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Adiabatic perturbation theory for atoms and molecules in the low-frequency regime

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There is an increasing interest in the photoinduced dynamics in the low frequency, ω, regime. The multiphoton absorptions by molecules in strong laser fields depend on the polarization of the laser and on the molecular structure. The unique properties of the interaction of atoms and molecules with lasers in the low-frequency regime imply new concepts and directions in strong-field light-matter interactions. Here we represent a perturbational approach for the calculations of the quasi-energy spectrum in the low-frequency regime, which avoids the construction of the Floquet operator with extremely large number of Floquet channels. The zero-order Hamiltonian in our perturbational approach is the adiabatic Hamiltonian where the atoms/molecules are exposed to a dc electric field rather than to ac-field. This is in the spirit of the first step in the Corkum three-step model. The second-order perturbation correction terms are obtained when $i\hbar\omega\frac{\partial}{\partial\tau}$ serves as a perturbation and τ is a dimensionless variable. The second-order adiabatic perturbation scheme is found to be an excellent approach for calculating the ac-field Floquet solutions in our test case studies of a simple one-dimensional time-periodic model Hamiltonian. It is straightforward to implement the perturbation approach presented here for calculating atomic and molecular energy shifts (positions) due to the interaction with low-frequency ac-fields using high-level electronic structure methods. This is enabled since standard quantum chemistry packages allow the calculations of atomic and molecular energy shifts due to the interaction with dc-fields. In addition to the shift of the energy positions, the energy widths (inverse lifetimes) can be obtained at the same level of theory. These energy shifts are functions of the laser parameters (low frequency, intensity, and polarization). *Published by AIP Publishing.*
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MOTIVATION AND INTRODUCTION

The possibility to create extremely short pulses, using high-order harmonics created by a low-frequency driving field, has stimulated studies of photoinduced dynamics in the low-frequency regime. Using low-frequency driver lasers for high-order harmonic generation (HHG) is attractive because the cutoff limit scales as one over the laser frequency squared. In 1994, Lewenstein *et al.*[1] published an analytic and fully quantum theory of HHG by low-frequency laser fields, opening the way for various studies on the topic. For example, there are studies on attosecond pulse emission by elliptically polarized low-frequency laser fields[2] as well as studies on the efficiency of the high harmonics that is reduced with the increasing of the wavelength.[3]

When long laser pulses of monochromatic radiation are used as the driving laser field to produce the high harmonics, only odd harmonics are produced. The obtained spectrum is comb-like, and it is not sufficient for producing isolated attosecond pulses. To produce an isolated short pulse, one needs to extend the plateau and to generate a denser spectrum. One of the methods is irradiation with short few-cycle femto-second pulses in the visible range. The problem with this method is the difficulty in producing driver pulses as these. Another method is using a bichromatic laser. Mauritsson *et al.*[4] showed in 2006 that combining a laser field with its second harmonic densifies the spectrum and also even harmonics are produced. Further studies were carried for different combinations of frequencies.[5,6] Fleischer and Moiseyev[7] showed that for the bichromatic case of $(\omega, \omega + \delta\omega)$, where $\delta\omega \ll \omega$, much longer irradiance pulses can be used to produce attosecond pulses, which simplifies the experimental setup.

There is a difficulty to solve the photoinduced dynamics in the low-frequency regime. When the frequency is taken to the low limit, $\omega \to 0$, the period, T, becomes extremely large. When trying to solve the dynamics using different propagation schemes, one needs to use a growing number of propagations steps. The calculations become heavy and troublesome. This also introduces numerical errors. In most of the propagation schemes, when the number of time steps is increased, the density of the grid must be increased as well. When using another approach and trying to solve the low-frequency problem using the Floquet method, one encounters a problem again: When ω is small, the Floquet states are nested together. This means that H_F needed for results accurate enough becomes very large, making the calculation laborious and difficult.

In order to overcome this difficulty, we propose the use of a perturbation theory with the adiabatic Hamiltonian, where time serves as an instantaneous parameter, used as a zero-order Hamiltonian.

Corkum[8,9] and Kulander and Schafer and Krause[10] showed that the three-step model (TSM) provides a classical interpretation of the HHG from atoms in strong laser fields without solving the time-dependent Schrödinger equation. Later Lewenstein *et al.* generalized the TSM to describe the interaction of arbitrary one-electron potentials with laser fields of arbitrary ellipticity and spectrum.[1] The adiabatic hypothesis is based on a comparison between the (estimated) tunneling time (the first step in the TSM) with the period of the laser field. For sufficiently low laser frequencies, the tunneling time is smaller than the periodic time of the oscillating electric field, $T = 2\pi/\omega$. The photoinduced dynamics can be described by the Floquet solutions which are eigenstates of the Floquet operator $\hat{H}^{ad}(t) - i\hbar\partial_t$. It is natural to apply perturbation theory where $\hat{H}^{ad}(t)$ is the zero-order Hamiltonian and $-i\hbar\partial_t$ is taken as a perturbation. By making a simple transformation to dimensionless time units $\tau = \omega t$, ω is obtained as the perturbational strength parameter. This approach was first demonstrated by Pont *et al.*[11]

In order to keep the adiabatic functions and energies as the leading dominant terms in the perturbation expansion of the Floquet eigenstates and eigenvalues, ω has to be a small parameter. For large values of ω, one should calculate the high-order terms in perturbation theory. Calculating the metastable photoionization states (so called resonances) using out-going boundary conditions (as used by Gamow to calculate the tunneling decay rates for radioactive reactions) enables one to use the standard time-independent perturbation theory. Moreover, the use of one of the complex scaling transformations is found to be most helpful even when the tunneling resonances are very narrow and can be considered as bound states in the continuum (see, for example, Chap. 5 in Ref. 12). In such a case, the use of one of the complex scaling transformations enables to isolate the bound states in the continuum, which are exponentially localized in the interaction region from the delocalized continuum states.

In this paper, the numerically exact quasi-energies (QE's) of a toy model were calculated for different frequencies using the (t,t′)-Floquet method. As a Padé approximant was calculated for them and expanded into Taylor series at $\omega = 0$, it appears that the leading term in the Taylor expansion in the low-frequency regime is the $\sim\omega^2$ term. This gives a motivation to study the system using perturbation theory second-order corrections.

The strategy of our paper is as follows: First we will briefly explain the use of the (t,t') method in the calculations of the numerically exact solutions of our "toy" model that illustrates the interaction of an atom with a high intensity ac-field in the low-frequency regime. We should emphasize here that the numerical calculations are carried out not only for illustration but also in order to confirm the validity of the expressions derived for the leading terms in the adiabatic perturbation theory where time is used as a parameter and $-i\hbar\partial_t$ as a perturbation. Second, we will show how, by applying the Schlessinger[13] approach to the Padé approximant to the numerically exact results for the quasi-energies as obtained by the (t,t') method, we can get the coefficients in the Taylor series expansion of the quasi-energies in ω when the maximum field amplitude is held fixed. In the section titled adiabatic perturbation theory for atoms and molecules in the low-frequency laser interaction regime, we represent the adiabatic perturbation theory that enables the calculations of quasi-energy narrow resonances from dc-field (Stark) resonances. In the last section, we conclude by emphasizing the ability of using the adiabatic perturbation theory for calculating the effect of the dc-field on the atomic or molecular spectrum to obtain the effect of low-frequency intense ac-field on the atomic/molecular spectrum.

(T,T′) METHOD

In our calculation, we used a toy model of a 1D effective model potential V(x), which crudely mimics a xenon atom and is given by

$$V(x) = -V_0 e^{-ax^2}, \tag{1}$$

where $V_0 = 0.63$ a.u. and $a = 0.1424\ \frac{1}{\text{a.u.}^2}$.

This potential has two bound states, with energies $E_0 = -0.4451$ a.u. and $E_1 = -0.1400$ a.u. This model has been used before for calculating the HHG spectra of xenon.[14] The atom interacts with a linearly polarized laser field $\varepsilon_0 x \sin(\omega t)$, where ω is the laser frequency. The calculations were carried for $\varepsilon_0 = 0.015$ a.u., which corresponds to a laser intensity of $I \simeq 7.9 \cdot 10^{12}\ \frac{\text{W}}{\text{cm}^2}$.

In the calculation of the eigenvalues of the full Floquet type Hamiltonian, we used complex scaling in spite of the fact that the resonances are very narrow. In this case, complex scaling is used not for calculating the lifetime but in order to isolate the bound states embedded in the continuum, which represent the dressed states of an atom that interacts with a strong laser field. Note that we are interested only in the real part of the energies. The imaginary part, which is proportional to the inverse of the lifetime of the state, is extremely small—numerically zero.

In order to calculate the numerically exact quasi-energies, we used the (t,t′) method, which is described in Ref. 15. The method is based on the use of Floquet operator in the extended Hilbert space for time-dependant Hamiltonians but avoiding the need to introduce the time ordering operator when integrating the time-dependant Schrödinger equation. The time variable t′ is used as a time coordinate in a generalized Hilbert space. This method applies not only for time-periodic Hamiltonians but also to the case of time-periodic boundary conditions. The method is usable also for short laser pulses, provided that the envelope of the pulse supports sufficiently large number of optical cycles (typically more than 15).[16] Thus, the great advantage of this method is enabling the use of computational techniques originally developed for time-independent Hamiltonians. See the results for the quasi-energies as obtained from the (t,t′) method presented in Fig. 1.

PADÉ APPROXIMANT

The well-known Padé approximant is the approximation of a function by a rational function of given order. The Padé approximant often gives a better approximation of the function than truncating its Taylor series, and it may still work where the Taylor series does not converge. One of the methods inspired by Padé is the Schlessinger point method.[13]

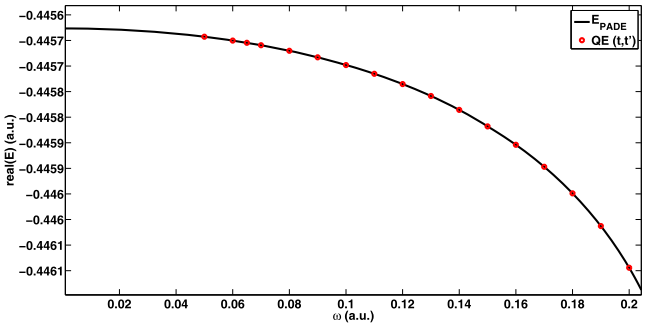

FIG. 1. Energies using Padé-Schlessinger point method: The real part of the energy as a function of the laser frequency ω (where $\omega \simeq 0.01$ a.u. is equivalent to $\lambda \simeq 4.56$ μm) calculated for $\varepsilon_0 = 0.015$ a.u., corresponding to a laser intensity of $I \simeq 7.9 \cdot 10^{12}$ $\frac{\mathrm{W}}{\mathrm{cm}^2}$. The red circles represent the exact quasi-energies (QE's). The black solid line represents the results from the Padé-Schlessinger point approximation calculated using 18 QE's from the (t,t′) calculation ($0.05 \le \omega \le 0.21$ a.u.).

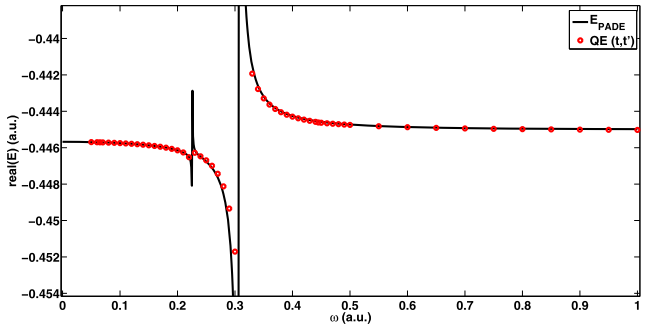

FIG. 2. Energies using Padé-Schlessinger point method. The real part of the energy as a function of the laser frequency ω ($\omega \simeq 0.01$ a.u. is equivalent to $\lambda \simeq 4.56$ μm) calculated for $\varepsilon_0 = 0.015$ a.u., corresponding to a laser intensity of $I \simeq 7.9 \cdot 10^{12}$ $\frac{\mathrm{W}}{\mathrm{cm}^2}$. The red circles represent the exact quasi-energies (QE's). The black solid line represents the results from the Padé-Schlessinger point approximation calculated using 18 QE's from the (t,t′) calculation ($0.05 \le \omega \le 0.21$ a.u.). Note the amazing agreement between the higher frequency QE points (those not used to create the Padé approximation) and the Padé approximation. This figure is the same as Fig. 1 but for a larger domain of frequencies.

The price we pay is that in order to use the Padé method, we need to calculate first the quasi-energies as function of the laser frequency, which is hard to do at the low-frequency regime.

The Padé approximant for the real part of the QE of the ground state in our model was calculated using the Schlessinger point method: In our calculations, it was calculated using 18 QE's from the (t,t′) calculation ($0.05 \le \omega \le 0.21$ a.u.). The real part of the Padé expression is given by

$$E_{Padé}(\omega) = \frac{\sum_{j=0}^{m} a_j \omega^j}{\sum_{k=0}^{n} b_k \omega^k} = \frac{a_0 + a_1\omega + a_2\omega^2 + \cdots + a_m\omega^m}{b_0 + b_1\omega + b_2\omega^2 + \cdots + b_n\omega^n}, \tag{2}$$

where the coefficients a_j and b_k are given in Table I.

The results of the Padé approximant are shown in Fig. 1. The red circles represent the real part of the numerically exact QE's. The black solid line represents the results from the Padé-Schlessinger point approximation. The Schlessinger point method enables analytically continuing the QE's calculated for higher frequencies down to the low-frequency field limit.

The beauty of the Padé approximation is clearly seen in Fig. 2 as the Padé approximation manages to find the points of singularity and bypass them. The higher frequency energies ($\omega > 0.21$ a.u.) calculated by the (t,t′) method have an amazing agreement with the energies predicted by the Padé approximation. There is a singularity at $\omega \approx 0.3$ a.u. which corresponds to the energy difference between the two states. This singularity is clearly seen from the Padé approximation graph. In addition, the Padé approximant manages to predict the discontinuity-like behaviour at $\omega \approx 0.22$ a.u., which raises from multiphoton effects.

TABLE I. Coefficients of the Padé approximant: The coefficients of the Padé approximant for the real part of the quasi-energies as a function of the laser frequency ω [See Eq. (2)]. The coefficients were obtained using the Schlessinger point method.

a_j	Value	b_k	Value
a_0	+0.000 000 246 069 95	b_0	−0.000 000 552 126 95
a_1	−0.000 011 598 22	b_1	+0.000 026 023 862
a_2	+0.000 223 669 11	b_2	−0.000 501 856 7
a_3	−0.002 220 116 4	b_3	+0.004 981 089 2
a_4	+0.011 296 681	b_4	−0.025 340 174
a_5	−0.019 618 022	b_5	+0.043 945 618
a_6	−0.067 292 28	b_6	+0.151 406 68
a_7	+0.354 285 96	b_7	−0.796 212 68
a_8	−0.444 928 28	b_8	+1.0
a_9	0	b_9	−0.000 292 557 6

The Padé expression can be expanded into Taylor series, $\sum_{n=0}^{\infty} \frac{E^{(n)}(\omega_0)}{n!}(\omega - \omega_0)^n$, by calculating the differentials. In this case, we get the following expression, when calculated for $\omega_0 = 0$ ($\hbar = 1$),

$$\begin{aligned} E(\omega) = &-0.445\,676\,53 + 0.000\,007\,14 \cdot \omega \\ &- 0.006\,523\,99 \cdot \omega^2 + 0.001\,921\,49 \cdot \omega^3 \\ &- 0.081\,325\,55 \cdot \omega^4 + 0.048\,939\,48 \cdot \omega^5 \cdots. \end{aligned} \tag{3}$$

It can clearly be seen that the odd coefficients are smaller than the even ones. For low frequencies, the most important

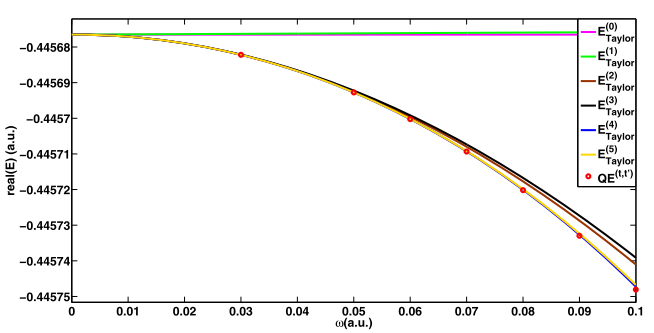

FIG. 3. Comparison between QE-obtained Taylor expansion to the Padé-Schlessinger point approximation: The real part of the energy as a function of the laser frequency ω (given here in atomic units where $\omega \simeq 0.01$ is equivalent to $\lambda \simeq 4.56$ μm) calculated for $\varepsilon_0 = 0.015$ a.u., corresponding to a laser intensity of $I \simeq 7.9 \cdot 10^{12}$ $\frac{\mathrm{W}}{\mathrm{cm}^2}$. The red circles represent the exact quasi-energies (QE's). The other graphs represent the Taylor series expansion to the Padé approximation, expanded at $\omega = 0$, up to the n-th degree—please see the legend on the side.

contribution comes from the second degree term, $E_{QE}^{(t,t')} \approx E^{(0)} + (\hbar\omega)^2 E^{(2)}$ (see Fig. 3). Note that here we use the Taylor series expansion based on the Padé calculations and not based on the results obtained from the adiabatic perturbation approach that will be presented in the section titled adiabatic perturbation theory for atoms and molecules in the low-frequency laser interaction regime.

ADIABATIC PERTURBATION THEORY FOR ATOMS AND MOLECULES IN THE LOW-FREQUENCY LASER INTERACTION REGIME

The Hamiltonian $H(t)$ stands for an atom or a molecule which interacts with a low-frequency laser field. The laser parameters are the frequency, ω, the intensity of the ac-field, I_0, and the polarization direction which is defined here as the x-coordinate. It is clear that for aligned molecules, the dipole transition matrix element, $d(\mathbf{R})$, depends on the polarization direction and also on the molecular structure. $d = \langle\phi_0|x|\phi_1\rangle$, where x is the polarization direction and ϕ_0 and ϕ_1 will be defined later in this section. For many electron systems, the dipole is given by $d = \langle\phi_0(\{x_j, y_j, z_j\}_{j=1,2,\ldots,N_e})|\sum_{j=1}^{N_e} x_j|\phi_1(\{x_j, y_j, z_j\}_{j=1,2,\ldots,N_e})\rangle$. For the sake of simplicity, in our derivations, we define here the laser parameter $\varepsilon_0 = \sqrt{I_0}d(\mathbf{R})$.

If the laser pulse is sufficiently long, the photoinduced dynamics of the atom/molecule-laser system can be described by the solutions of the Floquet operator $\hat{H}(t) - i\hbar\partial_t$. We use a perturbational approach and define $\hat{H}(t)$ as the zero-order Hamiltonian and $-i\hbar\partial_t$ as the perturbation.

The quasi-energy solutions of the time-dependent Schrödinger equation with time-periodic Hamiltonian, $H(t) = H(t+T)$, where $T = 2\pi/\omega$, (the so-called Floquet solutions) are given by

$$\Psi(x,t) = e^{-iEt/\hbar}\psi(x,t), \tag{4}$$

where $\psi(x,t) = \psi(x, t+T)$. The phase factor, E, and the time-periodic function $\psi(x,t)$ are correspondingly the eigenvalues and eigenfunctions of the Floquet operator,

$$(-i\hbar\frac{\partial}{\partial t} + H(t))\psi(x,t) = E\psi(x,t). \tag{5}$$

The adiabatic solutions are the eigenvalues and eigenfunctions of $H(t)$ where time is considered as a parameter and not as a dynamical variable as in Eq. (5),

$$H(t)\phi_j(x,t) = E_j(t)\phi_j(x,t). \tag{6}$$

The index $j = 0, 1, \ldots$ is associated with the quantization of the adiabatic Hamiltonian $H(t)$. The quantized electric field is associated with infinite number of photons since the electric field is classical. $n = 0$ is taken as a reference of infinite number of photons and $n = \pm1, \pm2, \ldots$ is associated with emission or absorption of photons due to the interaction of the laser with the atomic/molecular system. That is,

$$-i\hbar\frac{\partial}{\partial t}e^{i\omega nt} = \hbar\omega n e^{i\omega nt}. \tag{7}$$

Therefore, the zero-order states are taken as

$$\psi_{j,n}^{(0)}(x,t) = e^{i\omega nt}\phi_j(x,t) \tag{8}$$

and assign two good quantum numbers (j, n). The ground state is given by

$$\psi_{0,0}^{(0)} = \phi_0(x,t). \tag{9}$$

We define the first exited state with $n = 0$ and $j = 1$,

$$\psi_{1,0}^{(0)} = \phi_1(x,t). \tag{10}$$

According to perturbation theory,

$$E_0^{(0)} = \frac{1}{T}\int_0^T E_0(t)dt. \tag{11}$$

By making a simple transformation to dimensionless time units $\tau = \omega t$, ω is obtained as the perturbational strength parameter. Thus, $dt = \frac{d\tau}{\omega}$. From now on, we consider τ and ω to be two independent variables in spite that in the original Hamiltonian $\tau = t\omega$. Consequently, when the perturbation parameter, ω, is set to zero, then the zero-order Hamiltonian becomes the exact one. The zero-order term of the energy is given by

$$E_0^{(0)} = \frac{1}{2\pi}\int_0^{2\pi} E_0(\tau)d\tau. \tag{12}$$

The first-order term is given by

$$E_0^{(1)} = \frac{1}{T}\int_0^T (\phi_0(t)| - \frac{\hbar}{i}\frac{\partial}{\partial t}|\phi_0(t))dt \tag{13}$$

$$= \frac{1}{T}\int_0^T (-\frac{\hbar}{i}\frac{\partial}{\partial t})\frac{1}{2}(\phi_0|\phi_0)dt \tag{14}$$

$$= \frac{1}{T}\int_0^T 0dt \tag{15}$$

$$= 0, \tag{16}$$

where "(|)" stands for c-product. For similar reasons, every odd correction term will be zero.

The second-order correction term is given by

$$E_0^{(2)} = -\frac{\hbar^2}{T}\int_0^T \frac{(\phi_0(x,t)|\frac{\partial}{\partial t}|\phi_1(x,t))(\phi_1(x,t)|\frac{\partial}{\partial t}|\phi_0(x,t))}{E_1(t) - E_0(t)}dt \tag{17}$$

and since $\frac{\partial}{\partial t} = \omega\frac{\partial}{\partial\tau}$,

$$E_0^{(2)} = -\frac{\hbar^2\omega^2}{2\pi} \times \int_0^{2\pi} \frac{(\phi_0(x,\tau)|\frac{\partial}{\partial\tau}|\phi_1(x,\tau))(\phi_1(x,\tau)|\frac{\partial}{\partial\tau}|\phi_0(x,\tau))}{E_1(\tau) - E_0(\tau)}d\tau. \tag{18}$$

In the case of interaction with a linearly polarized laser field $\varepsilon_0 x\sin(\tau)$, using the complex Hellman-Feynman theorem as derived in Ref. 17, we get

$$E_0^{(2)} = -\frac{\hbar^2\omega^2}{2\pi}\int_0^{2\pi} \frac{(\phi_0|x\varepsilon_0\cos\tau|\phi_1)^2}{(E_1(\tau) - E_0(\tau))^3}d\tau \tag{19}$$

(notice that ε_0 is the maximal field amplitude and $E_j^{(0)}$ are the adiabatic eigenvalues).

The results, carried for $\varepsilon_0 = 0.015$ a.u., are shown in Fig. 4. The red circles represent the exact QE's. The black dashed line represents the zero-order QE's, calculated by using the perturbation theory. It is clear that as we approach the low frequencies, the "exact" energies approach the zero-order approximation. The blue solid line represents the QE obtained

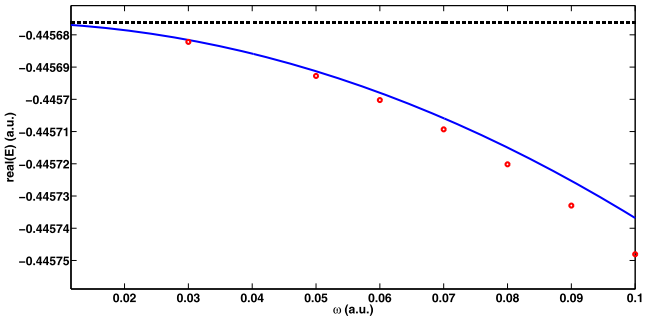

FIG. 4. Comparison between QE obtained by the (t,t′) method and the perturbation theory: The real part of the energy as a function of the laser frequency ω (given here in atomic units where $\omega \simeq 0.01$ a.u. is equivalent to $\lambda \simeq 4.56$ μm) calculated for $\varepsilon_0 = 0.015$ a.u., corresponding to a laser intensity of $I \simeq 7.9 \cdot 10^{12}\ \frac{\mathrm{W}}{\mathrm{cm}^2}$. The red circles represent the exact quasi-energies (QE's). The black dashed line represents the zero-order QE's, calculated by using the perturbation theory. It can be clearly seen that as we approach the low frequencies, the "exact" energies approach the zero-order approximation. The blue solid line represents the QE obtained by adding the second-order term.

by adding the second-order term. There is good agreement between the QE's calculated by the perturbation theory up to second order and the numerically exact QE's calculated using the (t,t′) method. The advantage of the perturbation theory is that it can be applied also for real systems, where calculating the QE's in another way would be numerically hard.

DISCUSSION AND CONCLUSIONS

The growing interest in low-frequency photoinduced dynamics encourages developing ways to calculate the energies of a given system for given laser frequency, ω. The second-order adiabatic perturbational method we propose enables the calculation of the QE of a system for a required frequency. The results are found to be in excellent agreement with energies calculated by other methods, such as the (t,t′) method. Using the (t,t′) method in the low-frequency limit becomes hard as many Floquet channels are nested together and involved in the dynamics of the system. The perturbational approach does not have this difficulty. Another essential advantage of this second-order perturbational approach is in the ability to use the standard quantum chemistry packages for calculating the effect of low-frequency ac-field on the atomic and molecular spectrum based on molecular calculation under dc-field.

The quantum chemistry packages provide the excited energy levels and the corresponding eigenfunctions. Due to the use of finite number of basis functions, the continuum spectrum is discrete, and narrow resonances (long lived metastable states) are described in standard quantum chemistry packages (such as Q-Chem) as bound states in the continuum. In such a case, the adiabatic approach presented in our paper is applicable, and ϕ_0, ϕ_1, E_0, and E_1 can be calculated by using the quantum chemistry packages without the need to use the complex scaling transformation as we used in our illustrative numerical study. Since uniform complex scaling can be applied to atoms interacting with static fields, the calculation of atomic dc-resonance positions and widths (inverse lifetimes) using the analytical continuation to the complex energy plane of the real energies, obtained by the quantum chemistry packages, by Padé is possible. In a very similar way, one can use Padé approximation to carry out the analytical continuation of the real corresponding eigenfunctions, obtained from the quantum chemistry packages, to the complex plane. This possibility has not been tried yet but should be doable. In particular, it seems doable since this approach for calculating the ϕ_0 and ϕ_1 functions is equivalent to the use of complex basis functions. Due to the fact that in some quantum chemistry packages the use of complex Gaussian basis functions is possible already, the resonance positions, widths, and corresponding eigenfunctions can be already calculated by the use of these packages. For example, resonance positions and widths were calculated for atoms in dc-field in Ref. 18 by using the Q-Chem package. The calculations of molecular ac-field induced resonances are not straightforward due to the non-analytical dilation property of the electron-nuclei potential energy terms (see discussion in Ref. 12). However, by using the stabilization approach, one can calculate the effect of dc-field on the spectrum of atomic and molecular systems similar to calculations of the energy of metastable molecular autoionization states [see, for example, the calculations of the energy curve of $He(^3 2s)$–H_2 using standard quantum chemistry package[19]]. The next step of the calculations involves the adiabatic second-order perturbation approach. Namely, the energy and wavefunctions for atoms and molecules in dc-field, as obtained from the stabilization graphs, are used in the calculations of energy shifts (position) by ac-field in the low-frequency regime. Moreover, the width (inverse lifetime) can be obtained using standard quantum chemistry packages nowadays, for example, via removing the artificial effects of complex absorbing potentials (CAPs), developed in Refs. 20 and 21, and using the analytical continuation via the Padé approach for calculating molecular resonances from stabilization graphs. Therefore, the strong intensity low-frequency ac-field effect on the atomic and molecular energy spectrum can be calculated while the dynamical electronic correlations are taken into consideration.

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