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Nonperturbative time-dependent theory of helium in a strong laser field

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We present a nonperturbative theory of the behavior of He in a strong pulsed laser. We address the question of the validity of frozen-core or single-active-electron approximations by providing direct quantitative comparisons with calculations including the complete two-electron behavior with correlation. Our results are illustrated with examples of nonlinear susceptibilities and ionization.

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In a previous paper [1], we introduced a different method for the nonperturbative solution of the time-dependent (TD) Schrödinger equation governing the interaction of an atom with strong, pulsed radiation (lasers). In that paper, the potential and effectiveness of the method was tested in hydrogen with the promise that results on the application of the method to atoms beyond single-electron H would follow. This problem represents uncharted territory as far as the nonperturbative behavior is concerned. It is the purpose of this Rapid Communication to report our results on He, which come at a rather opportune time, in view of a recent paper by Pindzola, Griffin, and Bottcher [2], who raised and explored, even if only within the confines of a one-dimensional (1D) soft-core model, the question of the validity of TD methods when more than one electron is involved.

Two additional reasons make this paper particularly relevant at this time. First, Kulander [3] has performed TD calculations based on a single-active-electron (SAE) model of He, while recently we provided a theoretical interpretation [4] of an experiment at fairly high intensity (up to $\sim 5\times10^{14}$ W/cm^2) by Perry, Szoke, and Kulander [5] using a semiperturbative theory based also on a SAE model; although we did explore the effects of electron correlation on at least some aspects of the problem. These papers seem to suggest that even at high intensity He responds as if only one electron is excited and/or ionized. Traditional single-photon absorption [6], on the other hand, has taught us that correlation is very important in He. As we shall see below, these apparently contradictory aspects are perfectly reconcilable and their explanation provides a clue as to what to expect from other two-electron atoms. To provide the resolution of this paradox, however, we must solve nonperturbatively the complete 3D problem for the real He atom and compare the result with a frozen-core (FC) calculation (similar in spirit to Kulander's SAE model) within the same representation and solution of the TD problem. At the same time, this paper represents (to the best of our knowledge) the only completely nonperturbative solution of the TD Schrödinger equation for a two-electron atom.

The essential steps of the technique have been presented in Ref. [1], while a somewhat more detailed exposé is to appear in [7]. As a brief reminder and summary of the steps necessary for the problem at hand, we recall that we solve the equation

$$(\partial/\partial t)\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = -(i/\hbar)H(t)\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$$

subject to the initial condition $\Psi(\mathbf{r}_1,\mathbf{r}_2;0)=g(\mathbf{r}_1,\mathbf{r}_2)$, with g being the ground state of He. The TD Hamiltonian is $H(t)=H^0+V(t)$ where, within the dipole approximation, the interaction $V(t)$ is for a two-electron atom written as $V(t)=-e\boldsymbol{\epsilon}\cdot(\mathbf{r}_1+\mathbf{r}_2)E(t)\sin\omega t$, with $\boldsymbol{\epsilon}$ being the unit polarization vector of the radiation, ω its frequency, and $\mathbf{r}_1,\mathbf{r}_2$ the position operators of the two electrons. The time evolution of the amplitude $E(t)$ of the pulse is represented as $E(t)=Ef(t/\tau)$, where $f(t)=1/\cosh(t/\tau)$ or $e^{-(1/2)(t/\tau)^2}$, depending on which form corresponds more closely to the experimental conditions. We refer to τ as the width of the pulse, but the integration of the differential equations is carried out from $-T$ to $+T$, where $|T|\geq 2.5\tau$ so that the end result is insensitive to the further increase of $|T|$.

In analogy with the approach we presented in Ref. [1], generalized now to two active electrons, we construct a set of two-particle wave functions $\phi_{nLM}(\mathbf{r}_1,\mathbf{r}_2)$ which satisfy the Schrödinger equation

$$H^0\phi_{nLM}(\mathbf{r}_1,\mathbf{r}_2)=E_{nL}\phi_{nLM}(\mathbf{r}_1,\mathbf{r}_2)\,,$$

with the atomic Hamiltonian H^0 and the boundary conditions

$$\phi_{nLM}(0,0)=\phi_{nLM}(r_1^{\max},r_2)=\phi_{nLM}(r_1,r_2^{\max})=0\,,$$

and where n is an abbreviation for the pair n_1n_2 of the principal quantum numbers for the single-particle wave functions $\phi_{n_1l_1m_1}(\mathbf{r}_1)$ and $\phi_{n_2l_2m_2}(\mathbf{r}_2)$ which enter in the antisymmetrized, linear combinations of products in terms of which the two-particle wave functions are constructed. The single-particle wave functions are constructed in terms of B splines in the manner we have discussed elsewhere [1]. With the wave functions ϕ_{nLM} in hand, we write the TD wave function as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t)=\sum_{nLM} b_{nLM}(t)\phi_{nLM}(\mathbf{r}_1,\mathbf{r}_2)\,, \tag{1}$$

which upon substitution into the TD Schrödinger equation leads to a set of coupled linear differential equations for the coefficients b_{nLM}, which can be written in the form

$$i\frac{d}{dt}b_{nLM}(t)=\sum_{n'L'M'}(E_{nLM}\delta_{nn'}\delta_{LL'}\delta_{MM'}-\langle\phi_{nLM}|V(t)|\phi_{n'L'M'}\rangle)b_{n'L'M'}\,, \tag{2}$$

where the dipole form of $V(t)$ leads only to matrix elements of r between the single-particle functions ϕ_{nlm}. The results of this paper have been obtained with light linearly polarized which limits the summation over M' only to terms $M'=0$ due to the selection rule $M'=M$ and the fact that our initial (ground) state of He has $M=0$.

The probability of ionization after time t can be expressed as

$$P(t)=\sum_{nL(E\geq 0)}|b_{nL}(t)|^2\,, \tag{3}$$

where the summation is extended over all states of positive energy of a given basis set. A result for $P(t)$ is deemed converged when it becomes insensitive to the further increase of the size of the box (i.e., the value of $r^{\max}$), the number of basis functions per angular momentum, as well as the number of angular momenta. For each basis employed in a calculation, it is checked that a number of negative energy states match the experimentally known values of the respective excited states of the atom below the first ionization threshold, which lies at 24.58 eV above the ground state. The second threshold (at 78.98 eV above the ground state) corresponds to doubly ionized helium. Those states of a given basis whose (positive) energies lie between the two thresholds represent doubly excited configurations, as well as singly ionized states. The basis does, of course, extend well above the double-ionization threshold. By increasing the number of configurations (nl) entering in the linear combination expressing the state $|nLM\rangle$ we obtain a description that includes the correlation between the two electrons. Depending on the number of configurations included in a calculation, we refer to the result as simply CI (configuration interaction) or ECI (extended CI) as indicated in each case below. To give an idea of the size of our TD calculations, we note that CI results such as those shown later on have been obtained with a basis that includes 10 total angular momenta (L), 12 orbital angular momenta (l), and 300 states for each l.

In order to investigate the difference between a CI and a FC calculation, we change the basis in terms of which we expand the wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$ in Eq. (1). Otherwise, the TD calculation does not change. This is one of the advantages of implementing the TD calculation in terms of a basis set; another advantage being that one can follow rather conveniently the role of the underlying atomic structure on the atom-field interaction. A FC calculation is not uniquely defined, as it depends on the manner and the state in which one of the electrons is frozen. In fact, it may be desirable to freeze the electron in different states, depending on the problem at hand. Given that our objective is to describe multiphoton ionization, which implies that the excited atomic states may play a more or less significant role (depending on whether they may be or come in near resonance), the electron is frozen in the ionic $1s$ (with $Z=2$) state. This is what we mean by FC in this paper. In implementing the FC calculation, we construct a basis with one electron frozen as mentioned above, which means that all atomic states are calculated consistently within this basis, and then we employ this basis in the TD calculation. Thus the CI and FC calculations are performed with the same TD method, but each is cast in terms of a different L^2 basis set consistently calculated so as to represent adequately the atom.

The first concern in constructing a basis set is to reproduce with sufficient accuracy the known energy spectrum of the atom. A sample of results illustrating the level of accuracy we obtain is shown in Table I. Clearly, all three models do very well for the excited states. As expected, the ground state where correlation is most important requires the ECI calculation (with more than 1000 configurations) to obtain agreement through the second decimal. For the same reason, the $1s2s$ exhibits the same behavior to a lesser degree. Good values for the energies of the basis states are not sufficient to guarantee equally good values for the transition moments entering the TD calculation. Their accuracy must be tested separately. A sample of the level of accuracy, in the sense of how well the different models agree with each other, is shown in Table II, where in addition to numbers for the three models in the L^2 basis, we also show a column we have obtained through single-channel quantum-defect theory (QDT). Again, dipole moments involving the ground state are most sensitive to correlation. That is why the respective numbers corresponding to QDT are significantly different from those of the other models. It should be noted, on the other hand, that dipole moments involving only excited states are represented fairly well even by QDT. One of the reasons for showing QDT results next to the much more sophisticated CI numbers is to provide a calibration for the importance of configuration interaction (channel couplings) in the excited states. When single-channel QDT provides a reasonably accurate number, correlation is not very important; a point to which we return later on. The message emerging from Tables I and II

TABLE I. Energies (Ry) of a sample of representative states of He.

State	Expt.	ECI	CI	FC
$1s^2$	−5.807088	−5.802624	−5.769211	−5.745014
$1s2s$	−4.291909	−4.291531	−4.288411	−4.286899
$1s2p$	−4.247645	−4.247084	−4.246507	−4.244912
$1s3s$	−4.122528	−4.122426	−4.121584	−4.121146
$1s3d$	−4.111227	−4.111230	−4.111154	−4.111092
$1s3p$	−4.110276	−4.110086	−4.109915	−4.109483
$1s4s$	−4.067165	−4.067125	−4.066783	−4.066601
$1s4d$	−4.062552	−4.062552	−4.062520	−4.062489
$1s4f$	−4.062493	−4.062492	−4.062507	−4.062499
$1s4p$	−4.062131	−4.062048	−4.061976	−4.061797
$1s5s$	−4.042349	−4.042330	−4.042158	−4.042066
$1s5d$	−4.040027	−4.040027	−4.040011	−4.039994
$1s5p$	−4.039806	−4.039764	−4.039727	−4.039637
$1s5f$	−4.040011	−4.040010	−4.040004	−4.040000

is that the importance of correlation in calculating single-electron transitions in He is concentrated mostly in the ground state. It should not be too surprising, therefore, if the FC approximation gives a reasonable approximation to single-electron multiphoton transitions or even to a TD calculation at high intensity.

Now we present some examples of calculations of nonlinear (multiphoton) transitions perturbatively as well as nonperturbatively. The perturbative examples shown in Figs. 1(a) and 1(b) represent values for the nonlinear susceptibilities $\chi(3)$ and $\chi(5)$ for third- and fifth-harmonic generation over a range of photon frequencies. The calculation here involves the well-known partial summations over complete sets of intermediate states. As we have discussed elsewhere [8], an L^2 basis provides a convenient way of performing such summations quite accurately. The curves in Figs. 1(a) and 1(b) represent the results for both FC and CI, which agree to within the thickness of the line of the drawing. The range of values spanned by $\chi(3)$ and $\chi(5)$ are in good agreement with earlier calculations by Mizuno [9] and the experimental result at the Nd-YAG (where YAG denotes yttrium aluminum garnet) laser frequency [10].

As an example of TD calculation, we present in Fig. 2 the ionization probability as a function of photon frequency and at high intensity. The pronounced peak corresponds to the contribution to ionization through a resonance created by the state $1s2p$ shifted into multiphoton resonance sometime during the pulse. This behavior is reminiscent of a similar feature obtained in our earlier paper [1] on the TD theory of H. The position of the pronounced peak can be related to the shift of the state $1s2p$. From its position at 4×10^{14} W cm^2, we deduce a shift of about 1.31 eV, while we calculate 1.43 eV for the lowest-order perturbation theory (linear in laser intensity) value. Therefore, there is a small departure from the linear shift. The behavior of the $1s2p$ under these circumstances is not

TABLE II. Transition moments between representative states of He in a.u.

States	CI	FC	QDT	ECI
$1s^2$ to $1s2p$	0.4252	0.4336	0.2786	0.4192
$1s^2$ to $1s3p$	−0.2102	−0.2150	−0.1375	−0.2073
$1s^2$ to $1s4p$	−0.1322	−0.1354	−0.0864	−0.1304
$1s2s$ to $1s2p$	−2.944	−2.970	−2.905	−2.9242
$1s2s$ to $1s3p$	−0.945	−0.939	−0.9024	−0.9072
$1s2s$ to $1s4p$	−0.475	−0.473	−0.4571	−0.4601
$1s2p$ to $1s3d$	−2.521	−2.548	−2.494	−2.511
$1s2p$ to $1s4d$	−0.885	−0.889	−0.881	−0.884
$1s3p$ to $1s3d$	−5.168	−5.167	−5.172	−5.168
$1s3p$ to $1s4d$	−4.085	−4.133	−4.034	−4.064
$1s3d$ to $1s4f$	−5.179	−5.189	−5.163	
$1s4f$ to $1s5g$	−8.928	−8.930		

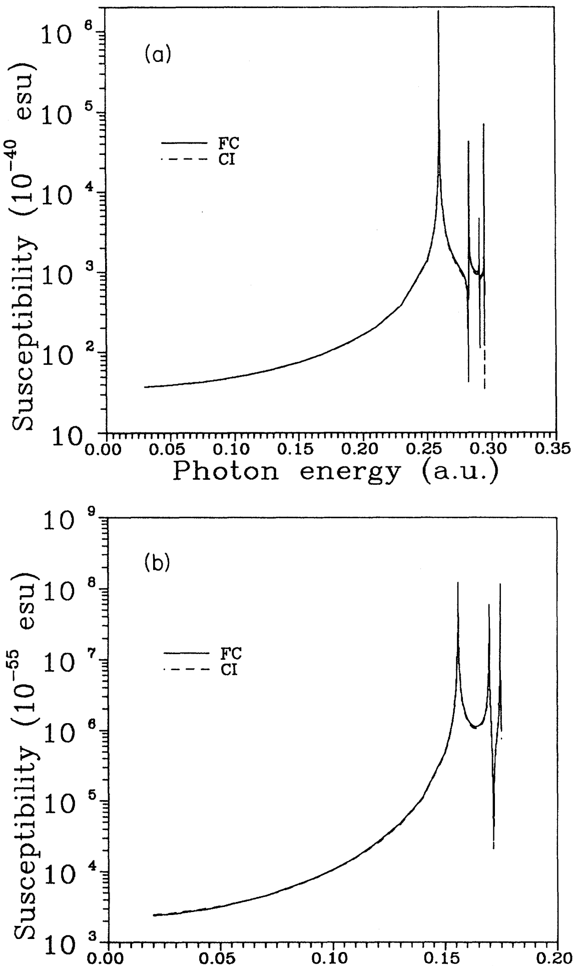

FIG. 1. Nonlinear susceptibilities $\chi(3)$ and $\chi(5)$ [(a) and (b), respectively] of He as a function of photon energy as given by FC and CI calculations. The peaks correspond to resonances with atomic bound states. Since FC and CI give somewhat different ground-state energies, we have shifted the FC results by that difference so as to provide a visually direct comparison of the susceptibilities.

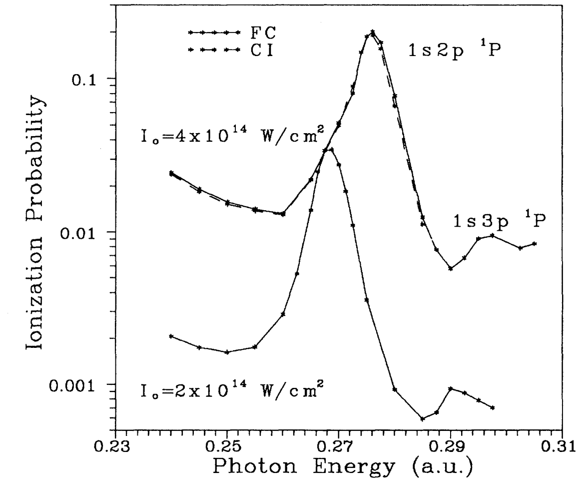

FIG. 2. Ionization probability for two different intensities as a function of photon energy at the end of a pulse with $\tau=10$ optical cycles integrated from -2.5τ to 2.5τ. The curves for FC have been shifted as in Fig. 1.

much different from that of the $2p$ in H reported in our earlier paper.

The different aspect here is the comparison between FC and CI. Again, as was the case with the susceptibilities, the agreement between FC and CI is within the thickness of the line of the drawing. We have thus demonstrated that, as long as correlation is included in the ground state, transitions in helium—from low to very high intensity (where total ionization occurs within a few cycles)—occur as if one electron is frozen in the ionic $1s$ state.

What are the conditions of validity of this picture and what does it say about the expected behavior of other two-electron atoms such as the alkaline earths? First of all, we should keep in mind that the photon frequencies employed in our examples here are considerably smaller than the energy of the first doubly excited state. This combined with the fact that the doubly excited states are energetically well separated from the singly excited ones (which entails the absence of perturbation in the spectrum of the Rydberg states) provides the basic physical justification for the success of the FC model. If we were to raise the photon energy, making it comparable to that of the doubly excited states, additional channels leading to double (electron) excitation and ionization will open. These processes cannot be described by any FC approximation and that represents one of the limits of validity of the FC model. Thus if we were to consider photons of about 28 eV, which would lead to two-photon excitation of states of the type $2s^2$ or $2p^2$, then a complete CI calculation including the autoionization widths of such states is necessary as we have discussed elsewhere [11].

Helium is a rather special two-electron atom, however, in that its doubly excited states are well separated from the first ionization threshold. The alkaline earths, on the other hand, have considerably different structure in that the doubly excited states begin very close to the first threshold, while for Ca, Sr, Ba, and Eu they begin well below the threshold, as a result of which the quantum defects of certain Rydberg series are seriously perturbed. We have already given examples [8] in perturbation theory (corroborated by experiment), showing that certain aspects of multiphoton absorption are then poorly described by FC approximations even if correlation is included in the ground state; correlation in the manifold of (even singly) excited states is then equally important. Note that one does not need a resonance with an excited state for this to be the case. Correlation plays its role through the summation over the manifold of the virtual intermediate states. On the basis of evidence that we have presented briefly elsewhere [12], we expect that TD nonperturbative calculations will exhibit much more severe CI effects on all aspects of strong-field transitions, even if one electron is ejected in the final state. We will report soon on this question.

In closing, we will venture a rule of thumb: If a multiphoton transition is described well by a FC approximation within perturbation theory, we expect the same to be true in the nonperturbative regime; with the usual exceptions that every good rule should possess.

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