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Effect of an improved molecular potential on strong-field tunneling ionization of molecules

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We study the effect of one-electron model potentials on the tunneling ionization rates of molecules in strong fields. By including electron correlation using the modified Leeuwen-Baerends (LB α) model, the binding energies of outer shells of molecules are significantly improved. However, we show that the tunneling ionization rates from the LB α do not differ much from the earlier calculations [Phys. Rev. A **81**, 033423 (2010)], in which the local correlation potential was neglected.

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The alignment-dependent ionization rate $P(\theta)$ for a molecule fixed in space is the first essential element for the understanding of molecules in strong laser fields. Despite its importance, there are few direct experimental measurements [1–5]. Thus in laser-molecule interactions, $P(\theta)$ is obtained entirely based on theoretical methods (θ is the angle between the molecular axis and the polarization direction of the laser's electric field). While in principle, ionization of a molecule in a strong laser field can be obtained by solving the time-dependent many-electron Schrödinger equation, such calculation is too large and the convergence is often difficult to evaluate. The multielectron effect of molecular ionization can be included partly within the framework of time-dependent density-functional theory (TDDFT) [6,7]. Since multielectron theories are very time-consuming, a single-active-electron (SAE) approximation is often used. Within SAE, one can obtain $P(\theta)$ by solving the time-dependent Schrödinger equation (TDSE) [8–10]. Even at this level of approximation, the calculation is still quite challenging. Thus, simpler models like the molecular strong field approximation (SFA) [11,12], or the molecular tunneling ionization theory (MO-ADK) [13] are quite desirable. In particular, the simple MO-ADK theory is of wide interest. According to MO-ADK [13], alignment-dependent ionization rates of each molecule can be obtained analytically once a few structure parameters for the molecule are obtained.

In MO-ADK theory, the ionization rate depends on the instantaneous electric field of the laser, the ionization potential, and structure parameters C_{lm} of the molecule. In Tong *et al.* [13], C_{lm} 's are expansion coefficients of the molecular electronic wave functions in the asymptotic region which can be expressed as

$$\psi^{(m)}(\mathbf{r}) = \sum_l C_{lm} r^{(Z_c/\kappa)-1} e^{-\kappa r} Y_{lm}(\theta, \varphi), \quad (1)$$

where Z_c and $Y_{lm}(\theta, \varphi)$ being the effective Coulomb charge and the spherical harmonics. Here, $\kappa = \sqrt{2I_p}$, and I_p is the ionization potential. These coefficients C_{lm} are originally extracted from molecular wave functions obtained from the multiple scattering theory [14]. Since molecular wave functions are more readily obtained these days using quantum chemistry packages such as GAMESS [15] or GAUSSIAN [16], it is desirable to obtain these parameters from such packages. Unfortunately, molecular wave functions from these chemistry packages do

not have the correct asymptotic behavior for the purpose of extracting accurate C_{lm} . Thus, accurate C_{lm} coefficients cannot be determined with molecular wave functions directly from the output of these codes [17,18]. In Zhao *et al.* [19], an iterative procedure was suggested to achieve accurate molecular wave function in the asymptotic region. The new C_{lm} 's have been shown to provide more accurate $P(\theta)$ for CO₂. The method has further been applied systematically to other linear molecules [20], including ionization from inner orbitals.

In order to calculate molecular wave functions with the correct asymptotic behavior, a one-electron model potential should be numerically created. The so-called LB94 potential, proposed by Leeuwen and Baerends [21], gives the proper asymptotic $-1/r$ behavior. In our previous works [19,20], we use a simplified version of LB94 potential (to be called “exchange-only” model in the following), in which the local correlation potential was neglected. The binding energies of atoms and molecules calculated within the LB94 model, however, often are not very accurate. The modified LB potential (called LB α) has been proposed [22] which is known to give more accurate binding energies of the occupied orbitals. In strong field physics, the LB α model has been used by Chu and collaborators in their TDDFT approach [23–25]. In this Brief Report, we obtain the one-electron molecular potential calculated using the LB α model and extract the new structure parameters C_{lm} to compare the MO-ADK rates with those from the exchange-only model [20].

Let us briefly describe how to construct one-electron model potential for linear molecules. Using a single-center expansion, the model potential can be expressed as

$$V(r, \theta) = \sum_{l=0}^{l_{\max}} v_l(r) P_l(\cos \theta). \quad (2)$$

Here, $v_l(r)$ is the radial component of the model potential and $P_l(\cos \theta)$ is the Legendre polynomial. The radial potential is given by

$$v_l(r) = v_l^{nuc}(r) + v_l^{el}(r) + v_l^{xc}(r), \quad (3)$$

where the first two terms represent the electrostatic potential (see Ref. [20]) and the last term is the exchange-correlation interaction.

In LB α , the partial exchange-correlation potential is written as

$$v_l^{xc}(r) = \frac{2l+1}{2} \int_{-1}^1 V_{xc,\sigma}^{\text{LB}\alpha}(r,\theta) P_l(\cos\theta) d(\cos\theta), \quad (4)$$

where

$$V_{xc,\sigma}^{\text{LB}\alpha}(r,\theta) = \alpha V_{xc,\sigma}^{\text{LDA}}(r,\theta) + V_{c,\sigma}^{\text{LDA}}(r,\theta) - \frac{\beta \chi_\sigma^2(r,\theta) \rho_\sigma^{1/3}(r,\theta)}{1 + 3\beta \chi_\sigma(r,\theta) \sinh^{-1}[\chi_\sigma(r,\theta)]}, \quad (5)$$

with $\chi_\sigma(r,\theta) = |\nabla \rho_\sigma(r,\theta)| \rho_\sigma^{-4/3}(r,\theta)$ and $\rho_\sigma(r,\theta)$ is spin density. Here $V_{xc,\sigma}^{\text{LDA}}(r,\theta)$ is the local density approximation (LDA) exchange potential,

$$V_{xc,\sigma}^{\text{LDA}}(r,\theta) = - \left[\frac{6}{\pi} \rho_\sigma(r,\theta) \right]^{1/3}. \quad (6)$$

We mention that the electron correlation term $V_{c,\sigma}^{\text{LDA}}(r,\theta)$ in Eq. (5) was neglected in the exchange-only model of Refs. [8,20]. In the present LB α calculations, we make $V_{c,\sigma}^{\text{LDA}}(r,\theta)$ the LDA correlation potential, and the Perdew-Wang representation is used for the correlation functionals [26],

$$V_{c,\sigma}^{\text{LDA}}(r,\theta) = \varepsilon_c(r_s, \zeta) - \frac{r_s}{3} \frac{\partial \varepsilon_c(r_s, \zeta)}{\partial r_s} - (\zeta - \text{sgn}\sigma) \frac{\partial \varepsilon_c(r_s, \zeta)}{\partial \zeta}, \quad (7)$$

with r_s and ζ being density parameter and relative spin polarization, respectively. $\varepsilon_c(r_s, \zeta)$ is the correlation energy. Parameters used in the correlation functionals are fitted beyond the random-phase approximation [26]. This potential is spin dependent. Note that $\text{sgn}\sigma$ is +1 for $\sigma = \uparrow$ and -1 for $\sigma = \downarrow$. We have checked that the neon exchange-correlation potential from our code agrees with the one given in Ref. [22].

Once the model potential is created, molecular wave functions can be obtained by solving the time-independent Schrödinger equation with basis functions consisting of B-spline functions. From the asymptotic wave function the structure parameters C_{lm} are extracted; see [19,20].

In Table I, ionization energies of three rare gas atoms with the present LB α model potential are compared to those of the exchange-only model [20] and with experimental values. It clearly shows that the results from the LB α model are more accurate than those from the exchange-only model [20]. The parameters $\alpha = 1.19$ and $\beta = 0.01$ [see Eq. (5)] are used in the present calculations.

TABLE I. Comparison of calculated ionization energies of rare gas atoms in the present LB α model, exchange-only model [20], and experimental values. Energies are in atomic units (a.u.).

Atom	LB α	Exchange only	I_p
He	0.815	0.786 ^a	0.904 ^b
Ne	0.793	0.722 ^a	0.793 ^b
Ar	0.592	0.524 ^a	0.579 ^b

^aReference [20].

^bReference [27].

TABLE II. Comparison of calculated binding energies of HOMO, HOMO-1, and HOMO-2 of N₂ and CO₂ in the present LB α model. Those from the exchange-only model [20] and experimental vertical ionization potential are also given. Energies are in eV. For HCl, only the energies of HOMO and HOMO-1 are considered.

Molecule	Spin orbital	LB α	Exchange only	I_p
N ₂	3 σ_g (HOMO)	15.5	15.0 ^a	15.6 ^b
	1 π_u (HOMO-1)	16.9	16.5 ^a	17.2 ^b
	2 σ_u (HOMO-2)	18.1	17.8 ^a	18.7 ^b
CO ₂	1 π_g (HOMO)	13.7	14.6 ^a	13.8 ^c
	1 π_u (HOMO-1)	17.5	18.3 ^a	17.6 ^c
	3 σ_u (HOMO-2)	15.9	16.8 ^a	18.1 ^c
HCl	2 π (HOMO)	12.8	11.4 ^a	12.8 ^d
	5 σ (HOMO-1)	16.4	15.0 ^a	16.3 ^d

^aReference [20].

^bReference [28].

^cReference [29].

^dReference [30].

In Table II, we compare the ionization energies of several occupied orbitals (such as HOMO, HOMO-1, and HOMO-2) for N₂, CO₂, and HCl, from the present calculations using LB α model potential, from the exchange-only model [20], and compare them to experimental vertical ionization energies. For N₂, the calculated ionization energies of HOMO, HOMO-1, and HOMO-2 using the LB α model agree well with experimental values within 0.6 electron volts (eV). For HOMO and HOMO-1 of CO₂ and HCl, the discrepancies between the present calculated and the experimental energies are within 0.1 eV. For HOMO-2 of CO₂, the error is larger than those of HOMO and HOMO-1. We mention that the same parameters $\alpha = 1.0$ and $\beta = 0.05$ are used in the exchange-only model for N₂, CO₂, and HCl [20]. For the present LB α calculations, we have used the parameters $\beta = 0.01$ and $\alpha = 1.12, 1.05,$ and 1.17 for N₂, CO₂, and HCl, respectively; see Eq. (5).

Since the one-electron molecular potentials obtained using the LB α model and the exchange-only model are different, the molecular wave functions will be different, thus resulting in different extracted structure parameters C_{lm} . How different are they? Using the methods employed in [19,20], the extracted C_{lm} parameters are shown in Table III, for the HOMO, HOMO-1, and HOMO-2 of N₂ and CO₂, and the HOMO and HOMO-1 of HCl. The comparison indicates that there are differences in the coefficients from the two different models. Careful examination shows that the relative magnitude of the coefficients is about the same, even though the actual values may differ somewhat. How much are the tunneling ionization rates modified because of the variations in the C_{lm} coefficients? Figure 1 shows the alignment-dependent ionization rates of HOMO, HOMO-1, and HOMO-2 for N₂, CO₂, and of HOMO and HOMO-1 for HCl. The solid lines are from the LB α model and the dashed lines are from the exchange-only model. The two sets of rates are normalized at the peak of the HOMO curve from the LB α model. The good agreement between the two sets of curves indicates that the relative tunneling ionization rates of different orbitals are the same using the exchange-only and LB α models. For each orbital, the alignment dependence of the ionization rates from both models also stays the same.

TABLE III. The newly fitted C_{lm} coefficients using the LB α potential versus values from earlier references [20,31] using the exchange-only model. $m = 0$ for σ orbital and $m = 1$ for π orbital.

Molecule	Spin orbital	C_{lm}				Ref.		
N ₂	$3\sigma_g$ (HOMO)	C_{0m}	C_{2m}	C_{4m}				
		3.39	1.40	0.05		[20]		
		2.68	1.10	0.06		[31]		
			C_{1m}	C_{3m}	C_{5m}			
	$1\pi_u$ (HOMO-1)	2.37	0.29	0.00		[20]		
	$2\sigma_u$ (HOMO-2)	4.49	0.39	0.01		[20]		
		3.72	0.34	0.01				
CO ₂	$1\pi_g$ (HOMO)	C_{2m}	C_{4m}	C_{6m}				
		1.74	0.33	0.03		[20]		
		1.97	0.40	0.04		[31]		
			C_{1m}	C_{3m}	C_{5m}	C_{7m}		
	$1\pi_u$ (HOMO-1)	3.12	1.16	0.15	0.01	[20]		
	$3\sigma_u$ (HOMO-2)	6.79	2.24	0.27	0.02	[20]		
		7.50	2.58	0.32	0.03	[20]		
HCl	2π (HOMO)	C_{1m}	C_{2m}	C_{3m}	C_{4m}	C_{5m}		
		1.57	0.01	0.07	0.01	0.01	[20]	
		1.23	0.01	0.05	0.01	0.01	[20]	
			C_{0m}	C_{1m}	C_{2m}	C_{3m}	C_{4m}	
	5σ (HOMO-1)	0.09	3.18	0.71	0.32	0.12	[20]	
			0.10	2.64	0.57	0.25	0.09	[20]

Note that the absolute tunneling rates are slightly different. In Fig. 1, the normalization factors $R(\text{LB } \alpha/\text{exchange-only})$ are 1.57, 0.76, and 1.61 for the three molecules, N₂, CO₂, and HCl, respectively. We comment that in calculating the tunneling ionization rates, experimental ionization energies are used for both models.

In conclusion, we investigate the sensitivity of molecular tunneling ionization rates on the one-electron model potentials used for several linear molecules. Using the potentials generated by the LB α versus the exchange-only model, we showed that the alignment dependence of tunneling ionization rates stays essentially the same. Thus, the structure coefficients derived using the exchange-only model for the calculations of MO-ADK rates reported in Ref. [20] do not need to be revised. The electron correlation [the $V_{c,\sigma}^{\text{LDA}}(r,\theta)$ term] partly included in the LB α model is important for improving the accuracy of binding energy; it has little effect on the tunneling ionization rates. This may be understood based on the fact that tunneling occurs at a large distance where an active electron approximation is relatively valid. As shown previously [20], ionization

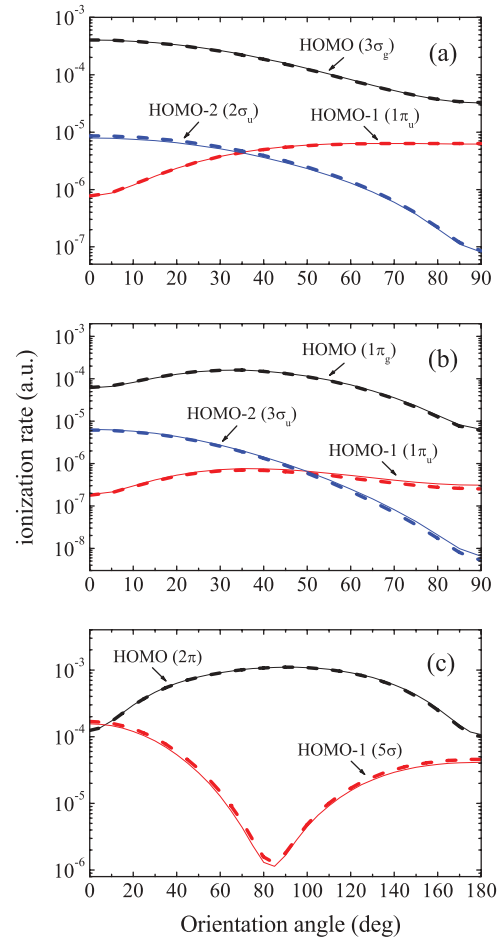


FIG. 1. (Color online) Alignment dependence of ionization rates. (a) N₂ at laser intensity of 1.5×10^{14} W/cm²; (b) CO₂ at 1.1×10^{14} W/cm²; (c) HCl at 1.4×10^{14} W/cm². Solid lines are from the LB α model and dashed lines from the exchange-only model.

rates calculated using the MO-ADK model reasonably agree with those from more elaborate theories. The simplicity the MO-ADK theory and the molecular structure calculations within the exchange-only model would make it possible to study strong field physics of polyatomic molecules.

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