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Diffraction patterns in ionization of the heteronuclear HeH^{2+} ion by attosecond x-ray radiation

Xiaoxu Guan, Ethan B. Secor,* Ryan C. Dutoit, and Klaus Bartschat

Department of Physics and Astronomy, Drake University, Des Moines, Iowa 50311, USA

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Single-photon ionization of the HeH^{2+} molecular ion exposed to an attosecond x-ray laser pulse is investigated for photon energies of 200 eV and 300 eV. In the fixed-nuclei approximation, the temporal response of the system is obtained by solving the time-dependent Schrödinger equation through an *ab initio* time-dependent grid-based discrete-variable representation formulated in two-center prolate spheroidal coordinates. The two-center interference effect is clearly observable in the excited $2p\sigma$ state, whereas interference patterns almost disappear, in both the parallel and perpendicular geometries, when the system is started from the $1s\sigma$ ground state. The angular distributions are asymmetric with respect to the center between the helium and hydrogen nuclei. For the $2p\sigma$ state in the parallel geometry, a dynamically forbidden mode of photoionization is observed only on one side of the two nuclei, with the details depending on the laser parameters and the internuclear separation. We also address the similarities and differences between a plane-wave model for the ejected electron with a linear combination of atomic orbitals for the molecular bound states and the classical double-slit-like interference pattern.

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I. INTRODUCTION

Interference has been a longlasting and fascinating topic over a wide variety of disciplines in both classical and quantum physics. In diatomic molecules specifically, interference phenomena are responsible for the confinement effect of a photoelectron's angular distributions driven by x-ray radiation [1–3] and also for the extrema in high-order harmonic generation [4, 5] through the rescattering process in an infrared (IR) laser pulse. Although the ionization mechanisms are entirely different, the two nuclei in diatomic molecules are responsible for these interference patterns, either by serving as two light “sources” for the emitted electronic waves in high-frequency radiation or as two rescattering centers in intense IR pulses. Young-type interference is observable not only in photoionization processes, but also in heavy-ion–molecule collisions [6].

The double-slit interference of diatomic molecules in the photon-energy regime of a few hundred eV was predicted by Cohen and Fano [7] for the angle-integrated cross sections, and also by Kaplan and Markin [8] for the angular distributions of photoionization. These previous works show that the interference patterns in the quantum molecular systems mimic their classical counterpart, at least to some extent. However, essential differences in the quantum microscopic and classical double-slit interferences were discussed in detail in our recent work [3].

Most previous works [3, 7, 8] in this area considered homonuclear diatomic molecules, such as N_2 , O_2 , H_2 , and H_2^+ . The essential idea behind these species is that classically the intensities of the two coherent light sources

are the same. This is equivalent to having identical probability density distributions of the valence electron in the ground state around the two nuclei. On the other hand, the orbital of the outer electron has a completely different probability density around two different nuclear charges in a heterodiatom molecule or molecular ion.

The single-electron HeH^{2+} ion serves as the simplest example for such heteronuclear systems, which may reveal even richer information than homonuclear systems regarding quantum-classical correspondence in terms of interference phenomena in a multi-center Coulomb system. It is reasonable to expect that some conclusions drawn for homonuclear diatomic molecules need to be modified to fit heteronuclear molecules. Intuitively, the photoelectron from heteronuclear molecules has different probabilities to be ionized in the region near the two different nuclear charges. This might be equivalent to having two coherent light sources with different intensities in a classical double-slit device. Therefore, the heteronuclear molecules provide an ideal test ground for the deeper understanding of interference phenomena in the quantum world.

Theoretical considerations of the field-free HeH^{2+} ion are far from new. They can be traced back to the work of Bates and Carson in 1956 [9]. Rather than the ground state $1s\sigma$, it was found that the potential energy curve of the electronic excited state $2p\sigma$ has a minimum around an internuclear separation of $R = 3.89$ bohr. (1 bohr = 1 a.u. = 0.529×10^{-10} m.) The existence of the bound state in the HeH^{2+} ion was experimentally established nearly four decades later by Ben-Itzhak *et al.* [10]. The lifetime of the metastable $2p\sigma$ state was found to be about 3.9 nanoseconds [11].

With the development in laser technology during recent years, the HeH^{2+} and HeH^+ ions will likely draw increasing interest to serve as benchmark laser-driven one-

* Present address: Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

and two-electron heteronuclear molecules. Using an analytical approximation to the two-center Coulomb wave function, Yudin *et al.* [12] already studied the asymmetric interference in photoionization of the HeH^{2+} molecular ion. As a single-electron molecular ion with a permanent dipole moment, HeH^{2+} was also used to examine the asymptotic theory of tunneling ionization [13]. Most recently, photoionization of as well as electron scattering from HeH^{2+} in its ground state were studied by Miyagi *et al.* [14].

In the present work, we employ our recently developed time-dependent grid-based approach [3, 15, 16] in its full dimensionality to study the double-slit interference effect of the fixed-in-space HeH^{2+} ion irradiated by an attosecond temporal x-ray laser pulse with central photon energies ($\hbar\omega_0$) of 200 eV and 300 eV, respectively. We refer the interested reader to our previous works [3, 15, 16] regarding the numerical implementations of the finite-element discrete-variable approach in molecular systems using prolate spheroidal coordinates and also the details in solving the time-dependent Schrödinger equation (TDSE) [17]. In short, the physical information such as angular distributions is extracted and analyzed by projecting the time-dependent wave packet onto the two-center Coulomb continuum states at the end of the time evolution. We emphasize that both the initial state and the continuum state are essentially exact (subject to numerical limitations, of course) solutions of the Schrödinger equation in its full dimensionality in the fixed-nuclei approximation.

The present paper is organized as follows. Angular distributions initiated from both the ground $1s\sigma$ and the first excited $2p\sigma$ states are investigated in detail for a variety of internuclear separations (R) in Sec. II. The connection between the present *ab initio* calculations and those using linear combinations of atomic orbitals (LCAO) as the initial state and a plane-wave representation for the ejected electron state is discussed as well. Furthermore, the time-evolved probability densities of the photoelectron in configuration and momentum space are presented in Sec. III. We will show results for both the “parallel” and “perpendicular” geometries, whose names refer to the relative orientation of the laser’s linear electric field polarization vector and the internuclear axis. Present experimental techniques, in principle, allow for the extraction of this information from “fixed-in-space” molecules, whose orientation at the moment of ionization can be determined from the pattern of Coulomb explosion, provided that the photo-fragmentation process is rapid compared to the molecular rotation [18]. We conclude with a brief summary in Sec. IV.

II. ANGULAR DISTRIBUTIONS

The computational details can be found in our previous work [3, 16]. The peak intensity of our sine-squared (electric field envelope) pulse in the present work

TABLE I. Electronic energies of the $1s\sigma$, $2p\sigma$, and $2p\pi$ states of the HeH^{2+} ion as a function of the internuclear separation R . All energies are in Hartrees.

R (bohr)	$1s\sigma$	$2p\sigma$	$2p\pi$
0.5	-3.665543943731	-1.197752634063	-1.093116322644
0.8	-3.240842100894	-1.286443588165	-1.055658003596
1.0	-3.033352518075	-1.338342137220	-1.028312852518
1.5	-2.695457797100	-1.388440272630	-0.960524570951
1.8	-2.573128762157	-1.369777569116	-0.922951609043
2.0	-2.512193016590	-1.345185686755	-0.899646912170
2.5	-2.404887411651	-1.264546966000	-0.847716080859
2.8	-2.360089794919	-1.212666999746	-0.820726287080
3.0	-2.335490938418	-1.178823245266	-0.804340585886
3.5	-2.286796500417	-1.099951888418	-0.768456143698
3.8	-2.263913082008	-1.057391943988	-0.750025563747
3.9	-2.257085241851	-1.044031965751	-0.744342427542
4.0	-2.250605387829	-1.031081311774	-0.738874455110
4.5	-2.222589705240	-0.972252504346	-0.714464187846
4.8	-2.208614012166	-0.941404964242	-0.701876505025
5.0	-2.200236965325	-0.922542873531	-0.694221996336

is $10^{12} - 10^{13}$ W/cm². Depending on the photon frequency, we are interested in short x-ray laser pulses of duration 344 – 517 attoseconds, corresponding to 25 optical cycles. The box of the “radial” variable $\xi = (r_1 + r_2)/R$ (where r_i is the distance of the electron from nucleus “ i ”) can be safely truncated at $\xi_{\text{max}} = 400$ to avoid any artificial boundary effects.

In this work, we consider the photoionization of the HeH^{2+} ion from two initial states, the ground state $1s\sigma$ and the first excited state $2p\sigma$, subjected to an attosecond x-ray laser pulse. The energies of these two initial states as well as the second excited state ($2p\pi$, shown to illustrate the accuracy of the method) are listed in Table I. All these energies were obtained by employing the method of imaginary time propagation. We first generate the energy and the wave function of the lowest state for a given magnetic quantum number. Then, in order to ensure that the system settles down in the desired excited state during the imaginary-time propagation, we subtract all components corresponding to the lower-lying states, so that the time propagation is carried out in a subspace orthogonal to the space spanned by all lower-lying states. The electronic energies presented in Table I agree to all digits given with the benchmark results reported in Ref. [19].

Due to the different nuclear charges in the HeH^{2+} ion, the spatial reflection symmetry or parity with respect to the midpoint of the two nuclei is no longer a conserved quantity. While a breakdown of the spatial parity conservation can also be caused by different masses of the two nuclei alone (e.g., in the HD^+ ion), its effect on the angular distributions is much more evident in heteronuclear targets with different nuclear charges. In the HD^+ ion,

FIG. 1. (Color online) Angular distributions of the HeH^{2+} ion from the initial ground state $1s\sigma$ at photon energies of 200 eV and 300 eV. The molecular axis (ϵ) is parallel (left two columns) or perpendicular (right two columns) to the direction of the linear laser polarization (ζ), respectively. The angular distributions were scaled to the same magnitude. The label in each panel denotes the internuclear separation distance R , which ranges from 1.5 to 5.0 bohr. The double-headed arrow specifies the direction of the laser polarization, while the large and small solid circles denote the He^{2+} and H^+ nuclei, respectively.

the effect would be attributed to higher-order corrections in the Hamiltonian and only becomes important when the degree of freedom of the nuclear motion is released [20].

A. Angular distributions from the initial $1s\sigma$ ground state

Figure 1 displays the angular distributions of the electron emitted from the HeH^{2+} ion at photon energies of 200 eV and 300 eV in both the parallel and perpendicular geometries. These results were obtained by solving the TDSE *ab initio*, starting the time propagation with the initial $1s\sigma$ ground state. We clearly see the asymmetric pattern in the angular distributions with respect to the two nuclei. In the parallel geometry, the photoelectron is more likely to be emitted on the H^+ side rather than on the He^{2+} side. Furthermore, the angular distributions are rather insensitive to the internuclear separation, except at the smallest R -value of 1.5 bohr. Finally, there is no obvious interference pattern in this case, even at the higher photon energy of 300 eV. This is particularly true for the perpendicular geometry.

As known from our previous study [3], an approximate plane-wave model combined with the LCAO expansion can be used to explain the interference patterns observed in homonuclear molecules such as the H_2^+ ion. Consequently, it seems worthwhile to explore to what extent the plane-wave model can capture the essential structures of the angular distributions in heteronuclear molecules. To begin with, the model fails to explain our first observation regarding the noticeable asymmetric mode of

electron ejection in the HeH^{2+} ion. At the largest internuclear separation considered in this work, $R = 5.0$ bohr, the kinetic energy of the photoelectron is about 140 eV at the photon energy of 200 eV. Its de Broglie wavelength, therefore, is about 2 bohr and thus much shorter than the separation in the “double-slit” device. Clearly, the internuclear separation is sufficiently large to fit several wavelengths. In contrast to what happens in homonuclear molecules, however, we observe neither noticeable interference nor the dynamic confinement effect (i.e., suppression of electron ejection along the laser polarization axis) in this particular case. Instead, the dominant ionization mode is still back-to-back emission along the polarization vector in both geometries.

The fundamental reason for the breakdown of the rule of thumb for interference effects to be visible or not is revealed by comparing the ground states of the HeH^{2+} and H_2^+ ions. The $1s\sigma$ state of the HeH^{2+} molecule corresponds to the dissociation channel of the H^+ ion (i.e., the proton) and the $1s$ state of the He^+ ion. In the lowest-order approximation at a fixed value of R , the wave function of the $1s\sigma$ state of the HeH^{2+} ion can be approximated as the $1s$ orbital of the He^+ ion. This also explains why the potential energy curve in the $1s\sigma$ ground state is purely repulsive: the probability density of finding the electron is larger around the helium nucleus due to its bigger charge compared to the proton. Consequently, the interference pattern in the photoionization process from the initial ground state almost disappears in this particular case, due to the approximate single-center character of the wave function obtained in this lowest-order picture. The result is in qualitative agreement with what we observe in Fig. 1. On the other hand, we also notice some asymmetric emission modes in the angular distributions for both geometries. This effect can only be captured by including electronic wave functions centered at both nuclei, i.e., by going beyond the lowest-order approximation discussed above.

B. Angular distributions from the excited $2p\sigma$ state

In the simplest treatment of photoionization of one-electron molecules, Cohen and Fano [7] and later Walter and Briggs [21] suggested to use the LCAO model to approximately represent the initial state, and to furthermore represent the final electron state by a plane wave. Before showing and discussing our accurate numerical results below, let us investigate what we might expect based on the predictions of this simple model.

In the LCAO approximation, the first excited $2p\sigma$ state is more complicated than the $1s\sigma$ ground state and also the $1s\sigma_g$ state of the H_2^+ ion. According to McCarroll and Moiseiwitsch [22], the molecular orbital (MO) of the $2p\sigma$ state in the LCAO model can be approximated by

$$\Phi_i^{\text{MO}}(\mathbf{r}) = \sum_{j=0}^3 c_j \Phi_j, \quad (1)$$

FIG. 2. (Color online) Angular distributions of the HeH^{2+} ion from the initial $2p\sigma$ excited state at the photon energy of 200 eV. The molecular axis is oriented horizontally along the direction of the laser polarization. The angular distributions were scaled to the same magnitude. The label in each panel denotes the internuclear separation R , which ranges from 1.0 to 4.9 bohr. The double-headed arrow on the left-bottom panel ($R = 1.0$ bohr) specifies the direction of the laser polarization, while the large and small solid circles denote the He^{2+} and H^+ nuclei, respectively.

where c_j ($j = 0 - 3$) are the expansion coefficients of the normalized hydrogenic atomic orbital Φ_j with nuclear charges $Z_1 = +2$ and $Z_2 = +1$ (in units of the elementary charge). Here $\Phi_0 = \Phi_{1s}^{(Z_2=1)}(\mathbf{r}_2)$, $\Phi_1 = \Phi_{1s}^{(Z_1=2)}(\mathbf{r}_1)$, $\Phi_2 = \Phi_{2p_z}^{(Z_1=2)}(\mathbf{r}_1)$, and $\Phi_3 = \Phi_{2s}^{(Z_1=2)}(\mathbf{r}_1)$, with $\mathbf{r}_1$ and $\mathbf{r}_2$ being measured from the nuclear charges Z_1 and Z_2 , respectively.

While the representation of the molecular states in the present work is much more accurate than what is obtained in the LCAO approximation, the latter allows us to highlight the essential scenario behind the interference phenomenon in heteronuclear molecules. The final continuum state of the photoelectron with momentum $\mathbf{k}$ is simply a plane wave, $\Phi_f = e^{i\mathbf{k}\cdot\mathbf{r}}$, in which $\mathbf{r}$ is measured with respect to the molecular center. In the velocity gauge, the ionization amplitude with light polarization

FIG. 3. (Color online) Same as Fig. 2, but for the photon energy of 300 eV.

vector ϵ is given by

$$T_{fi} = \langle \Phi_f | \epsilon \cdot \nabla_{\mathbf{r}} | \Phi_i^{\text{MO}} \rangle \\ = (i\epsilon \cdot \mathbf{k}) \times \left\{ e^{-i\mathbf{k}\cdot\mathbf{R}/2} \Phi_0(\mathbf{k}) + e^{i\mathbf{k}\cdot\mathbf{R}/2} \sum_{j=1}^3 \Phi_j(\mathbf{k}) \right\}. \quad (2)$$

After some algebra, the angular distribution can be written as

$$\frac{dP_{\text{ion}}}{d\Omega} \propto (\epsilon \cdot \mathbf{k})^2 \left\{ |\Phi_0(\mathbf{k})|^2 + \left| \sum_{j=1}^3 \Phi_j(\mathbf{k}) \right|^2 \right. \\ \left. + 2 \cos(\mathbf{k} \cdot \mathbf{R}) \Phi_0(\mathbf{k}) \sum_{j=1}^3 \Phi_j(\mathbf{k}) \right\}. \quad (3)$$

The $\Phi_j(\mathbf{k})$ are the Fourier transforms, i.e., the momentum space representations, of $\Phi_j(\mathbf{r}_1)$ and $\Phi_j(\mathbf{r}_2)$ after multiplication by c_j , with the vector of internuclear separation, $\mathbf{R}$, pointing from one nucleus to the other. As discussed in our previous work [3], $(\epsilon \cdot \mathbf{k})^2$ is a universal term for both molecules and atoms in single-photon ionization. It is determined by a quantum mechanical

FIG. 4. (Color online) Angular distributions of the HeH^{2+} ion from the initial $2p\sigma$ excited state at the photon energies of 200 eV and 300 eV. The molecular axis is perpendicular to the direction of the laser polarization. The angular distributions were scaled to the same magnitude. The label in each panel denotes the internuclear separation distance R , which ranges from 1.0 to 4.9 bohr. The double-headed arrow on the left-bottom panel ($R = 1.0$ bohr) specifies the direction of the laser polarization, while the large and small solid circles denote the He^{2+} and H^+ nuclei, respectively.

selection rule for the transition and hence is lacking a classical counterpart.

An important conclusion to be drawn immediately from the $(\epsilon \cdot \mathbf{k})^2$ term is the existence of a forbidden photoelectron emission mode along the direction normal to the laser polarization vector. This result neither depends on whether or not the nuclear charges are the same, nor on the relative orientation of the molecular axis and the laser polarization vector. If the nuclear charges are the same and only one atomic orbital is used ($1s\sigma_g$ state in H_2^+ , for example), the above expression for the angular distribution can be simplified to $(\epsilon \cdot \mathbf{k})^2 \cos^2(\mathbf{k} \cdot \mathbf{R}/2) |\Phi_0(\mathbf{k})|^2$. The Fourier transformation becomes spherically symmetric in this case, $\Phi_0(\mathbf{k}) \propto \Phi_0(k)$. Hence $|\Phi_0(\mathbf{k})|^2$ does not exhibit any angular dependence and effectively provides an isotropic background when the emission direction of the photoelectron is varied. Interference effects can only occur due to the term proportional to $\cos(\mathbf{k} \cdot \mathbf{R})$ in Eq. (3). When added to the background, it may lead to constructive increase or destructive cancellation in the resulting ionization signal.

Recall that the resulting intensity (I) of two coherent light beams with intensities I_1 and I_2 is given by $I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \delta$, where δ is the phase difference between the two paths [23]. Therefore, $|\Phi_0(\mathbf{k})|^2$ corresponds to I_1 while $|\sum_{j=1}^3 \Phi_j(\mathbf{k})|^2$ corresponds to I_2 . Assuming that the two light sources are in phase at the emitter, the classical phase difference

$\delta = \mathbf{k} \cdot \mathbf{r}_1 - \mathbf{k} \cdot \mathbf{r}_2 = \mathbf{k} \cdot \mathbf{R}$ is exactly the same as the oscillating term in Eq. (3). The angular distribution of the photoelectron thus shows that the probability densities of the atomic orbitals in *momentum space*, centered on the two nuclei, resemble the two “sources of lights” in the classical double-slit device. Nevertheless, a significant difference remains due to the term $(\epsilon \cdot \mathbf{k})^2$ in the photoionization signal for quantum atomic and molecular targets. This term, which does not have a classical analogue (see comments above), modulates the interference pattern expected from a classical double-slit device.

We now investigate how well the simplified plane-wave + LCAO picture works for the case of interest. Starting with the parallel geometry, Figs. 2 and 3 exhibit the angular distributions from the excited $2p\sigma$ state for photon energies of 200 eV and 300 eV from our *ab initio* calculations. We clearly see the dynamically forbidden ionization mode along the molecular axis at specific internuclear separations. Notice, however, that our numerical results show a strong asymmetry in the angular distributions with respect to the hydrogen and helium nuclei. The plane-wave model combined with the expansion of atomic orbitals, on the other hand, suggests that the angular distributions for $\mathbf{k} \parallel \mathbf{R}$ and $\mathbf{k} \parallel (-\mathbf{R})$ are the same [c.f. Eq. (3)]. Hence the simple model fails to predict the asymmetry observed in the accurate treatment of heteronuclear molecules. A similar observation was also presented in Ref. [12].

The reason for this failure is not the LCAO approximation. Instead, it is triggered by the plane-wave model. In our full time-dependent calculations, the angular distributions at the end of time evolution are extracted through

$$\frac{dP_{\text{ion}}}{d\Omega} = \int dk \left| \sum_{\ell m} (-i)^\ell e^{i\Delta_{\ell m}(k)} \mathcal{Y}_{\ell m}(\mathbf{k}) \mathcal{F}_{\ell m}(k) \right|^2, \quad (4)$$

where $\Delta_{\ell m}(k)$ is the two-center Coulomb phase shift and $\mathcal{F}_{\ell m}(k)$ is the complex amplitude in the ionization channel (ℓ, m) (see [3] for details of the notation). The essential source for the asymmetry in our formalism lies in the prolate spheroidal harmonics $\mathcal{Y}_{\ell m}(\mathbf{k})$. For the heteronuclear molecules, the inversion of the two nuclei is no longer a symmetry-conserving operation and therefore does not conserve the spatial parity operation of the electronic coordinates. While $\ell - |m|$ still refers to the number of nodes in the angular functions even when $Z_1 \neq Z_2$, we emphasize that $(-1)^\ell$ no longer relates to the parity conceptually. Hence, all ionization channels (ℓ, m) must be taken into account when calculating the cross sections.

A thorough examination of the angular function $\mathcal{Y}_{\ell m}(\mathbf{k})$ also indicates that it is generally not symmetric with respect to inversion of the momentum $\mathbf{k}$. The plane wave $e^{i\mathbf{k} \cdot \mathbf{r}}$ can, of course, also be expanded in two-center prolate spheroidal coordinates. In contrast to what we observe in a realistic heteronuclear molecule, however, the angular part $\mathcal{Y}_{\ell m}(\mathbf{k})$ in the plane wave expansion fulfills the parity symmetry since $Z_1 = Z_2 = 0$.

Note that the asymmetry in the HeH^{2+} molecular ion is sensitive to the internuclear separation where the ionization occurs. At some particular R and $\hbar\omega_0$ values, for example at $R = 1.8$ bohr and a photon energy of 300 eV [c.f. Fig. 3], the back-to-back dominant lobes are nearly the same on either side of the hydrogen and helium nuclei. For other combinations of R and $\hbar\omega_0$, however, a significant asymmetry is predicted. Such an asymmetry in the angular distributions is experimentally observable. As we can see from Figs. 2 and 3, the dynamically forbidden ionization mode may occur either on the side of the hydrogen or on the side of the helium nucleus. This selective mode of forbidden ionization suggests a practical way to identify the orientation of heteronuclear diatomic molecules experimentally.

Now we turn our attention to the perpendicular geometry. The corresponding results are shown in Fig. 4. As in the angular distributions of the H_2^+ ion, the dynamically forbidden ionization along the laser polarization direction completely vanishes in the HeH^{2+} ion as well. Furthermore, ionization along the molecular axis is also forbidden, as is the case for the H_2^+ ion.

However, a significant difference between the results obtained for the $1s\sigma_g$ state in H_2^+ and the $2p\sigma$ state in the HeH^{2+} ion should not be overlooked. When starting in the $1s\sigma$ state of H_2^+ , being ejected along the laser polarization axis is one of the favorite emission modes for the photoelectron in the perpendicular geometry. This fact can also be qualitatively explained by the plane-wave model. For the $2p\sigma$ state in the HeH^{2+} ion, however, the butterfly-shaped angular distributions in the perpendicular geometry reveal that the ionization along the polarization vector nearly vanishes [c.f. Fig. 4].

To summarize this section: The asymmetry seen in the angular distributions indicates a significant deviation from the classical double-slit interference pattern. The plane-wave model clearly fails in providing a satisfactory explanation for the HeH^{2+} case. In contrast to the H_2^+ ion, a simple relationship to predict how the confinement effect occurs does not seem to be available for heteronuclear molecules.

III. PROBABILITY DENSITIES IN THE PARALLEL AND PERPENDICULAR GEOMETRIES

At selected values of R , Fig. 5 depicts the probability densities ($|\Psi(\mathbf{r}, t)|^2$) in configuration space and the momentum distributions ($dP_{\text{ion}}/d\mathbf{k}$) at the end of the time evolution in the parallel and perpendicular geometries for the initial $1s\sigma$ state. Figures 6 and 7 present corresponding results for the initial $2p\sigma$ state. For these figures we reduced the pulse length to 15 optical cycles in order to broaden the energy width and thereby improve the visibility of the momentum distributions.

In our previous work on the H_2^+ ion [3], we established a relationship between the probability densities and the

momentum distributions. For both the $1s\sigma$ and $2p\sigma$ initial states, a similar correspondence also exists for the HeH^{2+} ion. Starting with the ground $1s\sigma$ state, we see from the shift of the distribution from the center in Fig. 5 that the probability density for finding the electron is large near the helium nucleus while it is almost negligible near the hydrogen nucleus. (Although the distribution is shown after the pulse, the overall ionization probability is small and hence the central part of the picture is also an approximate image of the initial state.) This result agrees with the predictions of the LCAO model. Consequently, the response of the molecular ion to the temporal laser pulse is nearly identical to that of He^+ , namely essentially back-to-back emission of the photoelectron from the $1s$ orbital in both the parallel and perpendicular geometries [c.f. Fig. 5 (a)-(d)]. The two-center interference effect, therefore, is minimized in this case.

For the initial $2p\sigma$ state, on the other hand, the electronic charge distribution is significant around both nuclei, instead of just one of them. This results in entirely different interference patterns than the emission from the $1s\sigma$ state. We notice, for example, a node-like structure in the $2p\sigma$ state. At the limit of the unified atom ($R \rightarrow 0$), it actually evolves into a nodal plane normal to the molecular axis. We emphasize again that the strength of our laser pulse does not significantly change the charge distributions in the region near the nuclei. Also, charge transfer between the two nuclei is not significant. Even at the end of the interaction with the laser, therefore, the electron remains largely surrounding the proton. The probability of finding it near the bare He^{2+} nucleus, however, is by no means not negligible, thereby allowing for significant interference effects.

There is a one-to-one correspondence between the configuration-space and momentum-space images regarding the preferential directions of the ionization modes. The probability densities alone show the dynamically forbidden modes and also the preferred directions of emission. For some cases in the parallel geometry (see, for example, Fig. 6 (c) at $R = 3.0$ bohr), the probability density for the electron emitted along the polarization axis on the side of the proton is negligible. This corresponds to the confinement effect observed in the angle-resolved momentum distribution [c.f. Fig. 6 (g) at the same R]. Here the ionization probability is largest for the electron knocked out on the He^{2+} side.

Similar correspondences can also be established for the perpendicular geometry (see Fig. 7). At large values of R , the well-resolved bouquet-shaped probability densities in the perpendicular geometry are directly related to the double-slit interference patterns observed in the momentum distributions.

IV. SUMMARY

We have investigated the photoionization of the heteronuclear HeH^{2+} ion irradiated by an attosecond x-ray laser

with photon energies of 200 eV and 300 eV. We solved the TDSE in two-center prolate spheroidal coordinates in the fixed-nuclei approximation for two initial states, $1s\sigma$ and $2p\sigma$, respectively. The connection between the angular distributions of the photoionized electron and the classical double-slit interference phenomenon was discussed for the parallel and perpendicular geometries. In an effort to study both homonuclear molecules in our previous work and heteronuclear molecules in the present work, we also employed a simplified plane-wave model in momentum space to investigate the similarities and differences in

the formalism for the quantum angular distributions and the classical interference pattern of two coherent light sources.

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FIG. 5. (Color online) Probability densities (a)-(d) and momentum distributions (e)-(h) of the electronic wave packets at the end of the laser pulse for the parallel and perpendicular geometries. The initial state is the $1s\sigma$ state. The nuclei are set from left (He) to right (H) for the parallel (||) geometry [panels (a),(b),(e),(f)], while they are from bottom (He) to top (H) for the perpendicular ($\perp$) geometry [panels (c),(d),(g),(h)]. The central frequency of the laser is 200 eV, the pulse duration is 15 cycles, and the peak intensity of the sine-squared (electric field envelope) pulse is 10^{12} W/cm². The laser polarization is oriented horizontally. The momentum distributions are presented in units of 10^{-8} per momentum in atomic units (a.u.). The axis dimensions in configuration space (left panels) are given in bohr, while those in momentum space (right panels) are in a.u.

FIG. 6. (Color online) Probability densities (a)-(d) and momentum distributions (e)-(h) of the electronic wave packets at the end of the laser pulse for the parallel geometry. The initial state is the $2p\sigma$ state. The nuclei are set from left (He) to right (H). The laser parameters are the same as those of Fig. 5. The momentum distributions are presented in units of 10^{-9} per momentum in a.u.

FIG. 7. (Color online) Same as Fig. 6, but at R -values of 1.0 and 4.5 bohr in the perpendicular geometry. The nuclei are set from bottom (He) to top (H). The laser polarization is oriented horizontally.