oscillations, because the excited state population is accelerated away from the resonance region faster than the Rabi oscillations take place [10–13]. Although our earlier studies were made for short pulses, the basic principle is the same. Thus the reservoir model works best for the excitation when $\alpha$ is large and wavepacket motion on state $|2\rangle$ takes place swiftly after excitation.

We have now established a loose criterion for obtaining exponential decay. Next we need to consider the validity of the perturbation result (11). The exponential behaviour is only a necessary but not a sufficient condition for equation (11) to hold. For suitably large values of $V_0$ the perturbation result may fail even if the criterion (14) is fulfilled and the decay is exponential. For this purpose we calculate the full perturbation result for our model in the following section.

4. Analytic considerations

The perturbative rate (11) contains the Condon factor

$$S_{01} = \langle \phi_0 | \psi_{E_0} \rangle$$

which is the overlap of the initial and final states (see e.g. [14–17]). This scalar product is most efficiently calculated in momentum space, where we need the Fourier transform of state (4). Calculating the continuum wavefunction $\psi_{E_0}$ for energy (3) we set $E = 0$, which gives

$$S_{01} = \frac{2^{5/8} \pi^{1/4}}{\sqrt{\alpha}} \int \frac{dk}{2\pi} \exp \left[ - \left( \frac{k^2}{\sqrt{2}} + i \frac{k^3}{3\alpha} \right) \right]$$

$$= \frac{e^{\alpha/\sqrt{2}}}{2^{3/8} \pi^{3/4} \sqrt{\alpha}} \int_{-\infty}^{\infty} du \exp \left[ i \left( \frac{\alpha u}{2} + \frac{u^3}{3\alpha} \right) \right]$$

where we have used the substitution $k = i\alpha/\sqrt{2} - u$. Using the Airy function

$$Ai(x) = \int_{-\infty}^{\infty} \frac{ds}{2\pi} \exp \left[ i \left( \frac{s^3}{3} + sx \right) \right]$$
we can write (after setting $u = \alpha^{1/3} s$ in equation (16))

$$S_{01} = \frac{2^{5/8} \pi^{1/4} e^{\alpha^{2/3}} \sqrt{\alpha}}{\alpha^{1/6}} \text{Ai} \left( \frac{\alpha^{4/3}}{2} \right).$$

(18)

The result (18) seems to contradict the simple dependence on $\alpha$ from (16), but the asymptotic relation $\text{Ai}(x) \simeq x^{-1/4} \exp(-2x^{3/2}/3)/\sqrt{4\pi}$, valid for large $x$, restores the correct scaling with $\alpha$ in the perturbative limit. In fact, the asymptotic result for the Franck–Condon factor becomes

$$\lim_{\alpha \to \infty} |S_{01}|^2 = \frac{1}{\alpha (2\pi^{2})^{1/4}}.$$  

(19)

This is exactly what the Condon reflection principle would predict [14, 16, 18]. According to it

$$\lim_{\alpha \to \infty} |S_{01}|^2 = \left| \frac{d(U_2 - U_1)}{dx} \right|_{x=x_0}^{-1} \left| \psi_0(x = x_0) \right|^2$$

(20)

where $x_0$ is the point where $U_2(x_0) = U_1(x_0)$; in our case $x_0$ approaches zero as $\alpha \to \infty$ and our ground state wavefunction contribution becomes $|\psi_0(x = 0)|^2 = (2\pi^{2})^{-1/4}$. The reflection principle simply means that the excited state wavefunctions for steep potentials are so localized to $x = x_0$ that they behave like $\delta$ functions inside the overlap integrals. Thus we get that

$$\lim_{\alpha \to \infty} \Gamma = \frac{1}{(2\pi^{2})^{1/4}} \Gamma_0.$$  

(21)

The interesting conclusion from equation (16) is that the decay rate is not the simple function of $\alpha$ suggested by equation (12) except in the asymptotic limit. The behaviour of $\Gamma(\alpha)$, however, is found to be simply monotonic with increasing $\alpha$ as shown in figure 9.

**Figure 9.** The $\alpha$ dependence of the decay rate $\Gamma$. We have plotted the wavepacket results (open circles), the full perturbation result (full curve) (equations (11) and (18)) and the asymptotic result (broken curve) (equation (21)). All selected data points correspond to exponential decay.
5. Discussion

We have shown that in the perturbation limit and for steep excited state potentials the Weisskopf–Wigner model can adequately describe laser-induced molecular excitation processes. Our numerical results are in good agreement with analytical perturbation theory results in the parameter region where we expect them to be applicable.

Although we have mainly considered the molecular excitation process, there are some interesting atomic systems that resemble the molecular model shown in figure 1(b). One can trap single ions electromagnetically and cool them down to the lowest motional state of the trap potential, which in this energy range corresponds to a harmonic potential [19–22]. Furthermore, one can also trap neutral atoms with magnetic fields and cool them evaporatively into the density–temperature region where Bose–Einstein condensation takes place [23, 24]. The behaviour of the condensed atoms can be described as a single wavefunction [25, 26]. Our model, therefore, resembles the recent studies for output couplers for the condensates, in which RF fields couple the trapping state to a nontrapping (continuum) state—such a system can be regarded as a first-generation atom laser [27, 28]. Thus our model may provide some insights when one wishes to move from pulsed atom lasers towards CW atom lasers.

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