Calculating the Keldysh adiabaticity parameter for atomic, diatomic, and polyatomic molecules

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A numerical model is presented to determine the Keldysh adiabaticity parameter for the interaction of an intense laser with a polyatomic molecule. The adiabaticity parameter is a guide to determining whether the ionization process is in the field or multiphoton ionization regime. The adiabaticity parameters are compared for potentials including the simple zero-range potential, the Coulomb potential, an atomic potential (Xe), a diatomic (N₂) molecular potential, and a polyatomic (C₆H₆) molecular potential. It is demonstrated that the Coulomb potential is approximately equal to the atomic and diatomic potentials and differs from the zero-range potential employed in the Keldysh model in a way which is predominantly dependent upon the ionization potential. Both simple models substantially overestimate the adiabaticity parameter for C₆H₆ at all field strengths and at fields above 1.25 V/Å both simple models become completely unphysical. This is because barrier suppression ionization is predicted to occur for benzene above 1.25 V/Å using the ab initio potential. This field for barrier suppression ionization is significantly lower than the 1.5 V/Å field predicted using the Coulomb model. © 1998 American Institute of Physics.

INTRODUCTION

The interaction of intense laser pulses with atomic and diatomic systems has generated considerable interest, in part because the electric field of the laser approaches the binding energy of the valence electrons. In the case of atomic systems models employing zero-range or Coulombic potentials have been shown to fit far-infrared photoionization experiments. For small molecules, e.g., H₂, H₂, H₃, and HCl, time-dependent quantum calculations have been performed and are in good agreement with experimental measurements. The interaction of intense pulses with larger polyatomic molecules has received less attention because of the increased complexity of the interaction and the substantial increase in accessible reaction channels. To develop some insight into the excitation mechanism in more complex polyatomic molecules we extend the Keldysh adiabaticity model by replacing the model zero-range potential with ab initio electrostatic potential energy surfaces.

The Keldysh adiabaticity parameter can be described by the ratio of the tunneling frequency to the laser frequency or equivalently by the square root of the ratio of the ionization potential to the ponderomotive potential of the laser pulse. In the original derivation the adiabaticity parameter was described by an electron tunneling through a barrier created by the electric field of the laser. The electric field is assumed to interact with a zero-range potential having a height equal to the binding energy of the electron; for atomic systems this energy is well approximated by the ionization potential (IP) of the atom. The length of the barrier through which the electron must tunnel is then given by

\[ t_{ZR} = \frac{IP}{eE_0}, \]  

where \( e \) is the charge of an electron and \( E_0 \) is the electric field strength of the laser pulse. The average kinetic energy of an electron is given by the virial theorem as IP and from this one can derive a simple expression for the electrons average velocity,

\[ \langle v \rangle = \left( \frac{2}{m_e} \right)^{1/2} IP^{1/2}, \]  

where \( m_e \) is the mass of an electron. Equations (1) and (2) can then be combined to determine the tunneling time or the tunneling frequency as given by

\[ t_{ZR} = \frac{1}{\langle v \rangle} = \frac{[IP_{m_e}]^{1/2}}{\sqrt{2eE_0}}, \]  

\[ v_{ZR} = \frac{1}{t_{ZR}} = \sqrt{2eE_0} \sqrt{[IP_{m_e}]^{1/2}}. \]  

Tunneling can occur if the mean tunneling time given by Eq. (3) is less than half the period of the laser. This leads to the definition of the Keldysh adiabaticity parameter which in fact may be defined by several equivalent expressions:

\[ \gamma = \frac{2v_0}{v_{ZR}} = \frac{l_{ZR}}{l_0} = v_0 \frac{\sqrt{2IP_{m_e}}}{eE_0}, \]  

where \( t_0 \) is the period of the laser, \( v_0 \) is the laser frequency, and \( l_0 \) is the mean distance which an electron travels during one half-period \((t_0/2)\) of the laser at a mean velocity of \( \langle v \rangle \).

The zero-range potential employed in the original Keldysh calculation provides a convenient analytical expression for calculating \( \gamma \). Conventionally, if \( \gamma < 0.5 \) and the strength of the field is below the value necessary to produce...
barrier suppression ionization, the system is in the tunnel ionization regime. If \( \gamma > 0.5 \) the system is in the multiphoton ionization (MPI) regime again as long as field strengths remain below that required for barrier suppression. However, this definition of the adiabaticity parameter takes no consideration of the actual shape of the potential surface. The shapes of the potentials of atoms can, to a good approximation, be considered as Coulombic. This causes the Keldysh approximation of a zero-range potential to produce a similar inaccuracy for all atoms. For the very different potential surfaces of polyatomic molecules both the zero range approximation, as well as a Coulomb approximation, can lead to rather significant errors. In this paper, a method for numerically determining the adiabaticity parameter is presented. This method depends upon the field free atomic or molecular potential energy surface and ionization potential, as well as the electric field strength and frequency of the laser. This numerical approach to calculating \( \gamma \) allows a more realistic determination of the adiabaticity parameter for larger molecules when compared to the Keldysh method employing a zero-range potential. This is primarily due to the fact that the extended molecular orbitals are not well described by the zero-range potential.

CALCULATIONS

The calculation of the atomic and molecular electrostatic potential energy surfaces was performed using \textit{ab initio} methods. Geometry optimization and electrostatic potential calculations for \( Z = 1 \) were performed using the \textsc{gaussian} program\textsuperscript{16} at the unrestricted Hartree–Fock level using the 6-311g(3df,2p) basis set for \( \text{N}_2 \) and \( \text{C}_6\text{H}_6 \). For the xenon calculation the LANL2MB frozen core basis set was employed. The criteria for convergence for these calculations was \( 10^{-6} \) \( \text{H} \). For the calculations of the barrier length for the molecular systems, the symmetry axis incorporating the maximum number of nuclei (along the NN bond for \( \text{N}_2 \) and through \( \text{C}_1 \) and \( \text{C}_4 \) for \( \text{C}_6\text{H}_6 \)) was used for the one-dimensional electrostatic potential. The resulting potentials are shown in Fig. 1 for the cases of the zero-range, Coulombic, xenon, \( \text{N}_2 \), and \( \text{C}_6\text{H}_6 \) systems. Comparison of the zero-range and Coulomb potentials with the \textit{ab initio} potentials demonstrates that the Coulomb potential is an appropriate model for the atomic Xe and the diatomic \( \text{N}_2 \) at displacements of over 1 \( \text{Å} \). Interestingly, the Xe and \( \text{N}_2 \) potentials more closely approximate one another at short range than does the Coulomb potential. Neither the zero-range nor the Coulomb potential accurately model the potential corresponding to the polyatomic \( \text{C}_6\text{H}_6 \) at distances below 4 \( \text{Å} \). This suggests that adiabaticity calculations employing simple model potentials for molecules such as \( \text{C}_6\text{H}_6 \) will not be accurate for electric field strengths in the range of 1 V/\( \text{Å} \).

To calculate the adiabaticity parameter as a function of electric field for a given system, we simply replace the length of the zero-range barrier developed in the Keldysh model with the analogous length determined by either the Coulomb or \textit{ab initio} potential surface. For example, to determine the length of the \textit{ab initio} barrier numerically, the electric field of the laser is superimposed onto the \textit{ab initio} atomic or molecular electrostatic potential. The length of the barrier is then evaluated at the ionization potential of the system. The adiabaticity parameter can be calculated by inserting the numerically determined length for \( l_{\text{Z}} \) in Eq. (5) as a function of the electric field strength of the laser pulse.

RESULTS AND DISCUSSION

The results of the numerical calculation of the Keldysh adiabaticity parameter using zero-range, Coulomb, and \textit{ab initio} potentials are shown in Fig. 2 over the range of electric field strengths employed in previous experiments. The atomic, diatomic, and polyatomic systems investigated were \( \text{Xe}, \text{N}_2, \text{, and C}_6\text{H}_6 \). The laser frequency employed in these calculations was 780 nm. Figure 2(a) represents Xe with an IP of 12.13 eV. For the case of Xe the adiabaticity parameters for the \textit{ab initio} potential and the Coulomb potential are essentially equivalent over the field strength range investigated here. Note that the zero-range potential overestimates the adiabaticity parameter by a factor of 1.5 to 2 for electric field strengths from 0.7 to 2 V/\( \text{Å} \). Figure 2(b) represents \( \text{N}_2 \) with an IP of 15.6 eV where the electric field is aligned along the molecular axis. Again, the adiabaticity parameter calculated for the Coulomb potential agrees with the \textit{ab initio} potential reasonably well. The zero-range potential again overestimates \( \gamma \), but to a lesser degree than Xe because of the higher IP for \( \text{N}_2 \). In general as the IP of an atom increases, the zero-range potential becomes a better approximation. Figure 2(c) represents the adiabaticity parameter as a function of electric field strength for the molecule \( \text{C}_6\text{H}_6 \) with an IP of 9.24 eV. In this case, both the zero-range and the Coulomb potentials overestimate the adiabaticity parameter considerably. For electric fields above 1.25 eV, the point at which barrier suppression ionization\textsuperscript{17} occurs, the Coulomb and zero-range potentials become completely unphysical for the molecule benzene. This data suggests that molecules with extended molecular orbitals can enter the field ionization regime at much lower laser intensities when compared to atoms or diatomics with similar ionization potentials. The conventional value for atomic systems entering the tunnel ionization regime is for Keldysh parameters of 0.5. This occurs for benzene in the region of 1.1 V/\( \text{Å} \). We also note that this is approximately the field required to observe ions using 780 nm Ti:sapphire radiation.\textsuperscript{11}
The correction to the adiabaticity parameter for real world systems has focused to this point on the width of the barrier through which an electron must tunnel. In the Keldysh zero-range model the barrier length decreases asymptotically to zero at infinite field strength. The barrier height, however, remains equivalent to the electron binding energy of the molecule regardless of field strength. Thus the zero-range model precludes barrier suppression ionization. The zero-range potential for \( \text{Xe} \), \( \text{N}_2 \), and \( \text{C}_6\text{H}_6 \) at their respective binding energies for each model. For \( \text{Xe} \) and \( \text{N}_2 \), both of which are well-modeled by the Coulomb potential, the WKB tunneling coefficient is enhanced by more than five orders of magnitude with respect to the simple zero-range model, at field strengths ranging from 1 to 2 V Å\(^{-1} \). For \( \text{C}_6\text{H}_6 \) the tunneling coefficient is enhanced by seven orders of magnitude at 1 V Å\(^{-1} \) in comparison to the zero-range model and 2 orders of magnitude in comparison with the Coulomb model. For the case of benzene, the onset of barrier suppression occurs at approximately 1.25 V Å\(^{-1} \). This is substantially lower than the 1.5 V/Å field predicted using the Coulomb model. Note that above 1.25 V Å\(^{-1} \) the ionization probability is 1. This emphasizes the enhanced tunneling probability of polyatomic aromatic molecules with respect to atoms and diatoms, and further illustrates the increasing impracticality of the zero-range Keldysh adiabaticity parameter for complex molecular systems as a result of extended length of the molecular electronic orbitals and the generally low electron binding energies of these systems. It should also be noted that a mechanism such as charge resonance-enhanced ionization (CREI) as demonstrated for diatomic molecular ions,\(^7\) may also play a role in the enhanced ionization rates observed experimentally.\(^11\)–\(^13\)

We have demonstrated that the zero-range potential employed in the conventional Keldysh adiabaticity parameter calculation substantially overestimates \( \gamma \) in comparison with a determination based on the calculated molecular electrostatic potential energy surface for the case of the polyatomic molecule benzene. We reported similar calculations for the atomic system \( \text{Xe} \) and the diatomic \( \text{N}_2 \) for comparison. For each of these smaller systems we have shown that approximating the calculated potential energy surface with a Coulombic potential leads to nearly identical values of the adiabaticity parameter. This explains why diatomic molecules

\[ T = \exp \left( -2 \int_a^b \left[ 2(E-V(x)) \right]^{1/2} \, dx \right), \]  

where \( E \) is the electron binding energy and \( V(x) \) is the one-dimensional potential surface, both in atomic units. The zero-range potential was first superimposed upon the one-dimensional potentials used previously. To accomplish this calculation the respective atom’s or molecule’s IP was listed in the text.

Note that each calculation employed the respective atom’s or molecule’s IP as listed in the text.

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\(^a\)The calculated tunneling probability reaches a maximum at \( F_{\text{BEI}} \) which occurs at approximately 1.1 V/Å for benzene.
such as N$_2$ are well-described by the zero-range model at high intensities in comparison with atoms.$^3$ For the C$_6$H$_6$ system, the zero-range and Coulombic potentials produce values of the adiabaticity parameter which significantly overestimate the adiabaticity values obtained via the calculated potentials. These calculations suggest that benzene is ionized via a field mechanism after excitation with an intense 780 nm pulse.

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$^{16}$ GAUSSIAN.