Role of Many-Electron Dynamics in High Harmonic Generation

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High harmonic generation (HHG) in many-electron atoms is studied theoretically. The breakdown of the frozen-core single active electron approximation is demonstrated, as it predicts roughly the same radiation amplitude in all noble gases. This is in contradiction with experiments, where heavier noble gases are known to emit much stronger HHG radiation than lighter ones. This experimental behavior of the noble gases can be qualitatively reproduced when many-electron dynamics, within a simple approximation, is taken into account.

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The first high harmonic generation (HHG) experiment was reported in 1987 [1]: gas atoms placed in an intense laser field were observed to emit coherent radiation in high-order harmonics of the laser frequency. Theoretical studies of the phenomenon followed shortly [2–8]. Common to the vast majority of the theories is the single active electron (SAE) approximation. References [2,5,7] represent frozen-core Hartree-Fock approaches. Numerical studies with one-dimensional model potentials [3] and analytical studies with a delta-function potential [4] belong to the same category. The widely accepted three-step model (TSM) [6] is another example of a SAE theory.

The SAE approximation is often motivated by the fact that in many HHG experimental situations predominantly only one electron is ionized during the process. However, this does not necessarily mean that the dynamics of the other electrons plays no role. In fact, the SAE approximation has no real justification in the HHG literature. Studies of HHG that go beyond the SAE approximation [8] are scarce due to the complexity of the problem.

SAE descriptions of HHG, often approximated by the TSM, have been successful explaining various features of HHG. Examples are the spectral cutoff formula [6], the phase structure of the spectrum [9], and the prediction [10] of attosecond pulses, which were later demonstrated and characterized [11]. However, there is one extremely prominent feature in HHG which, to the best of our knowledge, remains unexplained: the scaling of the HHG radiation intensity with the atomic number.

It seems to be common knowledge among HHG experimentalists that heavier noble gases emit stronger HHG radiation than lighter ones [12], the differences reaching a few orders of magnitude. Even though this behavior can be in part due to propagation effects, it is likely that there is a major contribution due to the single-atom response, since the behavior was sustained even in quasi-phase-matched experiments [13], and absorption generally becomes only stronger in heavier noble gases.

This behavior of the noble gases has been theoretically addressed in only a few studies. An example is Ref. [5], which employs an effective-potential SAE approach. Heavier noble gases are found to have stronger HHG intensities *when placed in the same laser field*. However, this effect can be attributed to the difference in ionization potentials. In contrast, experimentally the effect is observed even when the laser field intensity is matched to the medium to reach similar ionization rates [12], thus eliminating effects due to the differences in the latter.

The main conclusion of this Letter connects the question of the validity of the SAE approximation with the experimentally observed higher HHG intensities in heavier noble gases: first, we show that the SAE approximation predicts similar HHG emission in all noble gases. Hence, we may conclude that many-electron effects must be taken into account in the description of HHG. Second, we make a first attempt to provide a description of HHG that includes, within a simple approximation, many-electron effects and qualitatively reproduces the experimental trend mentioned above.

Let H_0 be the Hamiltonian of a many-electron atom with the atomic number Z (atomic units are adopted throughout the Letter):

$$H_0 = \sum_{j=1}^{Z}\left(\frac{\mathbf{p}_j^2}{2} - \frac{Z}{r_j}\right) + \sum_{j>k}\frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}. \tag{1}$$

The atom is placed in a linearly polarized laser field. The field is denoted by $E(t)$ and the direction of polarization is chosen to be x. The time-dependent Hamiltonian of the system is given by

$$H(t) = H_0 - E(t)\sum_{j=1}^{Z} x_j. \tag{2}$$

The amplitude of the HHG radiation can be found by computing the expectation value of the dipole moment

$$\langle x\rangle = \langle \Psi(t)|\sum_{j=1}^{Z} x_j|\Psi(t)\rangle \tag{3}$$

and then treating $\langle x\rangle$ as a classical dipole source. $|\Psi(t)\rangle$ is the time-dependent wave function of the many-electron atom, which solves the time-dependent Schrödinger equation $i|\dot{\Psi}(t)\rangle = H(t)|\Psi(t)\rangle$.

Finding $|\Psi(t)\rangle$ exactly is impossible, and an approximation is required. We assume, as explained in the introduction, that only one (the "active") electron is ionized during the HHG process and the others remain bound. At this point it is common [2–5] to adopt an effective-potential model, where the Hamiltonian of the active electron is written as

$$\tilde{H}(t) = H_1 - xE(t), \qquad H_1 \equiv \frac{\mathbf{p}^2}{2} + V. \tag{4}$$

V is the effective potential, which may be a central-field potential such as the Hartree-Slater potential [14]. [See, e.g., Ref. [5] for other possible choices.] The state vector $|\psi(t)\rangle$ of the active electron then satisfies

$$i|\dot{\psi}(t)\rangle = \tilde{H}(t)|\psi(t)\rangle, \tag{5}$$

and the time-dependent expectation value of the dipole moment is given by

$$\langle x\rangle = \langle \psi(t)|x|\psi(t)\rangle. \tag{6}$$

Central to this model is the fact that all electrons apart from one are kept frozen, and that the contribution of only one electron to the emitted radiation is calculated.

We argue that the model defined by Eqs. (4)–(6) typically gives similar HHG intensities for all noble gases for common experimental parameters [12]. $|\psi(t)\rangle$ may be written as a superposition of the most weakly bound orbital $|\varphi_0\rangle$ occupied in the ground state and the orbital $|\chi(t)\rangle$ describing the excited electron ($|\chi(t)\rangle$ is a superposition of eigenstates of H_1 that are energetically higher than $|\varphi_0\rangle$). Then it follows from Eq. (6) that the HHG emission is determined by the dipole matrix element between $|\varphi_0\rangle$ and $|\chi(t)\rangle$, times $\langle\varphi_0|\psi(t)\rangle$. The valence orbitals of all noble gases are of similar size. In matched field amplitude (MFA) conditions, that is, if the laser field amplitude is matched to each noble gas such that the respective Stark ionization rates are similar, the corresponding $|\chi(t)\rangle$ (and $\langle\varphi_0|\psi(t)\rangle$) are similar as well. This is true at least for momenta relevant to contemporary HHG experiments, which can hardly resolve the atomic core. One therefore expects that the model defined by Eqs. (4)–(6) does not account for orders-of-magnitude differences observed in experiments.

In order to substantiate the conclusions of the above discussion, we adopt a particular effective potential, namely, the Hartree-Slater [14] potential $V_{\mathrm{HS}}(\mathbf{r})$. With this potential, the binding energies and photoionization cross sections of the noble gases can be fairly well reproduced [15].

In the limit of a small Keldysh parameter, the HHG spectra obtained from the model described by Eqs. (4)–(6) are well approximated by the TSM [16,17]. For MFA, the amplitude of the HHG spectrum is determined by the TSM recombination amplitude. The latter is best evaluated in the acceleration form [16], and is given by $\langle\varphi_0| - \partial_x V|\mathbf{k}\rangle$, where $|\mathbf{k}\rangle$ is a momentum eigenstate. Since $|\varphi_0\rangle$ is technically an excited eigenstate of the Hamiltonian H_1 (excluding helium), the lower-lying eigenstates are kept unpopulated during the evolution, and the TSM is improved when the lower-lying states are projected out of $|\mathbf{k}\rangle$ [17]. This leads to a recombination amplitude given by

$$a_{\mathrm{rec}}(\mathbf{k}) = -\langle\varphi_0|\partial_x V|\mathbf{k}\rangle + \sum_j \langle\varphi_0|\partial_x V|\varphi_j\rangle\langle\varphi_j|\mathbf{k}\rangle. \tag{7}$$

The sum runs over all eigenstates $|\varphi_j\rangle$ of H_1 lying energetically below $|\varphi_0\rangle$.

$a_{\mathrm{rec}}(\mathbf{k})$ for the five lightest noble gases is displayed in Fig. 1. One can see that in the energy range where HHG experiments are done, $a_{\mathrm{rec}}(\mathbf{k})$ is of very similar magnitude for all noble gases. Therefore, for MFA, the model defined by Eqs. (4)–(6) gives similar spectral intensity in all noble gases. This statement is verified by extensive direct numerical calculations with Eqs. (4)–(6), which will appear elsewhere [18].

The finding that SAE models of the type defined by Eqs. (4)–(6) are orders of magnitude away from describing the scaling of the HHG intensity with the atomic number suggests that many-electron effects can play a crucial role in the HHG process. In what follows, we attempt to construct a model of HHG which goes beyond the standard SAE approximation and takes into account, within an approximation, the dynamics of many electrons during the HHG process.

If for the moment we ignore spin, which is taken into account later on, the single-electron wave function $|\psi\rangle$ in Eq. (5) can be given the meaning of being a part of an approximate many-electron wave function of the Hartree form

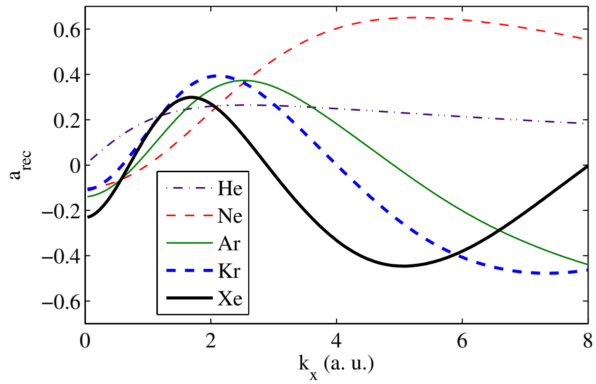

FIG. 1 (color online). $a_{\mathrm{rec}}(k_x)$ [Eq. (7)] for different noble gases.

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_Z, t) = \varphi_1(\mathbf{r}_1) \cdots \varphi_{Z-1}(\mathbf{r}_{Z-1}) \psi(\mathbf{r}_Z, t). \quad (8)$$

The potential V in Eq. (4) then represents the electrostatic potential generated by the $Z-1$ inner electrons, whose wave functions are frozen in time. Equation (3) then turns into Eq. (6).

However, one can use the wave function (8) differently: one can compute the second time derivative of Eq. (3) employing the Ehrenfest theorem with the exact Hamiltonian (2). The result is

$$\langle \ddot{x} \rangle = -Z \langle \Psi(t) | \sum_{j=1}^{Z} \frac{x_j}{r_j^3} | \Psi(t) \rangle + Z E(t). \quad (9)$$

Note that the electron-electron interaction term does not contribute.

If Ψ is the exact solution of the many-electron time-dependent Schrödinger equation, evaluating Eq. (9) gives the same result as differentiating Eq. (3) twice in time. However, for the approximate wave function (8) the results will be different. Using Eq. (8), Eq. (9) becomes

$$\langle \ddot{x} \rangle = -Z \langle \psi(t) | \frac{x}{r^3} | \psi(t) \rangle, \quad (10)$$

where the last term $[ZE(t)]$ in Eq. (9) has been dropped, as it does not contribute to the HHG spectrum. Because of the Z prefactor in Eq. (10), even if ψ is now obtained solving Eq. (5), it is now not surprising to obtain enhanced HHG emission for heavier noble gases compared to lighter ones.

In what follows, we study the HHG spectra produced with Eq. (10) and show that they reproduce the experimental behavior of the noble gases much better than Eqs. (4)–(6). However, before we proceed, we discuss why it is that Eq. (10) is more suitable than Eq. (6) for describing HHG in many-electron atoms.

First, if we had to select between an approximation for $\langle x \rangle$ and an approximation for $\langle \ddot{x} \rangle$, for calculating HHG the latter would be the natural choice. This is because the high frequency composition is much more pronounced in $\langle \ddot{x} \rangle$ than in $\langle x \rangle$. For a $|\psi\rangle$ that satisfies Eq. (5), differentiating Eq. (6) twice gives $\langle \psi | -\partial_x V | \psi \rangle$ rather than Eq. (10) [omitting $E(t)$ again]. While Eqs. (10) and (6) are evaluated with the same approximate wave function, only the dipole acceleration operator in Eq. (10) is exact, as it is obtained from the exact Hamiltonian (1).

The second argument in favor of Eq. (10) is based on the TSM. We begin with a classical argument. According to the TSM, an electron is pulled out of the atom by the laser field, accelerated by it, and after the field reverses its direction the electron recollides with the parent ion. The radiation is emitted due to the acceleration of the electron in the field of the cation (i.e., the nucleus of charge Z screened by $Z-1$ electrons of charge unity). Consider now a bound electron in its equilibrium position that repels the recolliding electron, screening thereby part of the nuclear charge. Exactly the same force is exerted by the recolliding electron on the bound one, causing the same acceleration and thus additional radiation in the same amount. The emitted radiation is thus enhanced by Z, as if one electron were moving in the potential of an unscreened nucleus. Said differently, the total body of charge composed of all electrons accelerates under the influence of the "external" nuclear force only. The internal electron-electron forces cancel out. This is why the electron-electron repulsion term is absent in Eq. (10).

Although this is a classical and rather simplistic picture, it is supported by quantum-mechanical many-body calculations of electron-ion collision processes. The emission due to the polarization of the target ion in response to the collision has been calculated in the context of bremsstrahlung [19,20] and recently in the context of recombination [21]. This mechanism has been termed "polarizational recombination" [21]. It was shown that the radiation emitted by all electrons can be approximately obtained by calculating the radiation from the recolliding electron only, but as if it were moving in a (usually not fully) descreened nuclear potential. On the other hand, using Eq. (6) is exactly equivalent to computing the acceleration in the fully screened potential V.

In order to illustrate the enhancement in the HHG emission in heavier noble gases obtained when Eq. (10) is used, we have computed HHG spectra for the four lightest noble gases with MFA. The many-electron wave function we construct goes one step beyond Eq. (8), taking spin into account. The equation of motion for the spatial orbital of the active electron is then systematically derived by a time-dependent configuration interaction singles (TDCIS) method, where the time-dependent wave function is restricted to spin-singlet conserving single-particle excitations of the ground-state determinant. A detailed derivation and discussion of this method will be given elsewhere [18], where it is also demonstrated that the TDCIS method better agrees with full many-body calculations than SAE calculations of the type defined by Eqs. (4)–(6). Here we only give a brief description of the method.

Our starting point is the expansion of $|\Psi(t)\rangle$ in terms of Slater determinants constructed from one-particle orbitals $|\varphi_j\rangle$ of a given one-particle Hamiltonian (H_1 with $V = V_{\mathrm{HS}}$ in this work). The initial state is the ground state, which is approximated by a single determinant. The expansion of $|\Psi(t)\rangle$ is restricted to single-particle excitations from the occupied orbitals. Here, we consider only excitations from the highest occupied p_x ($1s$ in He) orbital $|\varphi_0\rangle$. All other occupied orbitals are frozen. In contrast to other existing approaches, excitations preserve the spin-singlet symmetry of the system. TDCIS can be recast as an effective single-electron approach. Approximating $H(t)$ [Eq. (2)] by $\tilde{H}(t)$ [Eq. (4)] leads to the effective one-particle equation

$$\mathrm{i}\, |\dot{\psi}(t)\rangle = H_1 |\psi(t)\rangle - E(t)(\mathbb{1} - P + 2P_0) x |\psi(t)\rangle. \quad (11)$$

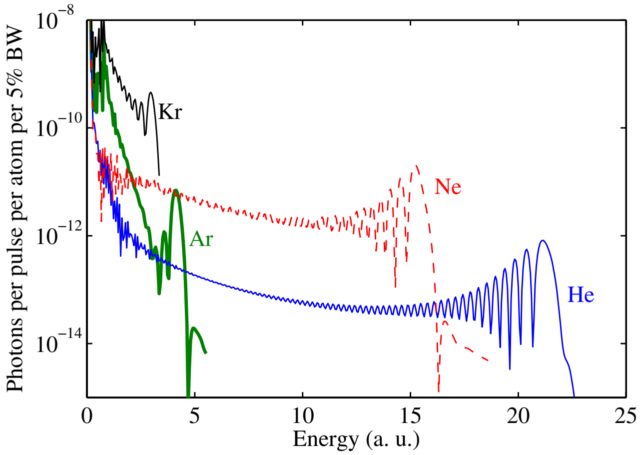

FIG. 2 (color online). HHG spectra in MFA conditions ($E_0 = 0.29, 0.245, 0.125, 0.1$ a.u. for He, Ne, Ar, and Kr, respectively) computed numerically using the TDCIS method.

The initial condition is $|\psi(0)\rangle = |\varphi_0\rangle$, $P_0 \equiv |\varphi_0\rangle\langle\varphi_0|$, and $P \equiv \sum_i |\varphi_i\rangle\langle\varphi_i|$, where the sum goes over all occupied orbitals of the ground-state determinant. Note that the evolution of the orbital $|\psi(t)\rangle$ is nonunitary. The norm of the many-body wave function constructed from $|\psi(t)\rangle$, however, is conserved. Expectation values of one-particle operators $\hat{D}$ can be expressed by means of the orbital $|\psi(t)\rangle$: $\langle\Psi(t)|\hat{D}|\Psi(t)\rangle = 2\langle\psi(t)|\hat{D}|\psi(t)\rangle$.

Figure 2 shows HHG spectra for MFA obtained numerically from the TDCIS method, with $\hat{D} = -Zx/r^3$ as in Eq. (10). The field amplitudes are given in the caption, and achieve equal static Stark ionization rates in all gases within 4%. The Stark ionization rates were calculated numerically from $V_{\rm HS}$ for each noble gas, using a suitably adapted version of the technique described in Ref. [22].

The general trend of stronger HHG yield in MFA conditions for heavier noble gases is clearly reproduced in Fig. 2. Yet, the results in Fig. 2 should not be interpreted as a quantitative prediction: they only indicate a trend. The calculations involve approximations and their validity needs further investigation. In particular, the role of electron correlation remains open.

In this work we have shown that frozen-core SAE models give similar HHG emission rates in all noble gases, which seems to significantly contradict the experiments. We have proposed a new approximation, which clearly goes beyond a frozen-core SAE model, and qualitatively agrees with experiments. The results are strongly suggestive of a crucial role that many-electron dynamics plays in determining the HHG emission rates in many-electron atoms.

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