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Solution of the Schrödinger equation for the Morse potential with an infinite barrier at long range

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Abstract
The Schrödinger equation is considered for a one-dimensional potential function composed of the Morse oscillator and an infinite barrier at long range. The boundary condition introduced by the barrier implies discretization of the unbound states. The eigenstates and eigenvalues are determined along with the discretization condition and the proper normalization for positive and negative energies. An analysis is presented for a particle in this potential driven by an external field coupled in through a dipole. Analytical formulae are derived for the matrix elements of an exponential and linear dipole function with respect to the eigenstates. Numerical time-dependent solutions to the Schrödinger equation are obtained for a periodic external field.

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1. Introduction

The driven Morse oscillator is a common model for investigating the dynamics of atoms and molecules in external fields. This system accounts for the anharmonicity of molecular vibrations and allows for the study of selective excitation [1–3], bond cleavage [4–8] and bond formation [9–13], as well as ionization and stabilization of electronic states [14–17]. The classically chaotic behaviour of this oscillator also makes it a natural model for comparison between the quantum and classical dynamics [18–23], which is important for consideration of quantum chaos [24–26]. Furthermore, the driven Morse potential provides a useful testing ground for controlling quantum dynamics [27–33].

The most common approach to obtain the time-dependent wavefunction for the driven Morse system is through direct numerical solution of the Schrödinger equation [4–11]. The wavefunction may be written on a position grid and the time propagation performed by the split-time operator technique [34, 35], but this methodology does not fully profit from the analytical nature of the model. Since the stationary solutions are available for the Morse potential, a standard technique is to expand the wavefunction in terms of the unperturbed eigenstate basis. One of the advantages of this approach is that the populations of the field-free quantum levels are directly determined in the procedure. However, the continuous positive energy sector of the oscillator causes some difficulty with a traditional basis state expansion, because the resulting equations of motion are a set of integro-differential equations. To overcome this problem, one can approximate the continuum with a set of square integrable orthogonal functions (e.g., derived from Laguerre polynomials), which transforms the integro-differential equations into ordinary differential equations [12, 36]. A different approach was recently applied to the Morse problem based on a state-specific expansion and on the numerical calculation of the continuum–continuum matrix elements [22], but at the expense of losing some of the analytical properties of the system.

In this work, we consider a potential function consisting of the Morse oscillator truncated at long range with an infinite barrier. The boundary condition imposed by the infinite wall implies discretization of the unbound states. We derive the discretization rule and the proper normalization factor for the eigenfunctions at positive and negative energies. The discretization of the continuum in this fashion allows for taking full advantage of the analytical nature of the model. The system driven by an external field coupled in through a dipole is then solved by the standard basis expansion approach, which permits a computationally simple implementation of the time-dependent solutions. As the barrier is placed outside the influence of the Morse potential, the solutions reproduce those of the Morse oscillator without the barrier.

The practical implementation of the driven model depends on the ready calculation of the matrix elements of the external field interaction in the unperturbed basis. The interaction Hamiltonian is considered in the semiclassical dipole formulation, $H_I = -\mu(x)\mathcal{E}(t)$. Provided that the dipole function $\mu(x)$ vanishes before the position of the barrier, previously determined formulae can be used for the matrix elements of the Morse oscillator eigenstates without the barrier (apart from a different normalization factor for the free eigenstates). For example, in [36] analytical forms were obtained considering a particular finite-range dipole function for all bound and free couplings. Even in the case that the dipole is not bounded as $x \to \infty$, the bound–bound and bound–free coupling results are similar for the Morse oscillator with and without the barrier, since the bound eigenfunctions die out rapidly at long range. However, this is not true for the free–free matrix element with a linear dipole function, $\mu(x) \propto x$. For the Morse potential without the barrier, this matrix element cannot be expressed in terms of analytical functions, due to both the asymptotic behaviour of the continuum eigenfunctions and the dipole; the matrix element in this case involves the derivatives of Dirac and Schwartz generalized functions [37]. In contrast, the corresponding dipole coupling between the free states of the Morse potential with the barrier has no singularities and can be represented by known analytical functions. This result will be presented below by first deriving formulae for the matrix elements for an exponential dipole function [38], and then obtaining explicit expressions for all the couplings of the linear dipole function. Finally, the methodology will be applied to the investigation of a driven particle in the potential well. The population dynamics for a periodic external field will be shown along with the convergence of the results with increasing position of the barrier.

2. Eigenvalue equation for the free oscillator

Consider the one-dimension potential function composed of a Morse oscillator and an infinite barrier placed at the position $x = L$

$$V(x) = \begin{cases} V_M(x), & \text{if} \quad x \leqslant L \\ \infty, & \text{otherwise,} \end{cases} \tag{1}$$

where the Morse potential V_M is given by

$$V_M(x) = D[\mathrm{e}^{-2\alpha(x-x_e)} - 2\mathrm{e}^{-\alpha(x-x_e)}]. \tag{2}$$

Here D is the classical dissociation or ionization energy, α^{-1} gives the potential range and x_e is the equilibrium position.

The potential function has a depth of $-D$ at $x = x_e$ and the barrier is assumed to be outside the influence of the Morse oscillator, which means that $L \gg \alpha^{-1} + x_e$ and $V_M(x = L) \approx 0$. The eigenvalue equation for the time-independent Hamiltonian H_o of a particle of mass m under the influence of the potential is

$$H_o\phi(x) = \left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right]\phi(x) = E\phi(x). \tag{3}$$

There are two cases to be considered: the bound eigenfunctions with negative energies $-D < E < 0$ and the free eigenfunctions with positive energy $E > 0$. In order to solve the eigenvalue equation, it is convenient to eliminate the exponential factors present in the potential function $V(x)$ and rewrite it in terms of the dimensionless variable z defined by

$$z = (2N + 1)\,\mathrm{e}^{-\alpha(x-x_e)}, \tag{4}$$

where the $2N + 1 = \sqrt{8mD}/(\hbar\alpha)$. The limit $x = L \to \infty$ corresponds to $z \to 0$, and the limit $x \to -\infty$ leads to $z \to \infty$. For $x \leqslant L$, the eigenvalue equation (3) reduces to that for a confluent hypergeometric equation with a solution of the form $\phi(z) = z^\rho \exp(-z/2)\chi(N, \rho, z)$ [39]. The function $\chi(N, \rho, z)$ can be expressed in terms of Kummer functions of the first and second kinds [40], where $\rho^2 = -\epsilon$ and ϵ is the rescaled energy $\epsilon = 2mE/(\hbar^2\alpha^2)$. The boundary conditions and eigenfunctions are discussed below in two cases for $\epsilon < 0$ and $\epsilon > 0$.

2.1. Case $\epsilon < 0$

In this circumstance $\rho = |\epsilon|^{1/2}$ corresponds to the bound states of $V_M(x)$, and the eigenfunctions may be written in terms of the Kummer function of the first kind [36, 39]

$$\phi_\nu(z) = \mathcal{N}_\nu z^{N-\nu}\,\mathrm{e}^{-z/2} M(-\nu, 1 + 2N - 2\nu, z), \tag{5}$$

where $\mathcal{N}_\nu$ is a normalization constant. In order to satisfy the boundary conditions, the eigenstates obey the relation

$$N - \sqrt{|\epsilon|} = \nu, \tag{6}$$

where ν is a positive integer. It follows that the number of bound states is finite and ν runs from 0 to the integer part of *N*. In the presence of the infinite barrier, the ortho-normalization condition is

$$\int_{z_L}^{\infty} \phi(z)^*_\nu \phi_{\nu'}(z)\frac{\mathrm{d}z}{z} = \delta_{\nu,\nu'}, \tag{7}$$

where $z_L = z(x = L) = (2N + 1)\exp[-\alpha(L - x_e)]$. We can evaluate the above integral by substituting in eigenfunctions (5) along with the definition of the incomplete gamma function

$$\Gamma(y, z_L) = \int_{z_L}^{\infty} \mathrm{e}^{-z} z^{y-1}\,\mathrm{d}z = \Gamma(y) - y^{-1} z_L^y\,\mathrm{e}^{-z_L} M(1, y + 1, z_L), \tag{8}$$

where y is an arbitrary complex number. The first argument y of the incomplete gamma function resulting from integration (7) is real, positive and depends on the constant N, on the quantum numbers ν and ν' and on the indexes of the summations of the Kummer series. Since the infinite wall is placed far beyond the range of the Morse oscillator, the bound states vanish before the position of the wall and we can safely take the limit $\Gamma(y, z_L \to 0) \approx \Gamma(y)$. Therefore, the calculation reduces to the standard Morse potential without the barrier and the normalization constant $\mathcal{N}_\nu$ is the real factor given by [36]

$$\mathcal{N}_\nu = \left[\frac{(2N - 2\nu)\Gamma(2N - \nu + 1)}{\nu!\Gamma(2N - 2\nu + 1)^2} \right]^{1/2}. \tag{9}$$

2.2. *Case* $\epsilon > 0$

In this circumstance $\rho = \mathrm{i}\epsilon^{1/2}$ corresponds to the free states of $V_M(x)$, and the coefficients of the Kummer functions are complex numbers. The wavefunctions for positive energies have the form [36, 41]

$$\phi(k, z) = \mathcal{N}(k) z^{\mathrm{i}k} \,\mathrm{e}^{-z/2} U(-N + \mathrm{i}k, 1 + 2\mathrm{i}k, z), \tag{10}$$

where $k = \sqrt{\epsilon}$ and $\mathcal{N}_k$ is a normalization constant. The presence of the infinite barrier imposes the condition that the wavefunctions satisfy $\phi(k, x = L) = 0$. Since we assumed that the position of the wall satisfies $L \gg \alpha^{-1} + x_e$, the eigenfunctions at L are faithfully described by their asymptotic forms as $x = L \to \infty$ or equivalently $z \to 0$. From (10), we can write the eigenfunction in the proximity of the infinite wall as

$$\lim_{z\to 0} \phi(k, z) = \frac{\mathcal{N}(k)}{k} \Im \left\{ \frac{\Gamma(1 + 2\mathrm{i}k)}{\Gamma(-N + \mathrm{i}k)} z^{-\mathrm{i}k} \right\}. \tag{11}$$

This expression can be written in terms of the variable x,

$$\lim_{x\to\infty} \phi(k, x) = \frac{\mathcal{N}(k)}{k} \frac{|\Gamma(1 + 2\mathrm{i}k)|}{|\Gamma(-N + \mathrm{i}k)|} \sin[\alpha k(x - x_e) + \theta(k)], \tag{12}$$

where the phase-shift $\theta(k)$ depends on the energy through the relation

$$\theta(k) = \arg \left\{ \frac{\Gamma(1 + 2\mathrm{i}k)(2N + 1)^{-\mathrm{i}k}}{\Gamma(-N + \mathrm{i}k)} \right\}. \tag{13}$$

It is clear from (12) that in order to satisfy the boundary condition at the wall the eigenfunctions must obey the discretization rule

$$\alpha k(L - x_e) + \theta(k) = \eta\pi, \tag{14}$$

where η is an integer. The latter expression should be contrasted with the corresponding relation (6). Unlike the case for the bound eigenfunctions, the discretization condition for the free eigenfunctions does not impose an upper limit in the number of states, i.e., there is an infinite number of positive eigenvalues. Equation (14) is a transcendental equation for k, which needs to be solved numerically. The solutions of this equation are sought only for positive values of η. For reasonable choices of L, the term $k\alpha(L - x_e)$ is always greater than $|\theta(k)|$ and the left-hand side of (14) cannot be negative. Therefore, we ascribe the quantum number k_η to each value of k, which assures satisfaction of the boundary condition for a given η. In the limit $L \to \infty$, (14) reduces to the discretization condition for a particle in a box, $\alpha k = \eta\pi/L$.

As for the bound states, the normalization factors $\mathcal{N}(k_\eta)$ for the free eigenfunctions are obtained by imposing the corresponding orthogonality condition given in (7). The integral can be calculated by substituting in the corresponding eigenfunctions and using the definition of the Kummer series. The integration results in incomplete gamma functions (8) for which the first argument has a positive real part that depends on the constant N and on the indexes of the summations, and an imaginary part that depends on the quantum numbers k_η and $k_{\eta'}$. Unlike the case for the bound states, we cannot simply assume that the free states are zero in the vicinity of the wall and set the incomplete gamma function equal to the gamma function, because of its complex argument. However, since z_L is comparably smaller than the other parameters associated with the integration, it is still legitimate to take the limit from (8):

$$\lim_{z_L\to 0}\Gamma(y, z_L) = \Gamma(y) - (y)^{-1} z_L^y \tag{15}$$

With the help of the above expression along with the Gauss hypergeometric formula,

$$\sum_{n=0}^{\infty}\frac{(a)_n(c)_n}{(b)_n n!} = \frac{\Gamma(b)\Gamma(b-a-c)}{\Gamma(b-a)\Gamma(b-c)}, \tag{16}$$

where $(a)_n = \Gamma(a+n)/\Gamma(a)$ is the Pochhammer symbol, we can write the normalization integral as

$$\begin{aligned}\int_{z_L}^{\infty}\phi(k_\eta, z)^*\phi(k_{\eta'}, z)\frac{\mathrm{d}z}{z} = {}& \frac{\mathcal{N}(k_\eta)\mathcal{N}(k_{\eta'})^*}{2k_\eta k_{\eta'}}\left|\frac{\Gamma(1+2\mathrm{i}k_\eta)\Gamma(1+2\mathrm{i}k_{\eta'})}{\Gamma(-N+\mathrm{i}k_\eta)\Gamma(-N+\mathrm{i}k_{\eta'})}\right| \\ &\times\left[\frac{\sin[\alpha(k_\eta - k_{\eta'})(L-x_e)+\theta(k_\eta)-\theta(k_{\eta'})]}{k_\eta - k_{\eta'}}\right. \\ &\left.-\frac{\sin[\alpha(k_\eta + k_{\eta'})(L-x_e)+\theta(k_\eta)+\theta(k_{\eta'})]}{k_\eta + k_{\eta'}}\right].\end{aligned} \tag{17}$$

The discretization condition for the free states (14) guarantees that the above expression is zero except for $k_\eta = k_{\eta'}$, in which case we find the normalization constant to be

$$\mathcal{N}(k_\eta) = \left|\frac{\Gamma(-N+\mathrm{i}k_\eta)}{\Gamma(1+2\mathrm{i}k_\eta)}\right|\left[\frac{2k_\eta^2}{\alpha(L-x_e)+\frac{\mathrm{d}}{\mathrm{d}k_\eta}\theta(k_\eta)}\right]^{1/2} \tag{18}$$

The orthogonality between the bound eigenfunctions ϕ_v and free eigenfunctions $\phi(k_\eta)$ directly follows from the properties of the standard Morse oscillator eigenstates. Also note that the free and bound eigenfunctions are real.

3. Solutions for the driven system

The interaction between the external field and the particle is given in the semiclassical dipole formulation by the Hamiltonian H_I

$$H_I = -\mu(x)\mathcal{E}(t), \tag{19}$$

where $\mathcal{E}(t)$ is the time-dependent external field and $\mu(x)$ is the dipole function. The Schrödinger equation for the time-dependent wavefunction $\Phi(x,t)$ is governed by the Hamiltonian consisting of the unperturbed portion H_o and the interaction term H_I

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Phi(x,t) = H\Phi(x,t) = [H_o + H_I]\,\Phi(x,t). \tag{20}$$

In order to solve the dynamical equation, the wavefunction may be expanded in terms of bound and free states

$$\Phi(x,t) = \sum_{m=0}^{\infty} A_m(t)\phi_m(x), \tag{21}$$

where $m \leqslant \text{int}(N)$ refers to the bound states, i.e., $\phi_m = \phi_\nu$, whereas $m > \text{int}(N)$ refers to the free states $\phi_{m-\text{int}(N)} = \phi(k_\eta)$.

Substitution of (21) into the Schrödinger equation and use of the orthogonality properties of the eigenfunctions leads to a system of first-order ordinary differential equations for the time-dependent coefficients $A_m(t)$

$$\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t} A_m(t) = E_m A_m(t) - \mathcal{E}(t) \sum_{m'=0}^{\infty} A_{m'}(t) \langle m|\mu(x)|m'\rangle, \tag{22}$$

where E_m is accordingly the energy of either the bound or free levels and the matrix elements $\langle m|\mu(x)|m'\rangle$ are given by

$$\langle m|\mu(x)|m'\rangle = \int_{-\infty}^{L} \mathrm{d}x\, \phi_m(x)\mu(x)\phi_{m'}(x). \tag{23}$$

Provided that the matrix elements can be readily evaluated, the integration of the equations of motion (22) truncated at an appropriate level $M_{\max}$ can be performed by the use of standard algorithms like Runge–Kutta. The convergence of the procedure can be tested by increasing the value of $M_{\max}$.

The free wavefunction calculated in (10) is related to the Morse continuum wavefunction $\phi_C(k)$ by [36]

$$\sqrt{\frac{\mathrm{d}\eta}{\mathrm{d}k}} \phi(k, z) = \phi_C(k, z), \tag{24}$$

where $\phi_C(k)$ obeys the relation $\langle \phi_C(k)|\phi_C(k')\rangle = \delta(k - k')$ and $\mathrm{d}\eta/\mathrm{d}k$ is the density of states, which can be obtained from the discretization condition (14),

$$\frac{\mathrm{d}\eta}{\mathrm{d}k} = \frac{1}{\pi}\left[\alpha(L - x_e) + \frac{\mathrm{d}}{\mathrm{d}k}\theta(k)\right]. \tag{25}$$

It also follows from (24) that the projection of the wavefunction onto the continuum subspace is $(\mathrm{d}\eta/\mathrm{d}k)^{1/2}\langle\phi(k)|\Phi(t)\rangle$. Hence, in the limit $L \to \infty$, the summations over the free states in (21) and (22) will become integrals leading to the equations of motion for the Morse oscillator without the barrier.

4. Matrix elements

Assuming that the dipole interaction vanishes as the wall is approached, $\mu(x \to L) \approx 0$, then we can use the all of the formulae for the matrix elements derived in previous works for the Morse oscillator without the barrier. However, this is not true for the continuum–continuum matrix element with unbounded functions such as the linear dipole $\mu(x) \propto x$. For the Morse potential without the barrier, this matrix element with the latter dipole cannot be expressed in terms of analytical functions, due to both the asymptotic behaviour of the continuum eigenfunctions and dipole at $x \to \infty$ [37]. In contrast, we will show that the corresponding matrix element between the free states for the Morse potential with the barrier has no singularities and can be represented by known analytical functions.

First, we calculate the matrix elements for a dipole function given as a power of the z variable. This form is very convenient for the derivation of several other dipole functional forms and corresponds to an exponential function in the x variable, which reasonably describes collision-induced dipole functions [38]. Hence, consider the following matrix element given by the integral (23) in terms of z:

$$\langle m|z^{\xi}|m'\rangle = \int_{z_L}^{\infty} \frac{\mathrm{d}z}{z} \phi_m(z)^* z^{\xi} \phi_{m'}(z), \tag{26}$$

where ξ is a real positive constant.

Since the bound eigenfunctions have finite range and the position of the barrier is chosen far outside of the influence of the Morse potential, the bound states are of essentially null value well before the infinite wall, $\phi_\nu(z \to z_L) = 0$. Therefore, substitution of the bound eigenstates (5) into the above expression will result in a double summation of gamma functions. One of the double summations can be performed using the Gauss formula and the resulting matrix elements can be written as a finite summation

$$\langle \nu|z^{\xi}|\nu'\rangle = \frac{\mathcal{N}_\nu \mathcal{N}_{\nu'}}{(1+2N-2\nu')_{\nu'}} \sum_{n=0}^{\nu} \frac{(-\nu)_n (1+\nu-\nu'-n-\xi)_{\nu'}}{n!(1+2N-2\nu)_n} \Gamma(2N-\nu-\nu'+n+\xi). \tag{27}$$

The bound–free matrix elements can be calculated by the same line of reasoning, which also results in a finite summation

$$\begin{aligned}\langle \nu|z^{\xi}|k_\eta\rangle = {} & \frac{\mathcal{N}_\nu \mathcal{N}(k_\eta)}{k_\eta} |\Gamma(1+2\mathrm{i}k_\eta)|^2 \Im \left\{ \frac{\sin[\pi(N+\mathrm{i}k_\eta)]}{\pi} \right. \\ & \left. \times \sum_{n=0}^{\nu} \frac{(-\nu)_n \Gamma(1+\nu-n-\xi)}{n!(1+2N-2\nu)_n} \frac{\Gamma(N-\nu+n+\mathrm{i}k_\eta+\xi)}{\Gamma(1-N+\nu-n+\mathrm{i}k_\eta-\xi)} \right\}.\end{aligned} \tag{28}$$

For the free–free matrix elements the product of eigenfunctions no longer vanish before the infinite barrier. As a consequence, in order to evaluate the corresponding integral (26), we have to consider the incomplete gamma function defined by (8). Substituting the free eigenfunctions into integral (26), we use the incomplete gamma function definition along with the small z_L limit (15) to obtain a double infinite summation. As in the previous cases, one of the summations can be performed with the help of the Gauss formula. Finally, the matrix element can be written as

$$\begin{aligned}\langle k_\eta|z^{\xi}|k_{\eta'}\rangle = {} & \frac{\mathcal{N}(k_\eta)\mathcal{N}(k_{\eta'})}{2k_\eta k_{\eta'}} \Re[F(k_\eta, k_{\eta'}, \xi) - F(k_\eta, -k_{\eta'}, \xi) \\ & + G(k_\eta, k_{\eta'}, \xi) - G(k_\eta, -k_{\eta'}, \xi)],\end{aligned} \tag{29}$$

where the auxilliary functions F and G are given by

$$G(k_\eta, k_{\eta'}, \xi) = \frac{\Gamma(1-2\mathrm{i}k_\eta)}{\Gamma(-N-\mathrm{i}k_\eta)} \frac{\Gamma(1-2\mathrm{i}k_{\eta'})}{\Gamma(-N-\mathrm{i}k_{\eta'})} \frac{z_L^{\mathrm{i}(k_\eta+k_{\eta'})+\xi}}{\mathrm{i}(k_\eta+k_{\eta'})+\xi} \tag{30}$$

$$F(k_\eta, k_{\eta'}, \xi) = B(k_\eta, k_{\eta'}) \sum_{m=0}^{\infty} F_m(k_\eta, k_{\eta'}, \xi). \tag{31}$$

The summand coefficient in (31) is

$$F_m(k_\eta, k_{\eta'}, \xi) = \frac{(-N+\mathrm{i}k_\eta)_m}{m!(1+2\mathrm{i}k_\eta)_m} \frac{\Gamma[\mathrm{i}(k_\eta+k_{\eta'})+m+\xi]\Gamma(1+N-\mathrm{i}k_\eta-m-\xi)}{\Gamma[1-\mathrm{i}(k_\eta-k_{\eta'})-m-\xi]}, \tag{32}$$

and the term $B(k_\eta, k_{\eta'})$ is given by

$$B(k_\eta, k_{\eta'}) = |\Gamma(1+2\mathrm{i}k_{\eta'})|^2 \frac{\sin[\pi(N+\mathrm{i}k_{\eta'})]}{\pi} \frac{\Gamma(1-2\mathrm{i}k_\eta)}{\Gamma(-N-\mathrm{i}k_\eta)}. \tag{33}$$

Finally, the matrix elements for an exponential dipole function of x may be determined from (4) by the relation

$$\mu_e(x) = \frac{q}{\alpha}\,\mathrm{e}^{-\zeta x} = \frac{q}{\alpha}\frac{\mathrm{e}^{-\zeta x_e}}{(2N+1)^{\zeta/\alpha}} z^{\zeta/\alpha}. \tag{34}$$

The term $G(k_\eta, \pm k_{\eta'}, \xi)$ may be neglected for the calculation of matrix elements of the exponential dipole function. This is a good approximation given that the position of the wall L and the exponential damping factor ξ are such that z_L^ξ is very small, and the series $F(k_\eta, \pm k_{\eta'}, \xi)$ is much larger in magnitude than $G(k_\eta, \pm k_{\eta'}, \xi)$. However, as we show below, none of the above factors can be ignored for the calculation of the linear dipole function.

Consider the linear dipole function $\mu_l(x)$, which is related to $\mu_e(x)$ by a simple differentiation rule

$$\mu_l(x) = qx = -\alpha \frac{\partial}{\partial\zeta}\mu_e(x)\bigg|_{\zeta=0}. \tag{35}$$

From the above equation, the matrix elements for $\mu_l(x)$ can be evaluated according to the expression

$$\langle m|\mu_l(x)|m'\rangle = \frac{q}{\alpha}\left\{[\alpha x_e + \ln(2N+1)]\delta_{mm'} - \frac{\partial}{\partial\xi}\langle m|z^\xi|m'\rangle\bigg|_{\xi=0}\right\}. \tag{36}$$

Hence, we just need to evaluate the derivative of the matrix elements of z^ξ with respect to ξ, at $\xi = 0$, to obtain the corresponding expression for the linear dipole. This procedure leads to the formulae obtained previously for the bound–bound matrix element [37, 42–44]

$$\langle\nu|\alpha x|\nu'\rangle = \frac{2(-1)^{\nu'-\nu+1}}{(\nu'-\nu)(2N-\nu'-\nu)}\left[(N-\nu)(N-\nu')\frac{\Gamma(2N-\nu'+1)\nu'!}{\Gamma(2N-\nu+1)\nu!}\right]^{1/2} \tag{37}$$

for $\nu' > \nu$, and for the diagonal element $\nu = \nu'$

$$\langle\nu|\alpha x|\nu\rangle = \alpha x_e + \ln(2N+1) + \psi(2N-\nu+1) - \psi(2N-2\nu+1) - \psi(2N-2\nu), \tag{38}$$

where the ψ function satisfies $\Gamma'(z) = \psi(z)\Gamma(z)$. The bound–free matrix element is similar to that obtained in [37, 41, 45] apart from the normalization factor in (18) for the free states

$$\langle\nu|\alpha x|k_\eta\rangle = \mathcal{N}(k_\eta)\frac{(-1)^{\nu+1}|\Gamma(1+2\mathrm{i}k_\eta)|}{(N-\nu)^2+k_\eta^2}\left[\frac{\sinh(2\pi k_\eta)(2N-2\nu)}{2\pi k_\eta\Gamma(2N-\nu+1)\nu!}\right]^{1/2}|\Gamma(1+N+\mathrm{i}k_\eta)|^2. \tag{39}$$

For the free–free matrix elements we have

$$\frac{\partial}{\partial\xi}\langle k_\eta|z^\xi|k_{\eta'}\rangle\bigg|_{\xi=0} = \frac{\mathcal{N}(k_\eta)\mathcal{N}(k_{\eta'})}{2k_\eta k_{\eta'}} \times \Re[f_l(k_\eta,k_{\eta'}) - f_l(k_\eta,-k_{\eta'}) + g_l(k_\eta,k_{\eta'}) - g_l(k_\eta,-k_{\eta'})], \tag{40}$$

where the auxilliary functions f_l and g_l are

$$g_l(k_\eta,k_{\eta'}) = \frac{\Gamma(1-2\mathrm{i}k_\eta)}{\Gamma(-N-\mathrm{i}k_\eta)}\frac{\Gamma(1-2\mathrm{i}k_{\eta'})}{\Gamma(-N-\mathrm{i}k_{\eta'})}z_L^{\mathrm{i}(k_\eta+k_{\eta'})}\left[\frac{\ln(z_L)}{\mathrm{i}(k_\eta+k_{\eta'})} + \frac{1}{(k_\eta+k_{\eta'})^2}\right], \tag{41}$$

$$f_l(k_\eta,k_{\eta'}) = B(k_\eta,k_{\eta'})\sum_{m=0}^{\infty}\{F_m(k_\eta,k_{\eta'},\xi=0)[\psi(\mathrm{i}(k_\eta+k_{\eta'})+m) - \psi(1+N-\mathrm{i}k_\eta-m) + \psi(1-\mathrm{i}(k_\eta-k_{\eta'})-m)]\}. \tag{42}$$

The above formulae can be used to calculate the off-diagonal $\eta \neq \eta'$ matrix elements. However, in order to determine suitable formulae for numerical computation of the diagonal elements $\eta = \eta'$, it is necessary to go one step further as there is a singularity in the function $g_l(k_{\eta'}, -k_{\eta'})$ at $\eta = \eta'$, which exactly cancels the singularity in $f_l(k_{\eta'}, -k_{\eta'})$. To this end, consider the limit

$$\Re\left\{\lim_{\eta\to\eta'} g_l(k_{\eta'}, -k_{\eta'})\right\} = \frac{|\Gamma(1-2\mathrm{i}k_\eta)|^2}{|\Gamma(-N+\mathrm{i}k_\eta)|^2}\left[\ln(z_L)^2 + \lim_{\eta\to\eta'}\frac{\cos[(k_\eta - k_{\eta'})\ln(z_L)]}{(k_\eta - k_{\eta'})^2}\right]. \tag{43}$$

Taking the same limit for the first term of the summation in $f_l(k_{\eta'}, -k_{\eta'})$ of (42) yields

$$-\frac{|\Gamma(1-2\mathrm{i}k_\eta)|^2}{|\Gamma(-N+\mathrm{i}k_\eta)|^2}\Gamma[\mathrm{i}(k_\eta - k_{\eta'})]\psi[\mathrm{i}(k_\eta - k_{\eta'})], \tag{44}$$

and the singularities cancel such that

$$\lim_{\eta'\to\eta}\left\{\Gamma[\mathrm{i}(k_\eta - k_{\eta'})]\psi[\mathrm{i}(k_\eta - k_{\eta'})] - \frac{\cos[(k_\eta - k_{\eta'})\ln(z_L)]}{(k_\eta - k_{\eta'})^2}\right\} = \frac{\pi^2}{12} + \frac{1}{2}\gamma^2 + \frac{1}{2}\ln(z_L)^2, \tag{45}$$

where γ is the Euler constant. With the help of the above relations, the diagonal matrix elements can be written as

$$\frac{\partial}{\partial\xi}\langle k_\eta|z^\xi|k_\eta\rangle\bigg|_{\xi=0} = \frac{\mathcal{N}(k_\eta)^2}{2k_\eta^2}\Re[s_1(k_\eta) - s_2(k_\eta) + g_l(k_\eta, k_\eta)], \tag{46}$$

where s_1 and s_2 are given by

$$s_1(k_\eta) = B(k_\eta, k_\eta)\left\{\Gamma(1+2\mathrm{i}k_\eta)\sum_{m=1}^{\infty}\frac{(-1)^m}{m}\frac{(-N+\mathrm{i}k_\eta)_m\Gamma(1+N-\mathrm{i}k_\eta - m)}{(2\mathrm{i}k_\eta + m)}\right.$$
$$\left. + \Gamma(2\mathrm{i}k_\eta)\Gamma(1+N-\mathrm{i}k_\eta)[\psi(2\mathrm{i}k_\eta) - \psi(1+N-\mathrm{i}k_\eta) - \gamma]\right\}, \tag{47}$$

$$s_2(k_\eta) = B(k_\eta, -k_\eta)\sum_{m=1}^{\infty}\left\{\frac{(-N+\mathrm{i}k_\eta)_m}{(1+2\mathrm{i}k_\eta)_m}\frac{\Gamma(1+N-\mathrm{i}k_\eta - m)}{m\Gamma(1-2\mathrm{i}k_\eta - m)}\right.$$
$$\left.\times[\psi(m) - \psi(1+N-\mathrm{i}k_\eta - m) + \psi(1-2\mathrm{i}k_\eta - m)]\right\}$$
$$-\left|\frac{\Gamma(1-2\mathrm{i}k_\eta)}{\Gamma(-N+\mathrm{i}k_\eta)}\right|^2\left[\frac{\pi^2}{12} + \frac{1}{2}\gamma^2 - \frac{1}{2}\ln(z_L)^2\right]. \tag{48}$$

The dependence of the free–free matrix elements on L arises from the normalization factor $\mathcal{N}(k_\eta)$ and the integration limit z_L. As shown at the end of section 3, the L dependence of the normalization factors are counterbalanced by the density of states in the limit of large L. On the other hand, the apparent singularity at $L = \infty$ originated from the integration is a consequence of the distribution nature of the matrix elements of the Morse oscillator without the barrier. The limit $L \to \infty$ should be taken in the space of generalized functions and the convergence analysed in the Schwartz sense [46]. A proper calculation of the free–free matrix elements in this limit can be found in [37], where is shown that these couplings can be expressed in terms of derivatives of Dirac and Cauchy principal value distributions.

5. Numerical results

In this section, we consider a particle in the potential well $V(x)$ of (1). The parameters are taken from [17]. In atomic units, the Morse parameters are $D = 0.6643$, $\alpha = 0.417$, $x_e = 0$

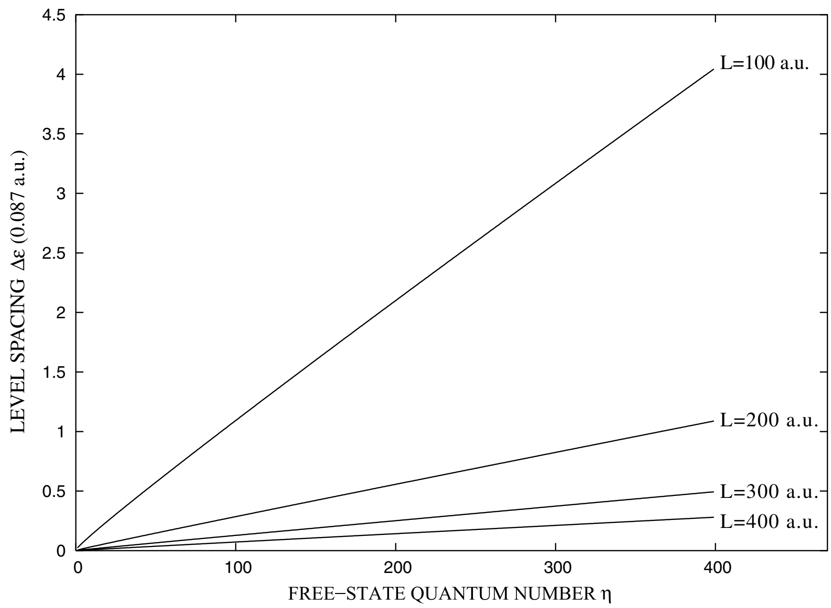

Figure 1. Spacing between free state levels $\Delta\epsilon = \epsilon(k_{\eta+1}) - \epsilon(k_\eta)$ for several locations L of the barrier.

and $m = 1$. For those parameters, we obtain $N \approx 2.26$, implying that there are three bound states with energies $E_0 = -0.4457$ au, $E_1 = -0.1389$ au and $E_2 = -0.0061$ au. Figure 1 shows the energy spacing of adjacent free state levels $\Delta\epsilon = \epsilon_{\eta+1} - \epsilon_\eta$ as a function of the state number η for several positions L of the barrier. The spacing grows linearly with the quantum number except for small values of η. For a given η, the density of states with respect to the energy $\Delta\epsilon^{-1}$ is roughly proportional to L^2. The behaviour in figure 1 at high quantum numbers is expected from the near particle in a box character in that limit.

The free–free matrix elements are shown in figure 2 for the barrier position $L = 400$ au. The plot was obtained with the fixed value of $E(k_{\eta'}) = 0.0064$ au and calculating the matrix element in (36) as a function of $E(k_\eta)$. The inset shows the same for $E(k_{\eta'}) = 0.56$ au, 2.21 au and 4.92 au. The figure clearly shows the diagonal dominance at $\eta = \eta'$ and a somewhat damped oscillatory coupling with neighbouring states. These matrix elements can be compared with different free–free couplings obtained in early works [36, 37], which show relatively similar energy dependence.

We assume that the particle is driven by a time periodic radiation field $\mathcal{E}(t) = V_o \cos(\omega t)$ and consider the linear dipole given in (35). Before proceeding to the calculation of the dynamics, we need to establish a value of L where the calculations are reliable. The external field parameters are set to $V_o = 13.8$ au and $\omega = 0.174$ au and the particle is assumed to be initially in the first excited bound state. Figure 3 shows the probability of the particle escaping from the Morse bound sector at $t = 11.5$ optical cycles as a function of the position of the barrier. There is clear convergence with the escape probability reaching a constant value above $L = 200$ au. This fact was verified as well for the bound-state populations. The convergence was also observed for other parameters of the external field.

Figure 4 shows the population dynamics for the same field parameters and initial condition used in figure 3, while the barrier is set to $L = 400$ au. The chosen frequency implies that

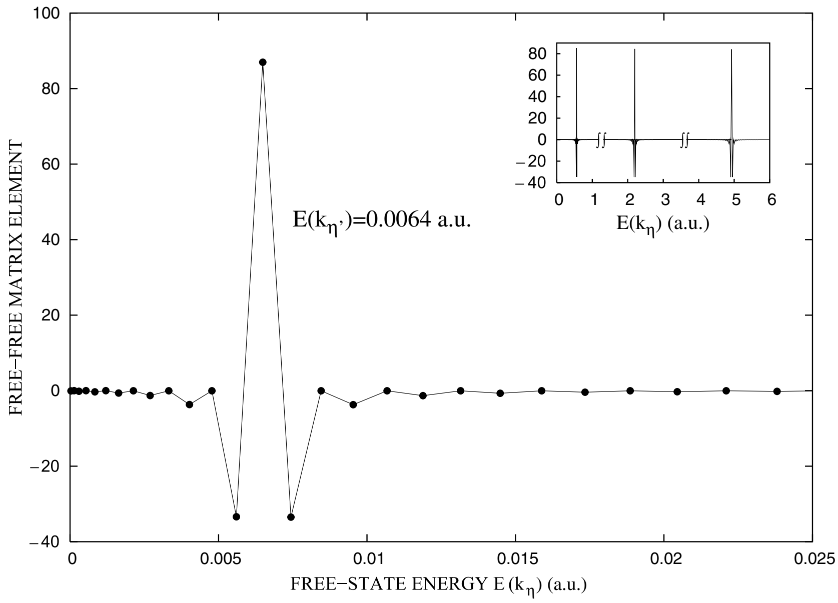

Figure 2. Free–free matrix elements for $L = 400$ au and $E(k_{\eta'}) = 0.0064$ au as a function of the free state energy. The inset shows the matrix elements for $E(k_{\eta'}) = 0.56$ au, 2.21 au, 4.92 au, successively indicated by the broken curves.

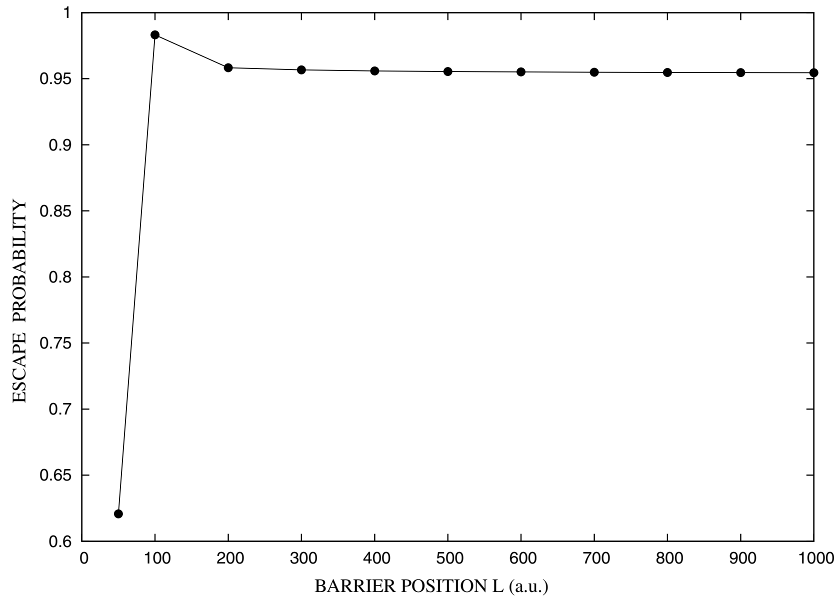

Figure 3. Probability of the particle escaping from the Morse bound sector at $t = 11.5$ optical cycles for the external field parameters $V_o = 13.8$ au and $\omega = 0.174$ au as a function of the position L of the barrier.

one photon of the external field is sufficient to remove the particle from the Morse well. The figure shows the population of the first and second excited bound states as well as the escape

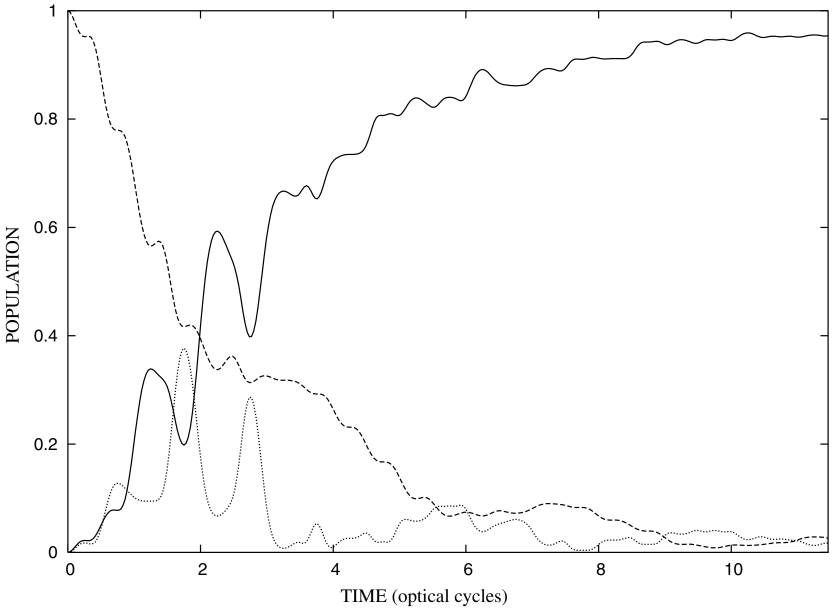

Figure 4. Population dynamics: first excited bound state (dashed curve), second excited bound state (dotted curve), escape probability (solid curve) (the ground-state population is not shown). The external field parameters are: $V_o = 13.8$ au and $\omega = 0.174$ au and the position of the barrier is $L = 400$ au.

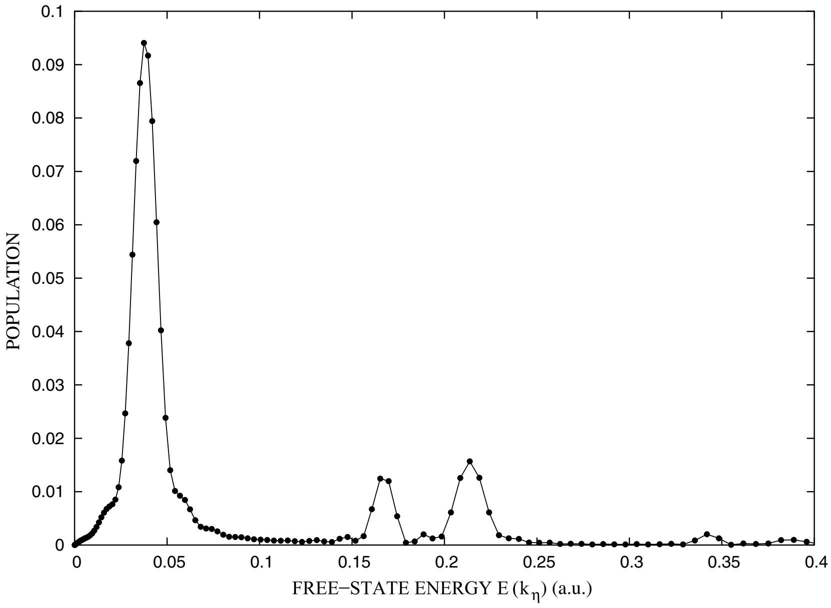

Figure 5. Free state population at $t = 11.5$ optical cycles. The position of the barrier is $L = 400$ au.

probability (the very small population of the ground state is omitted). There is a fast decrease in the initial-state population, which is accompanied by an increase of the escape probability and by some transient occupation of the second excited state. The escape probability reaches roughly 0.95 by nine optical cycles. Figure 5 shows the population of the free states at $t = 11.5$ optical cycles. The dominant peak at low energy is approximately the energy of one photon above the initial-bound state. The two peaks at 0.17 au and 0.21 au are due to the free–free transitions and to a two photon transition from the first excited bound level.

6. Conclusion

The methodology presented here provides an efficient technique to deal with the driven Morse oscillator taking advantage of the analytical characteristics of the problem. The treatment given to the unbound states allows for the time-dependent solutions to be found by the standard basis expansion approach, which permits a computationally simple implementation and is very convenient for obtaining the occupation probability of the unperturbed levels. Moreover, analytical formulae were derived for the matrix elements of an exponential and linear dipole function with respect to the Morse eigenstates. In addition to the numerical calculations shown here, we have compared the solutions of the present approach with those of the Morse potential without the barrier performed by the continuum Laguerre expansion technique [36]. The comparisons were carried out for the cases of dissociation from bound states and photoassociation from free Gaussian wavepackets, with the Morse, external field and dipole function parameters set to those of [12, 36]. In all situations, very good agreement was found between the results obtained from the two methods, which reinforces the validity of the current approach. The outcome of this work may be employed in many applications, including the study of controlling quantum dynamics.

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