Study of molecular orbitals in momentum space

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Abstract

Molecular orbitals are presented in configuration and momentum representations. We propose to minimize large oscillations present in calculated momentum wavefunctions by cancelling position factor phases. We illustrate the distortion introduced by different electron translation factors and show continuum states and dynamical wavefunctions in momentum coordinates.

I. INTRODUCTION

In the last decade, many experimental and theoretical studies have been carried out in the framework of the momentum representation (MR). In particular, the MR has been employed in the calculation of Compton profiles in molecular systems [1,2], and atomic and molecular collisions involving continuum states [3-5]. In this work we analyze the behaviour of the Fourier Transform (FT) of two centre molecular orbitals (MOs), the modification of these FT by the introduction of common [6] and non-common [7] translation factors in the molecular basis, as well as its use in in dynamical wavefunctions in ion-atom collisions.

A conpicuous feature is the oscillatory behaviour of MOs in the MR , which reflects interferences due to delocalisation effects. Unfortunately, this information usually appears blurred by other strongly oscillating phases comming from the so-called position factors (PF), which appear because the centre of electronic density does not coincide with the origin chosen to calculate the FT. In the following, we shall study how these unwanted oscillations can be reduced, and illustrate our findings with calculations of FT of exact one-electron diatomic model (OEDMs), and variational molecular orbitals (MOs) of the HeH^{2+} and H_2^+ quasimolecules.

II. DEFINITION AND PROPERTIES OF MOMENTUM WAVEFUNCTIONS

The Fourier Transforms (FT) and Inverse Fourier Transforms (IFT) are defined as

$$\Phi(\mathbf{p}) = (\frac{1}{2\,\pi})^{3/2} \int d\mathbf{r}\; e^{-i\mathbf{p}\cdot\mathbf{r}}\; \Psi(\mathbf{r}) \tag{1}$$

$$\Psi(\mathbf{r}) = (\frac{1}{2\,\pi})^{3/2} \int d\mathbf{r}\; e^{i\mathbf{p}\cdot\mathbf{r}}\; \Phi(\mathbf{p}) \tag{2}$$

The FT of real wavefunctions may be decomposed as

$$\Phi(\mathbf{p}) = \Phi_g(\mathbf{p}) + \Phi_u(\mathbf{p}) \tag{3}$$

with

$$\Phi_g(\mathbf{p}) = \Phi_g(\mathbf{p})^* = Real[\Phi(\mathbf{p})] \tag{4}$$

and

$$\Phi_u(\mathbf{p}) = -\Phi_u(\mathbf{p})^* = \mathrm{i}\,(\mathrm{Imag}[\Phi(\mathbf{p})]) \tag{5}$$

As a consequence, the FT associated with atomic functions with even angular quantum number l are real, while those with odd l are imaginary.

A Translation and Position Factors

In dynamical calculations, the wavefunction $\Psi(\mathbf{r}\,;t)$, describing the temporal evolution of a collisional system in the configuration representation (CR) is a solution of the equation

$$(H_{el} - i\partial/\partial t\,|_{\mathbf{r}})\Psi(\mathbf{r}\,;t) = 0 \tag{6}$$

where $\mathbf{r}$ denotes the electronic coordinates referred to an origin O, $H_{el}(\mathbf{r}\,;\mathbf{R})$ is the fixed nuclei Born-Oppenheimer electronic hamiltonian, and $i\partial/\partial t\,|_{\mathbf{r}}$ represents the non adiabatic coupling operator in a semiclassical Eikonal approach, where the relative nuclear motion is described in a laboratory reference frame by rectilinear classical trajectories $\mathbf{R}\,(t) = \mathbf{b} + \mathbf{v}\,t$ with constant velocity $\mathbf{v}$ and impact parameter $\mathbf{b}$.

Solutions $\Psi(\mathbf{r}\,;t)$, and $\Psi'(\mathbf{r}'\,;t)$, of the dynamical equation (6) obtained for two origins, O and O' respectively, with O'= O + $\delta\mathbf{R}$, ($\mathbf{r}' = \mathbf{r} - \delta\mathbf{R}$), fulfill

$$\Psi'(\mathbf{r}'\,;t) = \Psi(\mathbf{r}\,;t)e^{i\delta\mathbf{v}\cdot\mathbf{r}} \tag{7}$$

The exponential phase $e^{i\delta\mathbf{v}\cdot\mathbf{r}}$, is called a translation factor (TF), and ensures the Galilean invariance of cross sections. From equation (1) and $\mathcal{O}_{p'} = \mathcal{O}_p + \delta\mathbf{v}$, the corresponding FT functions $\Phi(\mathbf{p})$ and $\Phi'(\mathbf{p}')$ fulfill

$$\Phi'(\mathbf{p}') = \Phi(\mathbf{p} - \delta\mathbf{v})e^{i\delta\mathbf{p}\cdot\mathbf{R}} \tag{8}$$

and the effect of the TF has two different contributions: the shift in $\delta\mathbf{v}$ in $\mathbf{p}' = \mathbf{p} - \delta\mathbf{v}$ and an additional momentum phase $e^{i\delta\mathbf{p}\cdot\mathbf{R}}$, or Position Factor (PF) that represents the shift of the electron position with respect to the new origin, O' in the CR.

Despite the apparent similarity between the two TF and PF, we note that the PF emerges naturally in the MR, $\Phi(\mathbf{p})$ (eq. (8)), while no TF appears when MOs are obtained for fixed nuclei positions (v=0 in eq. (7)), and they must be included "ad-hoc" in the dynamics. For instance, the molecular expansion of the dynamical wavefunction usually is taken of the form

$$\Psi(\mathbf{r}\,;t) = \Sigma_i a_i(t)\,\phi_i(\mathbf{r}\,;\mathbf{R})e^{iU_i} \tag{9}$$

where e^{U_i} a molecular translation factor similar to the phase $\mathrm{e}^{i\delta\mathbf{v}\cdot\mathbf{r}}$ of equation (7), and $H_{el}(\mathbf{r}\,;\mathbf{R})\phi_i(\mathbf{r}\,;\mathbf{R}) = \varepsilon_i(\mathbf{R})\phi_i(\mathbf{r}\,;\mathbf{R})$

The choice of the $e^{i\,U_i}$ TF is not unique, and many analytical forms of U_i have been proposed in the literature. We consider in this work three ways of including them.

1 Bates and McCarroll Translation Factors

In this approach [7], a MO Ψ_j asymptotically describing a target (A) or projectile (B) atomic function, is multiplied by a target (D_A) or projectile (D_B) plane wave:

$$\Psi_j^{BM}(\mathbf{r}) = \Psi_j(\mathbf{r})D_j \tag{10}$$

so that unitarity is preserved. For an origin placed on the target

$$D_A = 1.0, D_B = e^{i\mathbf{v}\cdot\mathbf{r} - \frac{i}{2}v^2 t} \tag{11}$$

Momentum functions associated to MOs asymptotically localised at the target are:

$$\Phi_j^{BM}(\mathbf{p}) = (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}\ e^{-i\mathbf{p}\cdot\mathbf{r}}\ \Psi(\mathbf{r}) = \Phi_j(\mathbf{p}) \tag{12}$$

while those associated to projectile functions are

$$\begin{aligned}\Phi(\mathbf{p})^{BM} &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}\ e^{-i\mathbf{p}\cdot\mathbf{r}}\ \Psi(\mathbf{r})\, e^{i\mathbf{v}\cdot\mathbf{r} - \frac{i}{2}v^2 t} \\ &= e^{-\frac{i}{2}\mathbf{v}\cdot\mathbf{R}}\,\Phi(\mathbf{p} - \mathbf{v})\end{aligned} \tag{13}$$

which indicates a translation in $\mathbf{v}$ in the momentum space, with respect to the original FT, multiplied by a momentum-independent phase.

2 Common Translation Factor

As molecular orbitals are delocalized at small and intermediate distances, a more flexible and simpler alternative, which also preserves unitarity is the Common translation Factor (CTF) [6]:

$$\Psi_j^{CTF}(\mathbf{r}) = D\,\Psi_j(\mathbf{r}) = e^{iU}\ \Psi_j(\mathbf{r}) \tag{14}$$

with

$$U = f(\mathbf{r}, R)\mathbf{v}\cdot\mathbf{r} - \frac{f^2}{2}v^2 t \tag{15}$$

which defines through $\nabla U \simeq f\mathbf{v}$ a local velocity field. For the illustrations of this work we have chosen the switching function f($\mathbf{r}$, R) proposed in reference [8]. The corresponding momentum functions are:

$$\begin{aligned}\Phi_j^{CTF}(\mathbf{p}) &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}\ e^{-i\mathbf{p}\cdot\mathbf{r}}\ e^{iU}\ \Psi(\mathbf{r}) \\ &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}\ e^{-i\mathbf{p}\cdot\mathbf{r}\ f(\mathbf{r},R)\mathbf{v}\cdot\mathbf{r} - \frac{if^2}{2}v^2 t}\Psi(\mathbf{r})\end{aligned} \tag{16}$$

and have been calculated numerically using the Fast Fourier algorithm [9].

3 Projection over Atomic Components (PCA)

Variational molecular orbitals are usually built as linear combinations of target and projectile atomic orbitals

$$\Psi_j = \Psi_j^A(\mathbf{r}_A) + \Psi_j^B(\mathbf{r}_B) \tag{17}$$

In this approach, we multiply each atomic component by atomic plane waves D_j, (j=A,B)

$$\Psi_j^{PCA}(\mathbf{r}) = \Psi_j^A(\mathbf{r}_A)\, D_A + \Psi_j^B(\mathbf{r}_B)\, D_B \tag{18}$$

The PCA-TF modified momentum functions are

$$\begin{aligned}\Phi_j^{PCA}(\mathbf{p}) &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_A\, \Psi_j^A(\mathbf{r}_A)\; e^{-i\mathbf{p}\cdot\mathbf{r}_A} D_A + \int d\mathbf{r}_A\, \Psi_j^B(\mathbf{r}_B)\; e^{-i\mathbf{p}\cdot\mathbf{r}_A} D_B \\ &= \Phi_{jA}(\mathbf{p}) + \; e^{-i(\mathbf{p}-\mathbf{v}/2)\cdot\mathbf{R}}\; \Phi_{jB}(\mathbf{p}-\mathbf{v})\end{aligned} \tag{19}$$

that assign a translational target ($\mathbf{v}_A$) or projectile ($\mathbf{v}_B$) velocity to the electron depending on the relative weight the atomic components $\Psi_j^{A,B}$ have in the MO Ψ_j. The PF $e^{-i(\mathbf{p}-\mathbf{v}/2)\cdot\mathbf{R}}$ due to the delocalized character of the MO may be observed in (19).

III. CALCULATIONS

A Atomic calculations

We have diagonalised the Hydrogen hamiltonian in a large basis of STOs and spherical Bessel functions. Ground and first excited bound atomic states in the MR are identical to the exact ones [10] and are not shown. We present in figure 1 our results for atomic orbitals with positive energy (pseudostates), as functions of the radial coordinates, in both CR and MR. The ability of the variational method to describe continuum orbitals in the MR will be noted.

B HeH^{2+}

For the sake of clarity, and to minimize oscillations arising from the PF using OEDMs, a careful selection of the origin of calculations in eq. (1) is indispensable, and the center of electronic density seems to be the best choice. At small and intermediate distances (R $\leq$ 3 a.u.), the nuclear center of charges (n.c.c.) has been proved to be a good approximation to this point. Asymptotically, as the electron is localised on either the target or projectile, one of these centers must be chosen as origin. When variational molecular orbitals are used, an analytical identification of the PF is possible, which enable us to focus on that part of the phase resulting from the mixture between different angular momentum atomic functions, that are responsible for delocalisation effects.

Figure 2 illustrates the MR of the 1sσ MO. We plot in this figure the real and imaginary parts of $\Phi_{1s\sigma}(p_x = p_y = 0, p_z)$. Since this MO dissociates into He^+ (1s) + H^+, the momentum wavefunction calculated with respect to the proton, $\Phi(\mathbf{p})$, shows a PF phase $e^{i\mathbf{p}\cdot\mathbf{R}}$, which precludes the interpretation of the MR at large R, where the most adequate momentum function is that calculated using the projectile nucleus (He^{2+}) as origin. At intermediate distances, the FT calculated on the n.c.c. presents a smoother behaviour, with an almost negligible imaginary component. Using the "best" origin for each region, we can see that molecular effects show up in the imaginary component of the momentum function, providing a direct measure of the delocalisation in this state; we note that both the united (Li^{2+}(1s)) and asymptotic (He^+(1s)) atomic limits, correspond to even angular momentum, and yield real FT without PF.

Figure 3 shows the FT of the 2pσ MO for different internuclear distances, with the n.c.c. (at small and intermediate R) and the proton (at large R) as the "best" origins. An increasing real component of the FT is expected as R increases, given the united atom (Li^+(2p)) and asymptotic (H(1s)) limits. At internuclear distances around 1.5 a.u., the polarisation experienced by this MO appears in figure 3 in the real component of the FT calculated in the n.c.c. On the other hand, for distances around 6-8 a.u. the imaginary component reflects the delocalisation of the electronic cloud due to the 3dσ-2pσ avoided crossing, where these orbitals exchange character.

In figure 4 we plot $\Psi_{3d\sigma}(\mathbf{r})$ and $\phi_{3d\sigma}(\mathbf{p})$ functions. A similar analysis to that performed for the 1sσ may be applied, except that the real and imaginary parts have similar asymptotic values, which is consistent with the Stark hybrid limit (He^+(2s+2p_z)) of the orbital. In the region of the 2pσ - 3dσ crossing (R $\simeq$ 6-8 a.u.), the large delocalized density appears in the MR as oscillations in the imaginary component and in the accumulative probability around the origin (p = 0). Finally, as an illustration of the effect of TFs, we have plotted in figure 5 the CTF-and-BM-modified orbitals $\Phi^{CTF}_{3d\sigma}(\mathbf{p})$, (eq. (16)) and $\Phi^{BM}_{3d\sigma}(\mathbf{p})$, (eqs. (12) and (13)), respectively. While distortion introduced by a CTF in the MO is hardly observed in the CR, the effect is conspicuous in the MR, since, the unitarity relation $|\Psi^{CTF}(\mathbf{r})|^2 = |\Psi(\mathbf{r})|^2$, is not longer preserved in the MR. The FT of the Bates-McCarroll modified orbitals of figure 5 have been calculated with respect to the He^{2+} nucleus and the n.c.c. Multiplication of $\Phi_j(\mathbf{p})^{BM}$ by the phase $e^{\frac{i}{2}\mathbf{v}\cdot\mathbf{R}}$, (see equation (13)), provides the modified function $\Phi_j^{BMmod}(\mathbf{p}) = \Phi_j(\mathbf{p} - \mathbf{v})$, which clearly shows the shift in $\mathbf{v}$ induced by this TF in the electronic translation velocity.

1 He^{2+} + H(1s) collision

For illustrative purposes, we show in figure 6, the configuration and momentum density probabilities obtained using a semiclassical eikonal approach, and a 66-term molecular expansion (eqs. (6) and (9)), for three values of the nuclear coordinate Z = vt, along a nuclear trajectory with nuclear velocity v = 2 a.u., and impact parameter b = 2.0 a.u., that gives rise to a sizeable electron transfer probability.

For t $<$ 0, $\Psi(\mathbf{r};t)$ is described by the 1s atomic orbital of the Hydrogen. When the projectile approaches the target (Z $\simeq$ 0), an important fraction of the electronic density is polarised by the projectile. Then, as the nuclei recede (Z $\simeq$ 19) from each other, a part of this density has been completely transferred to the projectile, and the remainder describes the initial and excited target states. Although both CR and MR representations provide an equivalent description of the collisional process, a valuable information arises from the momentum representation, since a short and common range of the momentum values (p $\leq$ 3) is sufficient to describe the collisional process.

C $\mathbf{H}_2^+$

In homonuclear systems, delocalisation exists for all R values, so that PFs are always present. To minimize their influence in the study of the 1sσ_g and 2pσ_u OEDM orbitals, we have chosen the midpoint as origin. To better understand the form of the orbitals, we can assume that each MO admits an atomic decomposition

$$\Psi_j^{\pm} = \Psi_j^A(\mathbf{r}_A) \pm \Psi_j^B(\mathbf{r}_B) \tag{20}$$

where the $\pm$ combinations are gerade or ungerade orbitals. The corresponding momentum wavefunctions may be written as

$$\begin{aligned} \Phi_{j+}(\mathbf{p}) &= 2Real[\Phi_{j0}(\mathbf{p})\, e^{i\frac{\mathbf{p}\cdot\mathbf{R}}{2}}] \rightarrow_{R\to\infty} 2\Phi_{j0}(\mathbf{p})\, cos(\frac{\mathbf{p}\cdot\mathbf{R}}{2}) \\ \Phi_{j-}(\mathbf{p}) &= -2Im[\Phi_{j0}(\mathbf{p})\, e^{i\frac{\mathbf{p}\cdot\mathbf{R}}{2}}] \rightarrow_{R\to\infty} 2\Phi_{j0}(\mathbf{p})\, sin(\frac{\mathbf{p}\cdot\mathbf{R}}{2}) \end{aligned} \tag{21}$$

with

$$\Phi_{j0}(\mathbf{p}) = (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_A\, e^{-i\mathbf{p}\cdot\mathbf{r}_A} \Psi_j^A(\mathbf{r}_A) = (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_B\, e^{-i\mathbf{p}\cdot\mathbf{r}_B} \Psi_j^B(\mathbf{r}_B) \tag{22}$$

denoting the FT of the atomic components. In these equations, the new position factors are cos $(\frac{\mathbf{p}\cdot\mathbf{R}}{2})$ and sin$(\frac{\mathbf{p}\cdot\mathbf{R}}{2})$ which are not longer phases.

We may define corrected momentum functions

$$\begin{aligned} \Phi^c_{j+}(\mathbf{p}) &= \Phi_{j+}(\mathbf{p})/cos(\frac{\mathbf{p}\cdot\mathbf{R}}{2}) \\ \Phi^c_{j-}(\mathbf{p}) &= -\Phi_{j+}(\mathbf{p})/sen(\frac{\mathbf{p}\cdot\mathbf{R}}{2}) \end{aligned} \tag{23}$$

that asymptotically behave as

$$\lim_{R\to\infty} \Phi^c_{j\pm}(\mathbf{p}) = 2\Phi_{j0}(\mathbf{p}) \tag{24}$$

and present a smoother behaviour at large R, revealing the atomic components involved in the MO.

In figures 7 we present our calculations for the 1sσ_g orbital. We compare the original $\Phi_{1s\sigma g}(\mathbf{p})$, and corrected $\Phi^c_{1s\sigma g}(\mathbf{p})$, momentum functions. At small R, both descriptions are identical, since the position factors are small, and the momentum functions obtained using the midpoint, $\Phi_+(\mathbf{p})$ provides an accurate description.

At large R,(see e.g. R=10 a.u.), we can see in $\Phi^c_+(\mathbf{p})$ the gerade combination of 1s orbitals centred on each proton, structure that hardly may be obtained from the unmodified FT, which strongly oscillates with R. Comparison of MR and CR functions at small and intermediate distances, shows that as $\Psi_{1s\sigma g}(\mathbf{r})$ spreads with R, its momentum functions $\Phi_{1s\sigma_g}(\mathbf{p})$ becomes more compact, (as it should).

Figure 8 displays the information obtained for the 2pσ_u MO. While $\Phi_-(\mathbf{p})$ describes the ungerade character of the complete MO, $\Phi^c_-(\mathbf{p})$ shows a symmetric shape, with a maximum centred on p=0, which corresponds to the FT coming from the 1s atomic contributions of each hydrogen.

The 3dσ_g state has been obtained using the variational method in a basis of atomic orbitals. Then, the atomic decomposition $\Psi_j^{\pm} = \Psi_j^A(\mathbf{r}_A) \pm \Psi_j^B(\mathbf{r}_B)$ is possible in practice, and FT functions may be written as

$$\begin{aligned} \Phi_{j\pm}(\mathbf{p}) &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_A\, e^{-i\mathbf{p}\cdot\mathbf{r}_A} (\Psi_j^A(\mathbf{r}_A) \pm \Psi_j^B(\mathbf{r}_B)) \\ &= (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_A\, e^{-i\mathbf{p}\cdot\mathbf{r}_A} \Psi_j^A(\mathbf{r}_A) \\ &\pm (\frac{1}{2\pi})^{3/2} e^{-i\mathbf{p}\cdot\mathbf{R}} \int d\mathbf{r}_B\, e^{-i\mathbf{p}\cdot\mathbf{r}_B} \Psi_j^B(\mathbf{r}_B) \end{aligned} \tag{25}$$

Multiplication of each term by the inverse of the corresponding PF, 1.0 and $e^{i\mathbf{p}\cdot\mathbf{R}}$ respectively, allows us to define the modified functions

$$\Phi_{j\pm}^{mod}(\mathbf{p}) = (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_A \; e^{-i\mathbf{p}\cdot\mathbf{r}_A} \Psi_j^A(\mathbf{r}_A) \pm (\frac{1}{2\pi})^{3/2} \int d\mathbf{r}_B \; e^{-i\mathbf{p}\cdot\mathbf{r}_B} \Psi_j^B(\mathbf{r}_B)$$
$$\equiv \Phi_{jA}^{mod} \pm \Phi_{jB}^{mod} \tag{26}$$

valid for any value of R, and free of position factors. In figure 9 we have plotted this orbital, with and without the PCA translation factor, in the CR and MR. The use of equations (19) and (26) to incorporate this type of TF, and to remove unwanted oscillations due to position factors leads to final new momentum functions that stress the asymmetric distortion induced by this TF.

IV. CONCLUDING REMARKS

The presence of oscillations in molecular momentum functions, in particular in homonuclear systems, arise from the origin dependence of the definition of the FT functions, and are a consequence of the delocalized structure of MOs. Their minimisation through corrected (Φ_j^c) or modified (Φ_j^{mod}) functions is only a tool that facilitates the analysis of the molecular structure using the real part and imaginary part sharing the different atomic components present. Distortion induced in the MOs by different translation factors have been analysed in CR and MR. We have seen that the MR provides a valuable information that is not always available in the CR. Furthermore in dynamical problems, the use of both representations provides a description of the evaluation of the electronic momentum along the collision. For homonuclear systems, we have shown how variational MOs defined in a basis of atomic orbitals permit an analytical correction of position factors, providing new momentum functions which clearly reflect the atomic and molecular structure.

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a FIGURE CAPTIONS

Figure 1 Radial part of the Hydrogen continuum wavefunction with l = 0 and E = 0.104 a.u. a) Coordinate representation; b) momentum representation.

Figure 2 Plot of the FT of the 1sσ MO of the HeH^{2+} quasimolecule for several values of the internuclear distance R, indicated in the figure, and for different origins of electronic coordinates: a) Real $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on the proton. b)Im $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on the proton. c) Real $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+; $(- - -)$, $\mid \Phi(p_z) \mid$. d)Im $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+. e) Real $[\Phi(p_z)]$: (—–), origin on He^{2+}; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+. f)Im $[\Phi(p_z)]$: (—–), origin on He^{2+}; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+.

Figure 3 Plot of the FT of the 2pσ MO of the HeH^{2+} quasimolecule for several values of R, and for different origins of electronic coordinates: a) Real $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+. b)Im $[\Phi(p_z)]$: (—–), origin on the n.c.c. (this is indistinguishable from the corresponding line for the H^+ origin); ; $(- - -)$, $\mid \Phi(p_z) \mid$. c) Real $[\Phi(p_z)]$: (—–), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+. d)Im $[\Phi(p_z)]$: (— –), origin on the n.c.c.; $(\cdot\cdot\cdot\cdot\cdot)$, origin on H^+; . e) (—–), Real $[\Phi(p_z)]$; $(\cdot\cdot\cdot\cdot\cdot)$, Imag $[\Phi(p_z)]$, origin on H^+ ($\mid \Phi(p_z) \mid$ is indistinguishable from Real $[\Phi(p_z)]$ for this origin); f) (—–), Real $[\Phi(p_z)]$; $(\cdot\cdot\cdot\cdot\cdot)$, Imag $[\Phi(p_z)]$, origin on H^+ ($\mid \Phi(p_z) \mid$ is indistinguishable from Real $[\Phi(p_z)]$ for this origin).

Figure 4 Comparison of CR (panels a,c,e) and MR (panels b,d,f) of the 3dσ MO of the HeH^{2+} quasimolecule. In panels b,d and f full lines correspond to Real $[\Phi_{3d\sigma}(p_z)]$ and dotted lines to Imag $[\Phi_{3d\sigma}(p_z)]$.In panels b and d, the origin of electronic coordinates is on the n.c.c. In panel f it is on the He^{2+} nucleus.

Figure 5 Comparison of $\Phi^{CTF}_{3d\sigma}(p_z)$ (panels a,c,e) and $\Phi^{BM}_{3d\sigma}(p_z)$ (panels b,d,f) for v=1a.u. . In panels a,b,c,d the origin is on the n.c.c. In panels e and f it is on the He^{2+} nucleus. In panels a,d,c full lines represent real parts, and dotted lines the corresponding imaginary parts. In panels b,d,f thick lines represent real parts, and thin lines the corresponding imaginary parts.

Figure 6 Contour plots of the electronic density in the CR ($\int dy \mid \Psi(\mathbf{r}\,, Z) \mid^2$), and in the MR ($\int dp_y \mid \Phi(\mathbf{p}\,, Z) \mid^2$).

Figure 7 Comparison of the CR (a,c,e) and MR (b,d,e) of the MO 1sσ_g of the H_2^+ quasimolecule. The dotted line in panel f is the corrected function (eq. (23)).

Figure 8 Same as fig. 7 for the MO 2pσ_u of the H_2^+ quasimolecule. Dotted lines in panels b, d and f correspond to the uncorrected functions (eq. (21)), and full lines to the corrected functions of eq. (23).

Figure 9 Same as fig. 7 for the MO 3dσ_g of the H_2^+ quasimolecule. Dotted lines in panels b, d and f represent the FT of the orbital without translation factors, and full lines the MO modified by the PCA translation factor (eq. (18)).

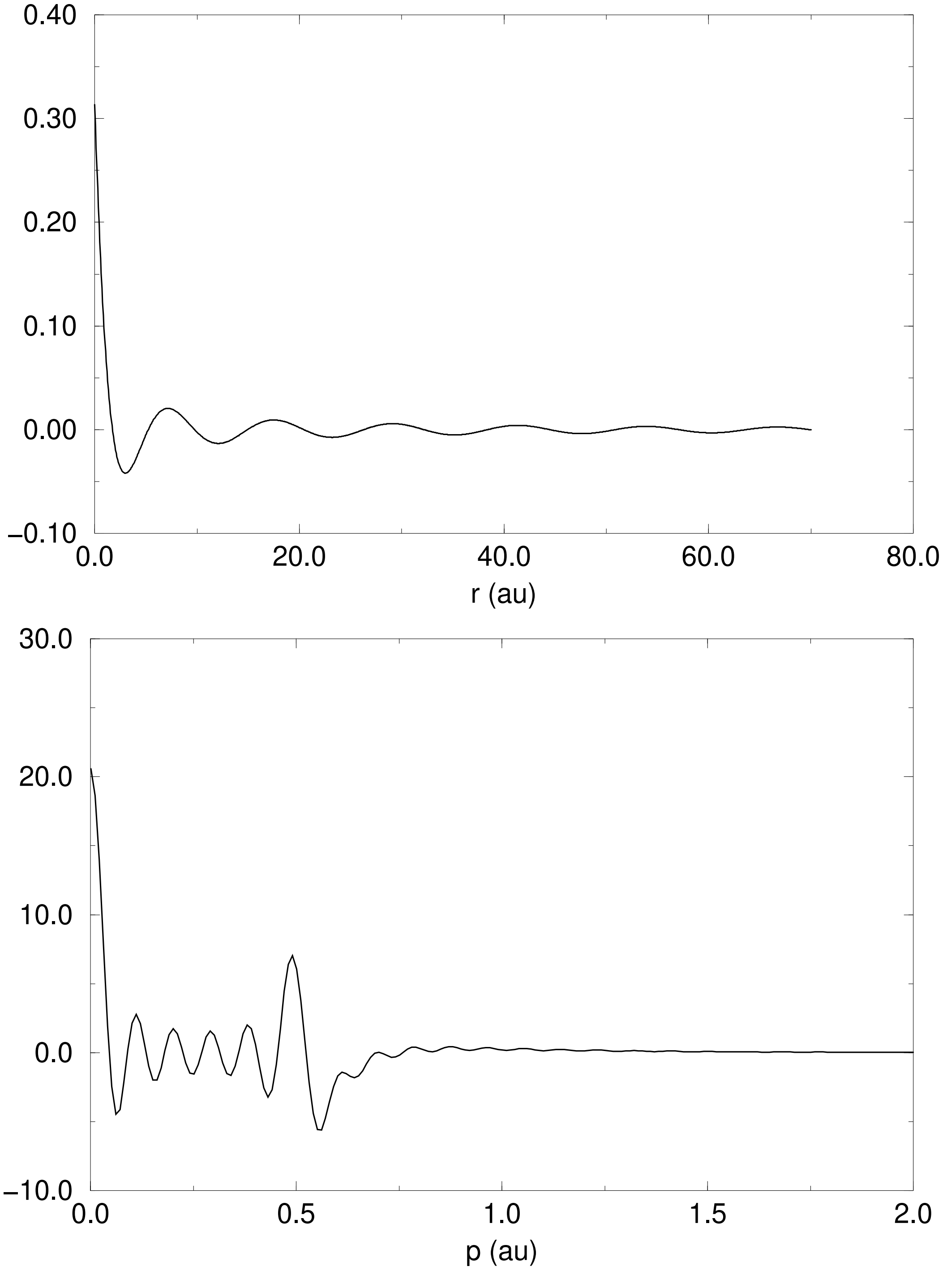

0.40
0.30
0.20
0.10
0.00
–0.10
0.0
20.0
40.0
60.0
80.0
r (au)
30.0
20.0
10.0
0.0
–10.0
0.0
0.5
1.0
1.5
2.0
p (au)

FIG. 1:

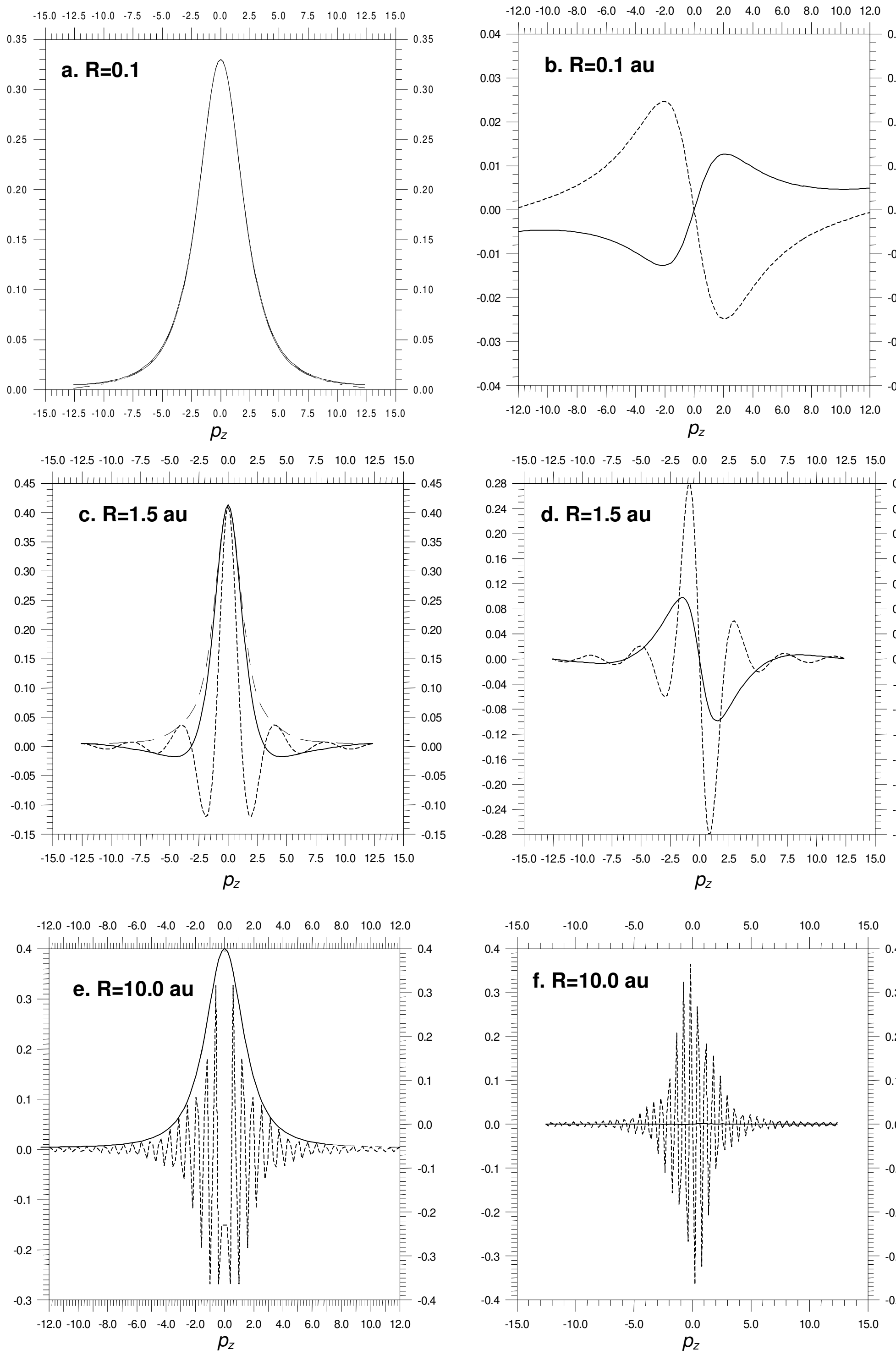


FIG. 2:

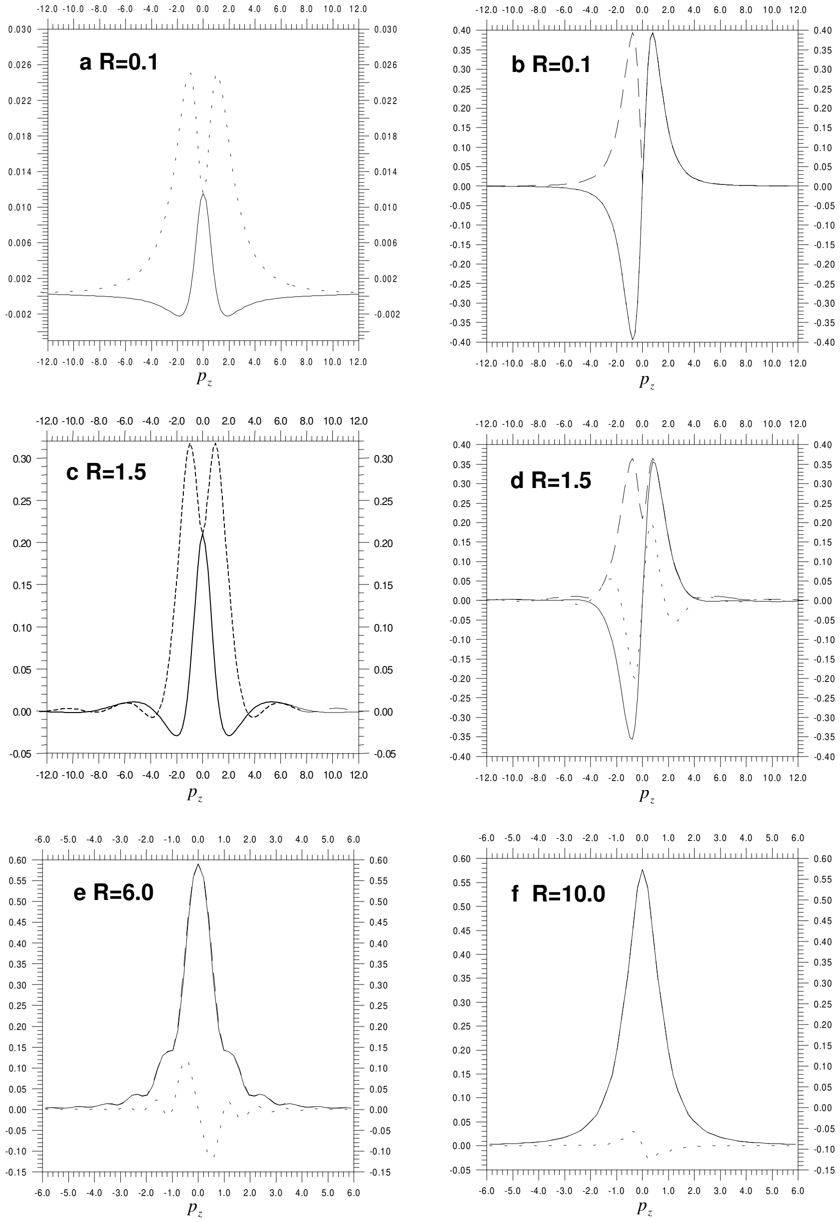


FIG. 3:

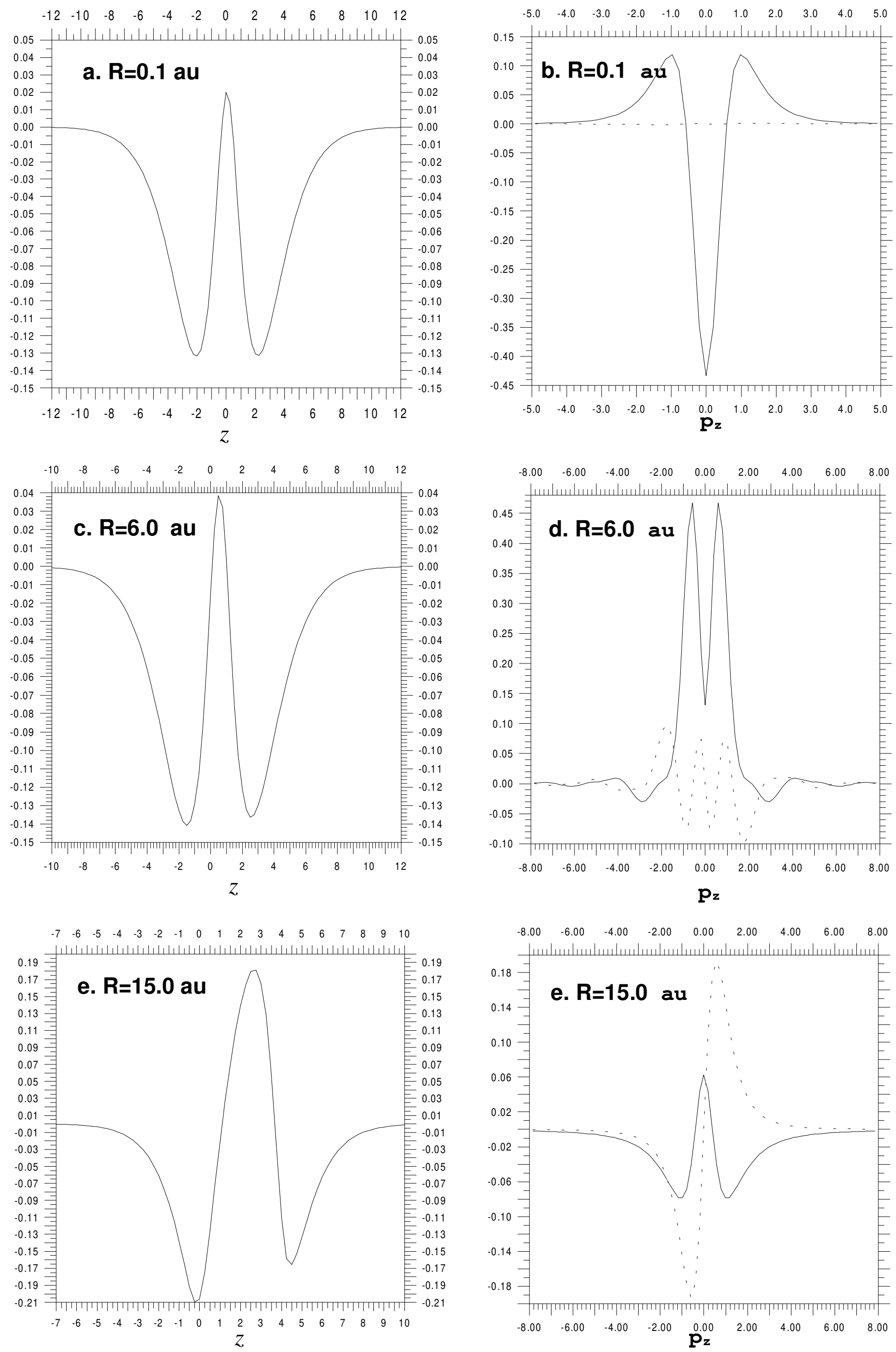


FIG. 4:

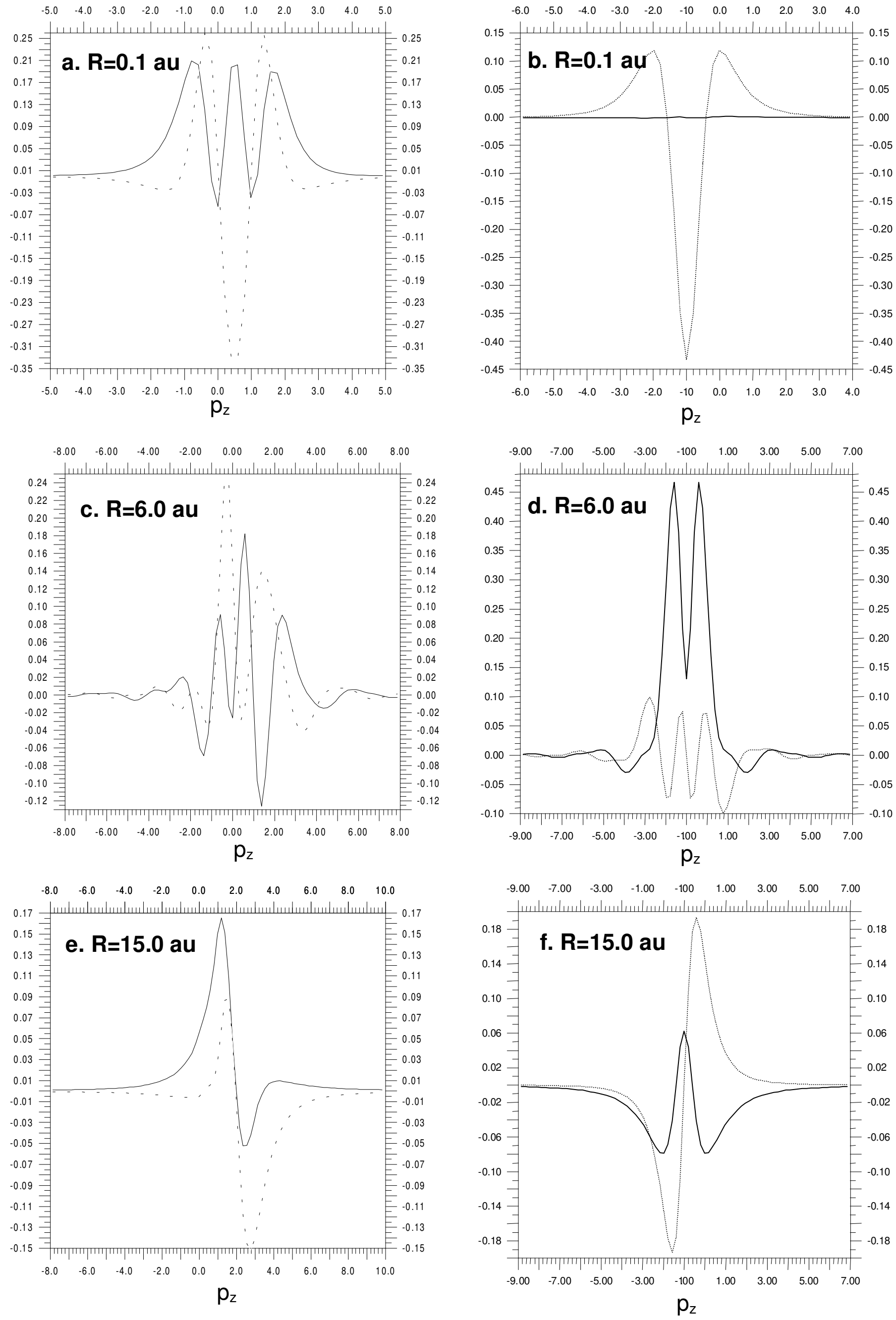
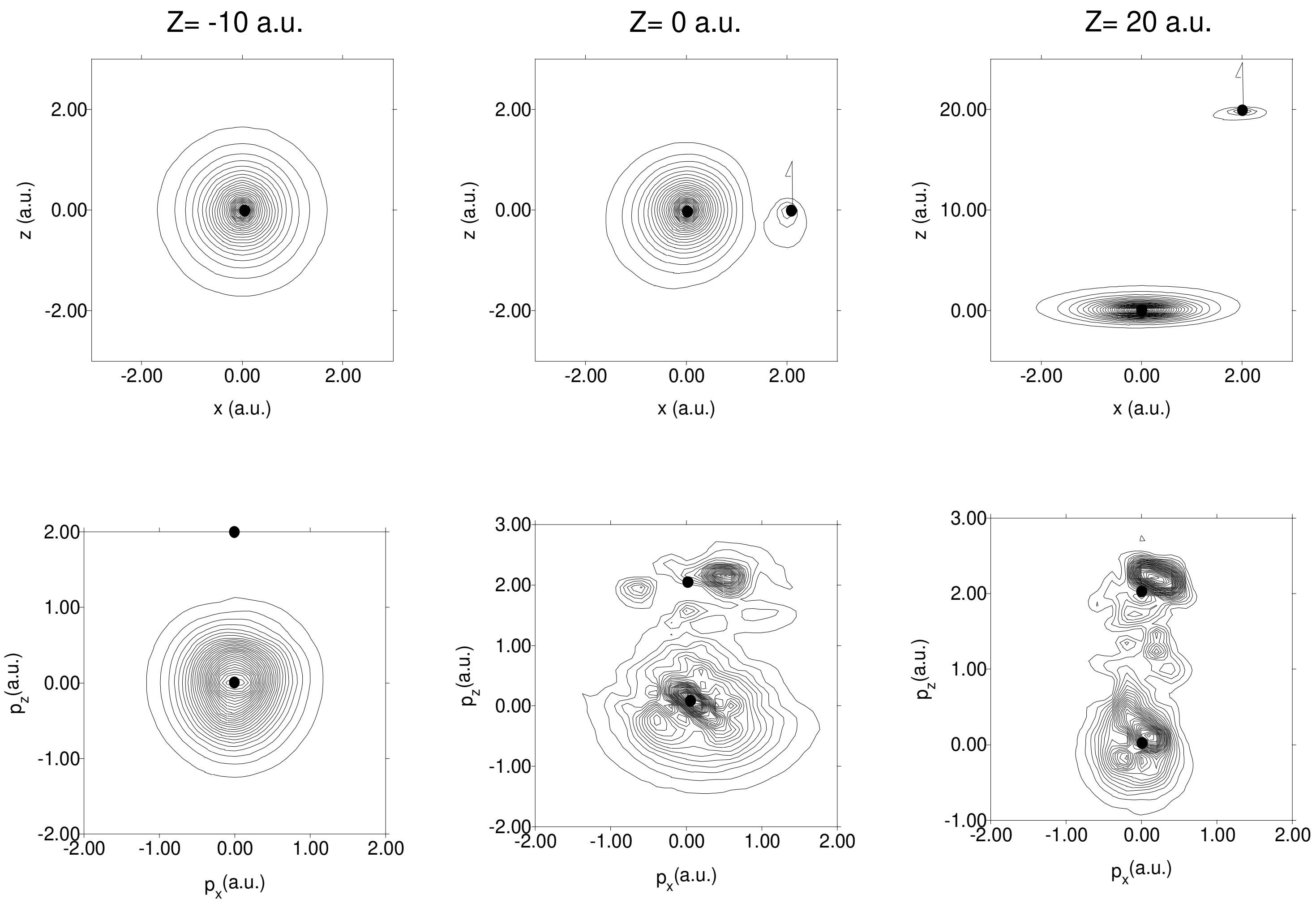


FIG. 5: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Z= 0 a.u.
Z= 20 a.u.
z (a.u.)
x (a.u.)
2.00
0.00
-2.00
10.00
20.00
p_z(a.u.)
p_x(a.u.)
-2.00
-1.00
0.00
1.00
2.00
3.00

FIG. 6:

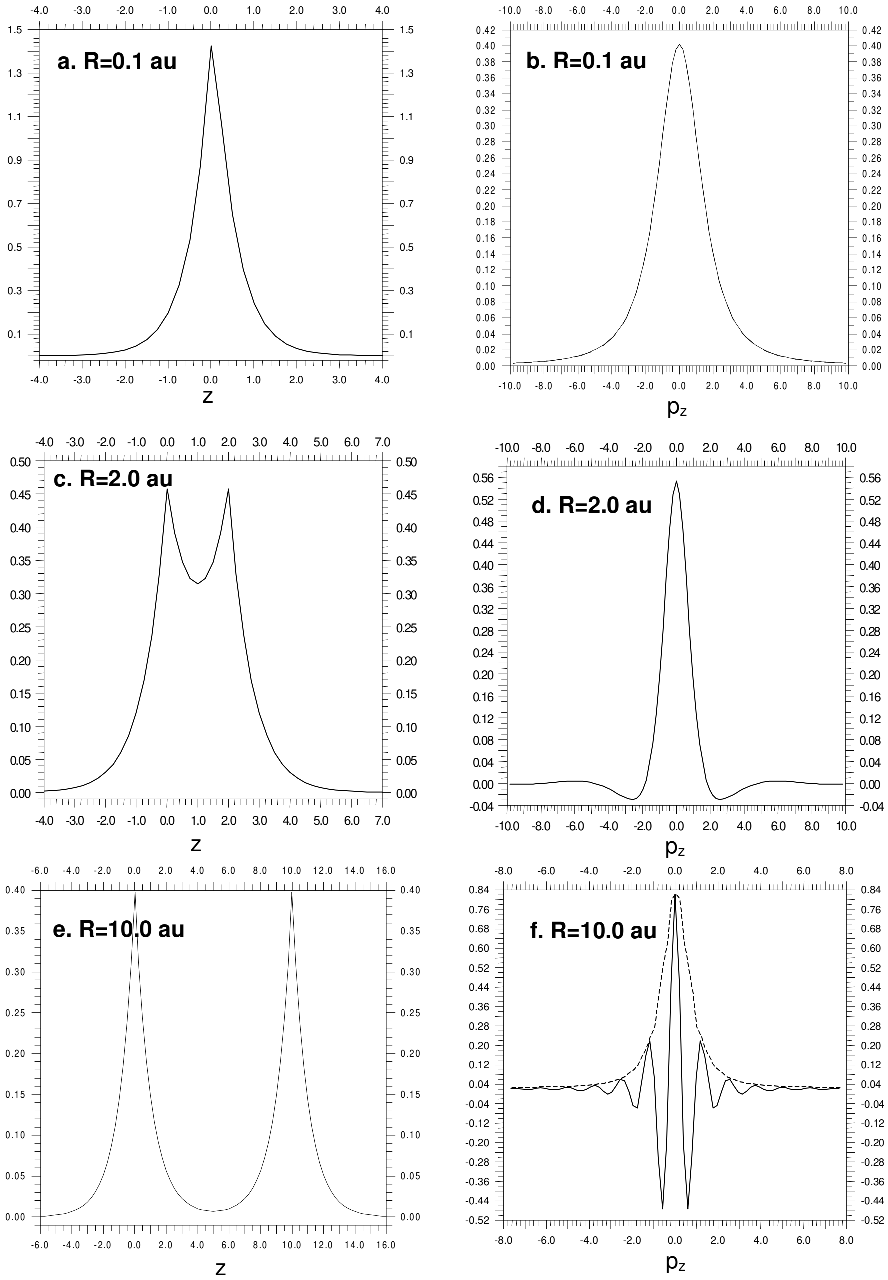

FIG. 7:

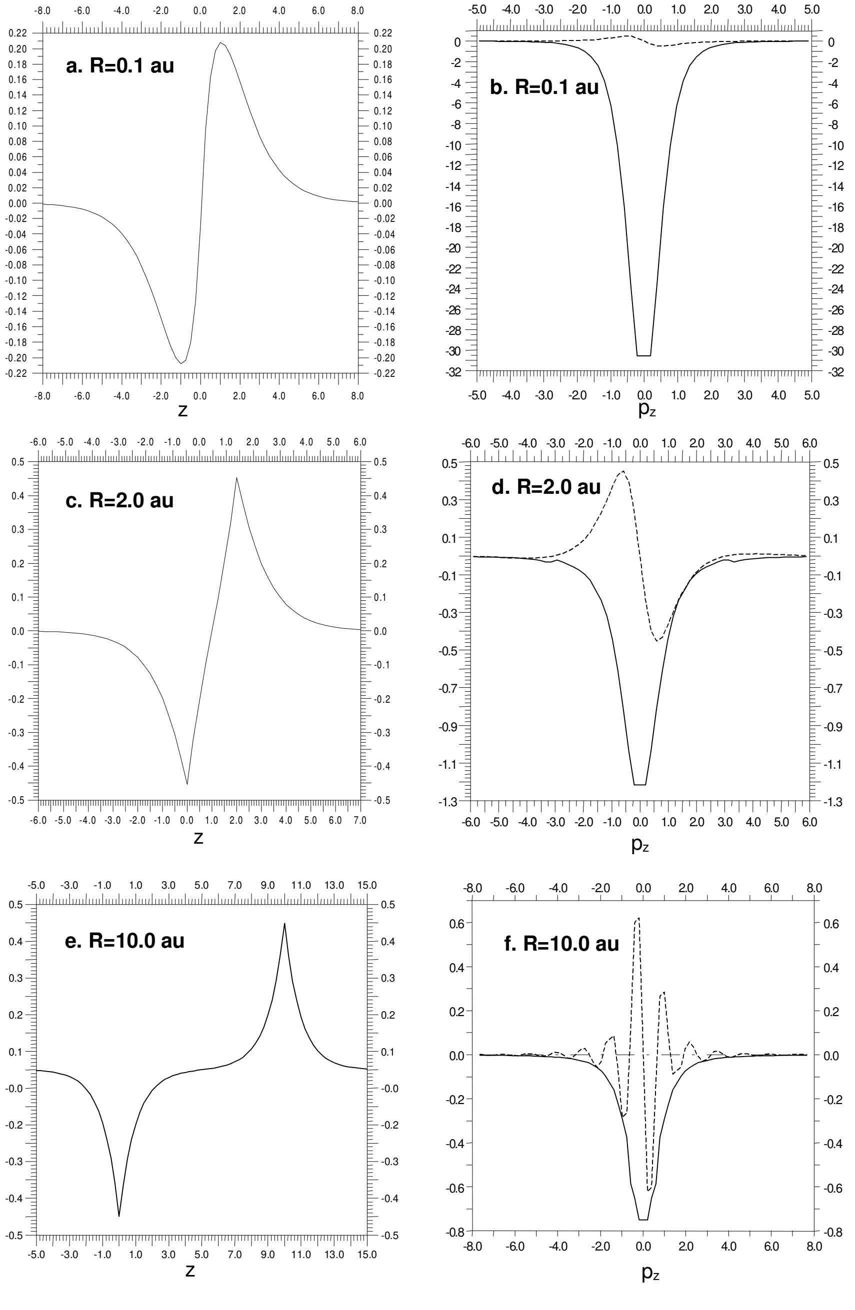

FIG. 8:

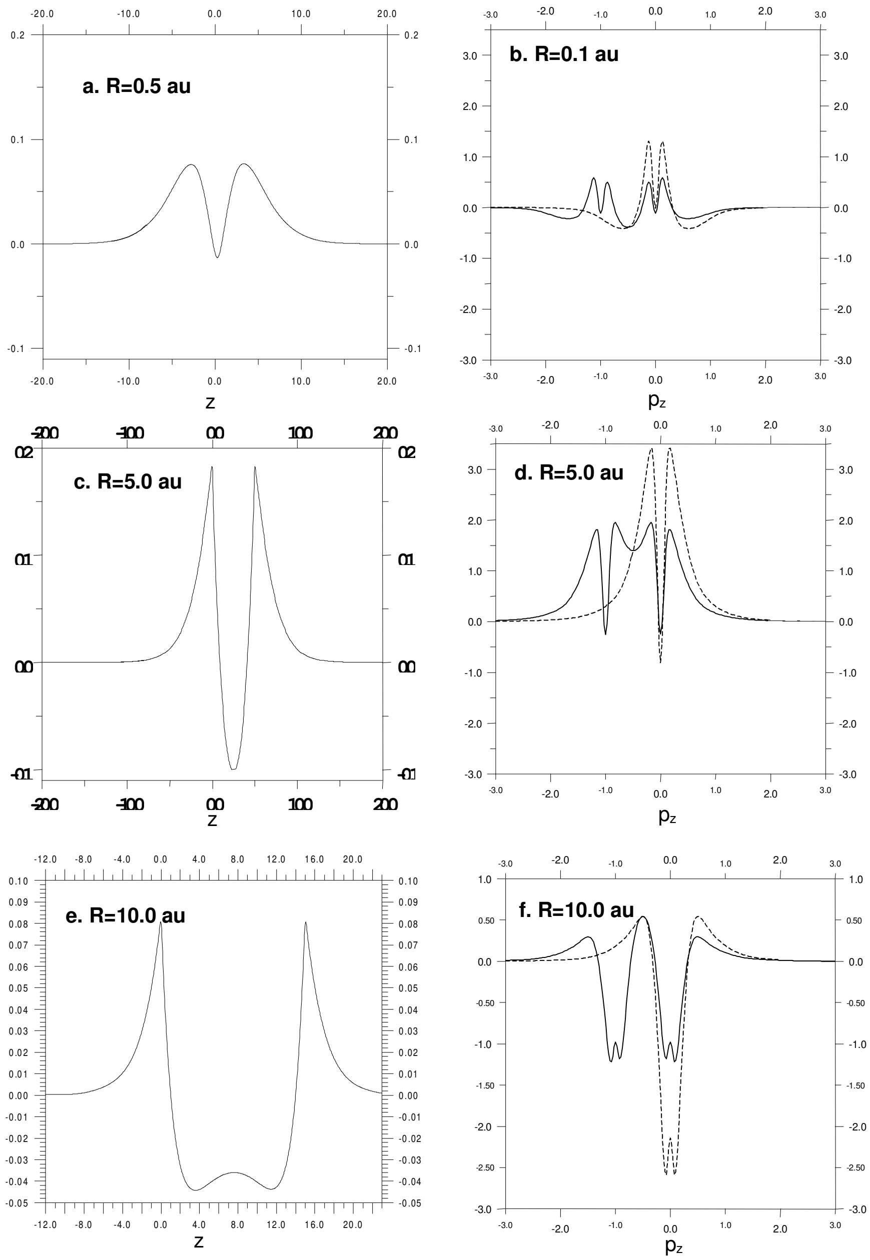

FIG. 9: