Anharmonic Potentials Analysis through the Floquet Representation

Mohammed Janati Idrissi, Abdelaziz Fedoul, Salaheddine Sayouri, Ibrahim Amila

Laboratory of Theoretical and Applied Physics, Faculty of Sciences Dhar Al Mahraz, University of Sidi Mohamed Ben Abdellah, Fez, Morocco
Email: jan123med@gmail.com, afedoul@yahoo.fr, ssayouri@gmail.com, ibrahimamila@gmail.com

Abstract
We propose an approach based on Floquet theorem combined with the resonating averages method (RAM), to solve the time-dependent Schrödinger equation with a time-periodic Hamiltonian. This approach provides an alternative way to determine directly the evolution operator, and then we deduct the wave functions and the corresponding quasi-energies, of quantum systems. An application is operated for the driven cubic or/and quartic anharmonic as well as for the Morse potential. Comparisons of our results with those of other authors are discussed, and numerical evaluations are performed, to determine the dissociation energy of (HCl) and (CO) molecules.

Keywords
Floquet Theorem, Resonating Averages, Anharmonic Potential

1. Introduction
Several physical systems have been modeled by a simple harmonic oscillator as a first approximation devoted to the construction of elegant formalism, to understand their dynamics and are dealing with the description of the nature of various physical phenomena under certain conditions. Moreover, it is possible to compare solutions derived from these studies to experimental results obtained by studying laser-matter interaction problems in many branches of physics, ranging from black body radiation to vibrations of crystal lattices [1] [2] [3] [4]. It is now generally realized that interesting connections of numerous real classical or quantum systems are a consequence of the anharmonic non-linear character of evolution in these systems, such as vibrations of the real molecules, graded alloys and irregular semiconductor structures.

In this regard, several approaches have been used, among them the well-
known perturbation theory [1] [2] [5] [6], the variational method based on the squeezed states [7], Lie algebraic method using canonical transformations [8] and multiple scale method [9] which have been developed and introduced in some special cases of the time-dependent harmonic and anharmonic oscillators in the presence of an external excitation force, to obtain the evolution operator of these systems which in turn enables to find the explicit expressions of quasi-energies and wave functions. In the regime of strong field-matter interaction, a non-perturbative approach, based on the quantization version of the Floquet formalism [10] [11] [12], has been developed and applied to describe physical systems with time-periodic Hamiltonians. This was used to give explanation of various phenomena, including multiple high order harmonic generation in intense laser field [12], multi-photon ionisation [13], and to describe the motion of a charged particle in an oscillating electric field [14], etc. Our motivation consists especially in solving the problem of a quantum system driven by a periodic time-varying force. The key feature of the application of Floquet theorem is that it permits the reduction of the time-dependent Schrödinger equation of the system to an equivalent conservative eigenvalue problem. It is an efficiency tool in the case of a system submitted to strong time-periodic field, and consequently for which the usual stationary states, solutions to the time-independent Schrödinger equation when no external field acts, do not exist [4]. These derived quantum steady states, lead to set correspondences with stationary states of conservative systems [12] [13].

In previous works, we have applied the above mentioned approach, to the case of harmonic oscillator with time-periodic frequency and to the simple forced harmonic oscillator [15]. Thus, some properties of the Floquet states for this system were elucidated. Moreover, we used resonating averages method (RAM) [16] which provides a useful tool for constructing the evolution operators in a whole resonance zone, which enabled us to obtain readily steady states and the associated quasi-energies of the time-periodic Hamiltonian of these systems. In this work, we apply our method, to first and second ameliorated order approximations, to some driven anharmonic potentials. A comparison of our analytical results with those of the literature was made and numerical evaluations, allowed calculation of the maximum vibrational quantum number to estimate the dissociation energy for the (HCl) and (CO) molecules.

The paper is organized as follows. In Section 2, we review the basic formulation of our approach. Section 3 consists of its application to the driven cubic and quartic anharmonic oscillators, and to the Morse potential expansion. In Section 4, some comparisons of our results with those of other published works are presented and discussed and an example of numerical evaluations was performed for the (HCl) and (CO) molecules. Concluding remarks are given in Section 5.

2. Basic of the Proposed Approach [15]

A quantum system that is submitted to a perturbation may be described by the
following Hamiltonian;

\[ H(t) = H_0 + \lambda H'(t) \]  

(1)

where \( H_0 \) is the Hamiltonian of the unperturbed system, and \( H'(t) \) is the interaction Hamiltonian, which amplitude \( \lambda \) is taken as being very small.

In the case of a periodical perturbation, according to the Floquet theorem there exists a couple of operators \( (R, T(t)) \), so that the time-evolution operator can be written in the following form [10] [11] [12]

\[ U(t) = T(t)e^{-iRt} \]  

(2)

and \( U(0) = 1 \)

where \( T(t) \) is a periodic unitary operator of the same period as \( H'(t) \), and \( R \) is a constant Hermitian operator.

In the interaction picture, \( U(t) \) satisfies the following differential equation

\[ ih \frac{dU_i(t)}{dt} = \lambda H_i(t)U_i(t) \]  

(3)

where

\[ H_i(t) = e^{iH_0/t}H'(t)e^{-iH_0/t} \]  

(4)

A unitary transformation \( T(t) \) may be applied to Equation (3) to obtain the so-called reduced equation of the system such as,

\[ ih \frac{d\phi_n(t)}{dt} = R|\phi_n(t)\rangle \]  

(5a)

\[ |\phi_n(t)\rangle = e^{-iE_n/t}|n\rangle \]  

(5b)

where \( |\phi_n(t)\rangle \) are the eigenstates of the Floquet operator \( R \), corresponding to the eigenvalues \( E_n \), and where \( |n\rangle \) are the states of the unperturbed system. Consequently, the Floquet states (or steady states), solutions of the time-dependent Schrödinger equation, in the Floquet representation are defined such as,

\[ |\psi_n(t)\rangle = T(t)|\phi_n(t)\rangle \]  

(6)

The obtained steady states form a complete set of time-dependent solutions in the extended Hilbert space, and do not depend on the choice of the couple \( (R, T(t)) \).

Search of Floquet operators is based on the resonating averages method (RAM) [15] [16], which consists in the separation of the perturbed Hamiltonian \( H_i(t) \), written in the interaction picture Equation (4), into an averaging part, \( \bar{H}_i(t) \), and an oscillating part, \( \tilde{H}_i(t) \), such as:

\[ H_i(t) = \bar{H}_i(t) + \frac{d\bar{H}_i(t)}{dt} \]  

(7)

The application of the RAM to Equation (3) gives rise to the following solutions to first and second order in \( \lambda \)

\[ U_i(t) = \left[1 - \frac{i\lambda}{\hbar} \tilde{H}_i(t)\right]^{(1)}V_i(t) \]  

(8)
\[ \begin{align*}
(2a)U_j(t) &= \left[ 1 - \frac{i\lambda}{\hbar} \hat{H}_j(t) + \lambda^2 A_z(t) \right] G(t) 
\end{align*} \] (9)

The determination of the solutions \( (1a)U_j(t) \) and \( (2a)U_j(t) \) Equations ((8), (9)) and a comparison with Floquet representation of Equation (2), enabled us to obtain the first and second order couples \( \left\{ (1a)R, (1a)\mathcal{T}(t) \right\} \), \( \left\{ (2a)R, (2a)\mathcal{T}(t) \right\} \), and thence the quasi-energies \( (1a)E_a, (2a)E_a \) and Floquet-states \( \left\{ (1a)\psi_a(t) \right\} \), \( \left\{ (2a)\psi_a(t) \right\} \), respectively.

3. Applications

3.1. Driven Cubic Anharmonic Oscillator

The Hamiltonian of the considered quantum system is given by the following expression

\[ H_i(t) = \frac{\dot{q}^2}{2m} + \frac{1}{2} m\omega^2_0 \dot{q}^2 + \mu \hbar \omega_0 \dot{q}^3 + \mu \hbar \omega_0 \sin(vt) \dot{q} \] (10)

where \( \dot{q} = \sqrt{\frac{m\omega_0}{\hbar}} q \)

\( \mu \hbar \omega_0 \dot{q}^3 \) and \( \mu \hbar \omega_0 \sin(vt) \dot{q} \) are the conservative perturbation and the time-dependent perturbation due to an external force, respectively.

\( m \) and \( \omega_0 \) are the mass and the frequency of the simple harmonic oscillator, respectively, \( \nu \) is the driven oscillation frequency, and \( \mu \), \( \mu \), are very weak amplitudes of the perturbations.

Adjusting Equation (10) with the RAM formulation needs the following variables changes,

\( \mu_i = \lambda \gamma_1; \quad \mu = \lambda \gamma \) and \( \lambda \ll 1 \)

Thus, we can write \( H_i(t) \) in the form,

\[ H_i(t) = \frac{\dot{q}^2}{2m} + \frac{1}{2} m\omega^2_0 \dot{q}^2 + \lambda \left( \gamma \hbar \omega_0 \dot{q}^3 + \gamma \hbar \omega_0 \sin(vt) \dot{q} \right) \] (11)

Introduction of the creation and annihilation operators \( a^+ \) and \( a \) of the unperturbed Hamiltonian [15] allows to write \( H'(t) \) given in Equation (1) as,

\[ H'(t) = \frac{\hbar \omega_0}{\sqrt{2}} \left[ \gamma \left( a^{+3} + a^3 + 3a^+a^3 + 3(a^+a+1)a \right) + \gamma (a^{+3} + a^3) \sin(vt) \right] \] (12)

The RAM applied to the interaction picture form of \( H_i(t) \) (Equations ((4), (7))) gives

\[ \Pi_j(t) = 0 \] (13)

\[ \hat{H}_j(t) = \frac{i\gamma \hbar}{\sqrt{2}} \left[ e^{i\omega_0 t} a^{+3} + e^{-i\omega_0 t} a^3 - 9e^{i\omega_0 t} a^+a^3 + 9e^{-i\omega_0 t} (a^+a+1)a \right] 
+ \frac{\gamma \hbar \omega_0}{\sqrt{2}} \left( \alpha^+_0(t)e^{i\omega_0 t} + \alpha_0(t)e^{-i\omega_0 t} \right) \] (14)

where
\[
\alpha_0(t) = -\frac{\nu \cos(\nu t) + i\nu_b \sin(\nu t)}{\nu^2 - \omega_0^2}
\]  
\[\alpha_0^*(t)\] being the complex conjugate of \[\alpha_0(t)\]

From Equation (8), we obtain the evolution operator to the first ameliorated order such as

\[
(1a)U(t) = \left[1 + \frac{\mu}{\sqrt{2}} \left(-a'^3 + a'^3 - 9a'a'a' + 9(a'a + 1)a\right)\right] e^{-i\mu t/\hbar}
\]

By comparison with the formulation of Equation (2), we deduce the first ameliorate order Floquet operators \((R, T(t))\), such as:

\[
(1a)R = \hbar \alpha_b \left(a' + \frac{1}{2}\right)
\]

\[
(1a)T(t) = 1 + \frac{\mu}{\sqrt{2}} \left(-a'^3 + a'^3 - 9a'a'a' + 9(a'a + 1)a\right) e^{-i\mu t/\hbar}
\]

Thus, the quasi-energies, Floquet states and wave functions developed to the first order respectively are:

\[
(1a)E_n = \hbar \omega_b \left(n + \frac{1}{2}\right)
\]

\[
(1a)\psi_n(t) = e^{-i\mu t/\hbar} \left[ c_{-3} |n-3\rangle + c_{-1} |n-1\rangle + c_{+1} |n+1\rangle + c_{+3} |n+3\rangle \right]
\]

\[
(1a)\psi_n(q,t) = e^{-i\mu t/\hbar} \left[ c_{-3}\phi_{-3}(q) + c_{-1}\phi_{-1}(q) + c_{+1}\phi_{+1}(q) + c_{+3}\phi_{+3}(q) \right]
\]

where the coefficients \(c_{-3}\) and \(c_{+3}\) are given by

\[
c_{-3} = \frac{\mu}{2\sqrt{2}} \sqrt{n(n-1)(n-2)}
\]

\[
c_{-1} = \left[ \frac{3\mu}{2\sqrt{2}} n - i \frac{\mu\omega_b}{\sqrt{2}} \alpha_0(t) \right] \sqrt{n}
\]

\[
c_{+1} = -\left[ \frac{3\mu}{2\sqrt{2}} (n+1) + i \frac{\mu\omega_b}{\sqrt{2}} \alpha_0^*(t) \right] \sqrt{n+1}
\]

\[
c_{+3} = -\frac{\mu}{2\sqrt{2}} \sqrt{(n+1)(n+2)(n+3)}
\]

and

\[
\phi_n(q) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha q^2}{2}} H_n(\sqrt{\alpha} q)
\]

\(\phi_n(q)\) is the wave function of the simple oscillator, the parameter \(\alpha = \frac{m\omega_b}{h}\)
and \( H_{r} \left( \sqrt{2a}q \right) \) are the Hermite polynomials.

Using Equation (9) and with the help of Equations ((13), (14)) one can write the second ameliorated order evolution operator and deduce the Floquet operators \((^{(2a)}R_{1})\) in the following form

\[
(^{(2a)}R_{1}) = H_{0} - \mu_{5}^{2} \frac{15\hbar\omega_{0}}{4} \left( (a^{*}a)^{2} + a^{*}a + \frac{11}{30} \right) + \frac{\mu_{5}^{2}\hbar\omega_{0}}{4} (\nu^{2} - \omega_{0}^{2})
\]  

(23)

Thus, the quasi-energies of the system up to second ameliorated order is given by

\[
(^{(2a)}E_{n}) = \hbar\omega_{0} \left( n + \frac{1}{2} \right) \mu_{5}^{2} \frac{15\hbar\omega_{0}}{4} \left( n^{2} + n + \frac{11}{30} \right) + \frac{\mu_{5}^{2}\hbar\omega_{0}}{4} (\nu^{2} - \omega_{0}^{2})
\]  

(24)

We note that the correction effects on the quasi-energies to second order approximation, and the Floquet shift levels depend on the amplitudes \((\mu_{5}, \mu)\) of the perturbations and the quantum number \(n\).

### 3.2. Driven Quatric Anharmonic Oscillator

We consider the system which Hamiltonian is given by,

\[
H_{z}(t) = \frac{p^{2}}{2m} + \frac{1}{2} m\omega_{0}^{2} q^{2} + \mu_{5}\hbar\omega_{0} q^{4} + \mu\hbar\omega_{0} \sin(\nu t) \dot{q}
\]  

(25)

where 

\( \mu_{5}\hbar\omega_{0} q^{4} \) and \( \mu\hbar\omega_{0} \sin(\nu t) \dot{q} \) are the quatric anharmonic perturbation with amplitude \(\mu_{5}\) and the external time-dependent perturbation with amplitude \(\mu\) respectively.

We operate the change variable \(\mu_{5} = \lambda\gamma_{z} \) and \(\mu = \lambda\gamma\) on Equation (25), then we have,

\[
H_{*}(t) = \frac{p^{2}}{2m} + \frac{1}{2} m\omega_{0}^{2} q^{2} + \lambda \left( \gamma_{z} \hbar\omega_{0} q^{4} + \gamma \hbar\omega_{0} \sin(\nu t) \dot{q} \right)
\]  

(26)

Using the usual creation and annihilation operators yields to write \(H'(t)\) in Equation (1) as

\[
H'(t) = \gamma_{z} \hbar\omega_{0} \left[ a^{4} + a^{2} + 4a^{*}aa^{2} - 2a^{*}a + 4 \left( a^{*}a + 1 \right) a^{2} + 2a^{2}
\right.
\]

\[
+ 3 \left( a^{*}a \right)^{2} + 3 \left( a^{*}a + 1 \right)^{2} \left. \right] + \frac{\hbar\omega_{0}}{2} \left( a^{*}a \right) \sin(\nu t)
\]  

(27)

The RAM applied to the interaction picture form of \(H_{z}(t)\) (Equations ((4), (7))), gives

\[
\bar{H}_{1}(t) = 3 \gamma_{z} \hbar\omega_{0} \left( 2a^{*}a \right)^{2} + 2a^{*}a + 1
\]  

(28)

\[
\bar{H}_{1}(t) = \gamma_{z} \frac{\hbar}{16} \left[ -e^{-4i\omega_{0}a} + 2a^{2} - 4e^{2i\omega_{0}a} \left( 2a^{*}a - 1 \right) a^{2}
\right.
\]

\[
+ 4e^{-2i\omega_{0}a} \left( 2a^{*}a + 3a^{2} \right) \left. \right] + \frac{\hbar\omega_{0}}{\sqrt{2}} \left( \alpha_{7}^{*}(t)e^{i\omega_{0}a} + \alpha_{7}(t)e^{-i\omega_{0}a} \right)
\]  

(29)
where \( \alpha_0(t) \) is given by Equation (15).

Following the previous procedure given in the subsection 3.1, we obtain the time evolution operator, then the quasi-energies and Floquet states to the first ameliorated order, for this system, respectively such as,

\[
(1a)U_2(t) = \left[ 1 - \frac{i \lambda}{\hbar} \left[ \gamma_2 \frac{i \hbar}{16} \left[ -a^4 + a^3 - 4 (2a' a - 1)a^2 + 4 (2a' a + 3)a^2 \right] \right. \right.
\]
\[
+ \frac{\hbar \omega_b}{\sqrt{2}} \left( \alpha_0^*(t) a^* + \alpha_0(t) a \right) \left. \right] \right]
\]
\[
\times \exp \left( -i t \left[ \frac{3}{4} \mu_\omega \omega_b \left( 2 \left( a' a \right)^2 + 2a' a + 1 \right) + H_0 \right] \right) \]
\]
\[
(1a)E_n = \hbar \omega_b \left( n + \frac{1}{2} \right) + \frac{3}{4} \mu_\omega \omega_b \left( 2n^2 + 2n + 1 \right)
\]
\[
(1b)\psi_n(t) = e^{\frac{1}{\hbar} \int_{t_0}^{t} \omega(t') \, dt'} \left[ k_{-4} |n-4\rangle + k_{-3} |n-2\rangle + k_{-1} |n-1\rangle \right.
\]
\[
+ |n\rangle + k_{1} |n+1\rangle + k_{2} |n+2\rangle + k_{4} |n+4\rangle \right]
\]

where

\[
k_{-4} = \frac{\mu_\omega}{16} \sqrt{n(n-1)(n-2)(n-3)}
\]
\[
k_{-3} = \frac{\mu_\omega}{4} \sqrt{2(n-1) \sqrt{n}}
\]
\[
k_{-1} = -i \frac{\mu_\omega \omega_b}{\sqrt{2}} \alpha_0(t) \sqrt{n}
\]
\[
k_{1} = -i \frac{\mu_\omega \omega_b}{\sqrt{2}} \alpha_0^*(t) \sqrt{n+1}
\]
\[
k_{2} = -\frac{\mu_\omega}{4} \sqrt{2(n+3) \sqrt{n+1}(n+2)}
\]
\[
k_{4} = -\frac{\mu_\omega}{16} \sqrt{(n+1)(n+2)(n+3)(n+4)}
\]

Application of the RAM Equation (9) to second ameliorated order, gives the expressions of the Floquet operator and quasi-energies respectively, such as:

\[
(2a)R_2 = \hbar \omega_b \left( a^* a + \frac{1}{2} \right) + \mu_\omega^2 \frac{3}{4} \hbar \omega_b \left( 2 \left( a' a \right)^2 + 2a' a + 1 \right)
\]
\[
- \mu_\omega^2 \frac{\hbar \omega_b}{8} \left( 34 \left( a' a \right)^3 + 51 \left( a' a \right)^2 + 59a' a + 21 \right) + \frac{\mu_\omega^4 \omega_b^3}{4 (v^2 - w_0^2)}
\]
\[
(2a)E_n = \hbar \omega_b \left( n + \frac{1}{2} \right) + \mu_\omega^2 \frac{3}{4} \hbar \omega_b \left( 2n^2 + 2n + 1 \right)
\]
\[
- \mu_\omega^2 \frac{\hbar \omega_b}{8} \left( 34n^3 + 51n^2 + 59n + 21 \right) + \frac{\mu_\omega^4 \omega_b^3}{4 (v^2 - w_0^2)}
\]

We note that the correction on quasi-energies of this system exist to first and second orders, and the Floquet shift levels depends on the parameters \( (\mu_\omega, \mu) \)
and the quantum number \( n \), which means that these energies levels are not equidistants.

We also note that in the absence of the cubic and quartic anharmonic perturbations (\( \mu_1 = \mu_2 = 0 \)) we find the Floquet states and quasi-energies of the simple forced harmonic oscillator [15].

### 3.3. Morse Potential Expansion

The Morse potential \( V(q) \), is the agreed model for diatomic molecules and is given by [6] [7],

\[
V(q) = D_e \left( 1 - e^{-\rho q} \right)^2
\]

(36)

where \( \rho \) is a parameter that controls the width of attraction (or measure the curvature at the bottom of the well), \( D_e \) is a parameter that controls the depth of the attracting well (or the depth of potential well), and \( q \) is the variation of interatomic distance with respect to the equilibrium distance.

Let us consider the Taylor development of exponential term in \( V(q) \) to forth order, and collecting terms in this development gives,

\[
V(q) = D_e \rho^3 q^3 - D_e \rho^4 q^4 + \frac{7}{12} D_e \rho^4 q^4
\]

(37)

Then we make the following changes to the notations:

\[
\omega_0 = \rho \sqrt{\frac{2D_e}{m}}
\]

(38a)

\[
\mu_1 = -D_e \rho^3 \sqrt{\frac{h}{m \omega_0}}
\]

(38b)

\[
\mu_2 = \frac{7}{12} D_e \rho^4 \frac{h}{m^2 \omega_0^2}
\]

(38c)

where \( \omega_0 \) is the vibrational constant with the reduced mass \( m \) of the diatomic molecule.

With the help of Equations ((36), (37)), we obtain the similar situation given, by the cubic together with quartic anharmonic oscillator, in the absence of the time dependent perturbation (\( \mu = 0 \)), for which the Hamiltonian is given by,

\[
H_5(t) = \frac{p^2}{2m} + D_e \rho^3 q^3 - D_e \rho^4 q^4 + \frac{7}{12} D_e \rho^4 q^4
\]

(39)

Using Equations (24) and (35), one can obtain the full quasi-energy to second order as:

\[
\begin{align*}
^{(2a)}E_n &= \hbar \omega_0 \left( n + \frac{1}{2} \right) + \frac{7}{16} \frac{D_e \rho^4 h^2}{m^2 \omega_0^2} \left( 2n^2 + 2n + 1 \right) \\
&\quad - \frac{7}{16} \frac{D_e \rho^4 h^2}{m^2 \omega_0^2} \left( n^2 + n + \frac{11}{30} \right) \\
&\quad - \frac{49}{1152} \frac{D_e \rho^4 h^3}{m^2 \omega_0^3} \left( 34n^3 + 51n^2 + 59n + 21 \right)
\end{align*}
\]

(40)
The difference between two adjacent Floquet levels for the cubic and quatic anharmonic oscillators are given by,

$$
\Delta E = (2a)E_{n+1} - (2a)E_n
$$

$$
= \hbar \omega \left[ 1 + 3 \mu E (n+1) - \mu_1 \frac{15}{2} (n+1) - \mu_2 \frac{51}{4} \left( (n+1)^2 + \frac{7}{17} \right) \right] \quad \text{(41)}
$$

We note that when $n$ increases $\Delta E$ decreases, until becoming equal to zero when the energy level reached the dissociation energy of diatomic molecular system, then the quantum number takes the maximum value $n_{max}$.

4. Comparisons and Numerical Evaluations

In the previous paragraphs we have developed calculations to first and second orders, and presented a number of results of the quantum anharmonic oscillator (Floquet states, quasi-energies). Table 1 compares our results with the works, of some other published works that used perturbation theory method.

The coefficients $A(n)$, $B(n)$, $C(n)$, $D(n)$, $E(n)$, $F(n)$, $G(n)$, $H(n)$, $A^{(2)}(n)$, $B^{(1)}(n)$ and $B^{(2)}(n)$, are given by Equation (15) in page (77) of the reference [5].

We observe in Table 1 that our first order states of the anharmonic (cubic and quatic) oscillator are similar to those obtained by the application of the stationary perturbation theory given in the work of Wang et al. [5]. We also note that our quasi-energy expression to second order for the anharmonic oscillator agreed with those obtained by Wang et al. [5] for this system.

We express $(2a)E_n$ of the Equation (40) as a function of $\left( n + \frac{1}{2} \right)$ and since the experimental data show that the terms in $\left( n + \frac{1}{2} \right)^3$ are negligible [6], we obtain

$$
(2a)E_n \approx \hbar \rho \left[ \frac{2D}{m} \left( 1 - \frac{3283}{18432} \right) (n+\frac{1}{2})^2 - \frac{\hbar^2 \rho^2}{2m} \left( n + \frac{1}{2} \right)^2 \right] \quad \text{(42)}
$$

Table 1. Comparison of our energy and quantum states with those of Wang et al.

|                         | Our method                        | Wang et al. [5]                       |
|-------------------------|-----------------------------------|---------------------------------------|
| The states $|\psi_n(\tau)|$ | $|\psi_n(\tau)| = e^{-\frac{\hbar \omega}{4} \left[ k \omega (n-4) + c_1 (n-3) + k_2 (n-2) + c_4 n - k_1 n + 2 \right]} \left[ a \omega (n-1) + A(n) n - D(n) + B(n) n + 1 \right] + C(n) n - 2 + D(n) n + 2 + E(n) n - 3 + F(n) n + 3 + G(n) n - 4 + H(n) n + 4$ |
| (2a)E_n = \hbar \omega \left[ n + \frac{1}{2} \right] + \mu \frac{3}{4} \hbar \omega (2n^2 + 2n + 1) | $E_n = \hbar \omega \left[ n + \frac{1}{2} \right] \left[ \frac{\alpha}{\hbar \omega} \right]^2 A^{(2)} + \frac{\beta}{\hbar \omega} B^{(1)} + \frac{\beta}{\hbar \omega} B^{(2)}$ |
| Quasi-energies        | $- \mu_1 \frac{15 \hbar \omega}{4} \left( n^2 + n + \frac{11}{30} \right)$ | $- \mu_2 \frac{\hbar \omega}{8} \left( 34n^2 + 51n^2 + 59n + 21 \right)$ |

Notations: $m \rightarrow m'$, $\mu = 0$, $\mu_1 = \frac{\alpha}{\hbar \omega}$, $\mu_2 = \frac{\beta}{\hbar \omega}$, $\hat{z} = \frac{z}{L}$.
Table 2. Spectra parameters corresponding to (HCl) and (CO) molecules.

| Molecule | $D_e$ (eV) | $m$ (amu) | $\rho$ (m$^{-1}$) |
|----------|------------|----------|------------------|
| HCl [17] | 4.61907    | 0.9801045 | $1.86769967 \times 10^{10}$ |
| CO [17]  | 11.2256    | 6.8606719 | $2.29939732 \times 10^{10}$ |

Table 3. Maximum quantum numbers, theoretical dissociation energy and dissociation energy with respect to the zero point level corresponding to (HCl) and (CO) molecules.

| Molecule | $n_{\text{max}}$ | $D_e^\text{th}$ (eV) | $E_e$ (eV) | $D_e$ (eV) |
|----------|------------------|----------------------|------------|------------|
| HCl      | 24               | 4.6126               | 0.1835     | 4.4291     |
| CO       | 83               | 11.2244              | 0.1341     | 11.0903    |

Let us consider the values of the parameters corresponding of (HCl) and (CO) diatomic molecules given in Table 2.

The derivative of Equation (42) with respect to $n$ and setting it equal to zero gives the vibrational level associated with the dissociation limit $n_{\text{max}}$, which allowed us to find the values of the theoretical dissociation energy corresponding to the equilibrium point ($D_e^\text{th}$) and the dissociation energy with respect to the zero-point level ($D_e = D_e^\text{th} - E_e$) which are given in Table 3.

5. Conclusions

The Floquet theory is one of the most useful tools which provides an alternative way for solving the Schrödinger equation of quantum systems with time-periodic Hamiltonian. In this paper, this approach was applied to driven quantum anharmonic oscillators. We have given the Floquet operators, solutions of the Schrödinger evolution equation, with the help of the RAM applied to first and to second ameliorated orders approximation and then we have calculated the Floquet states and the corresponding quasi-energies as well as the wave functions. Indeed, the approach used in our study determined, in a natural way, the explicit expressions for the time-dependent states of the anharmonic potential systems. It can be noticed that when we switch off the time-perturbation, we obtain the conservative energies of the cubic and the quartic anharmonic potential, and that the energy levels spacing decrease with increasing values of $n$ and allows us to estimate the dissociation energy of the molecule.

The comparisons of our expressions with published works by other authors, which have used different methods [1] [2] [5] revealed a good concordance, and the numerical evaluation carried out for the values of the parameters of (HCl) and (CO) diatomic molecules, illustrated clearly our results. This approach can be a useful tool to solve the Schrödinger equation of other types of driven time-dependent quantum systems. Therefore, it can be applied to investigate transitions between excited states and evaluate the dissociation energy of diatomic and polyatomic molecules. The goal of future work will be the application of the established approach to the driven Mathieu oscillator.
Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix

\( H(t) \): Time-dependent Hamiltonian.
\( H_0 \): Unperturbed Hamiltonian.
\( H'(t) \): Interaction Hamiltonian.
\( \lambda \): Amplitude of the perturbation.
\( h \): Reduced Planck’s constant.
\( \phi_n(t) \): Eigenstates of the operator \( R \).
\( E_n \): Eigenvalues of \( R \) (Quasi-energies).
\( n \): States of the unperturbed system.
\( \psi_n(t) \): Floquet states.
\( \langle 2^aU(t) \rangle \): Second order ameliorated evolution operator.
\( p \): Impulsion operator.
\( q \): Position operator.
\( m \): Mass of the system
\( \omega_0 \): Unperturbed oscillator frequency.
\( \mu \): Amplitude of the cubic anharmonic oscillator.
\( \mu' \): Amplitude of the time-dependent perturbation.
\( \nu \): Frequency of the time-dependent perturbation.
\( a \): Annihilation operator.
\( a^+ \): Creation operator.
\( \mu_2 \): Amplitude of the quartic anharmonic oscillator.
\( D_e \): Depth of potential well.
\( \rho \): Parameter that controls the width of attraction.
\( D_e^t \): Theoretical dissociation energy corresponding to the equilibrium point.
\( E_0 \): Zero-point energy \((n = 0)\).
\( D_0 \): Dissociation energy with respect to the zero-point level.