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Quantum effects of nuclear motion in three-particle diatomic ions

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A high-accuracy, nonrelativistic wave function is used to study nuclear motion in the ground state of three-particle \( \{a_1^+ a_2^+ a_3^-\} \) electronic and muonic molecular systems without assuming the Born-Oppenheimer approximation. Intracule densities and center-of-mass particle densities show that as the mass ratio \( m_{a_i}/m_{a_{j}}, \) \( i = 1, 2, \) becomes smaller, the localization of the like-charged particles (nuclei) \( a_1 \) and \( a_2 \) decreases. A coordinate system is presented to calculate center-of-mass particle densities for systems where \( a_1 \neq a_2 \). It is shown that the nuclear motion is strongly correlated and depends on the relative masses of the nuclei \( a_1 \) and \( a_2 \) rather than just their absolute mass. The heavier particle is always more localized and the lighter the partner mass, the greater the localization. It is shown, for systems with \( m_{a_1} < m_{a_2} \), that the ratio of (i) the density maximum and (ii) the FWHM of the radial distribution of each nucleus from the center of mass is directly proportional to the mass ratio of the nuclei: \( m_{a_1}/m_{a_2} \) for the former and \( m_{a_2}/m_{a_1} \) for the latter, thus quantifying a quantum effect of nuclear correlation.

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I. INTRODUCTION

One of the standard assumptions utilized within molecular quantum mechanics is the Born-Oppenheimer approximation \([1][2]\). For decades this has provided a way to simplify the Schrödinger equation for a molecule by means of separating the nuclear and electronic motions. For most applications the Born-Oppenheimer approximation is very useful because it can provide great insight into the structure of a molecular system and produce accurate results. Electronic structure theory is very well developed but the quantum theory of nuclear motion has remained in the shadow of advancements in electronic structure. With increasingly accurate experimental work, it is important to make sure that theory can remain competitive, as well as being able to model systems as accurately as possible using the fewest assumptions. A major advantage of treating a molecule nonadiabatically is that the kinematic effects of rotation and vibration are automatically included in the solution.

In this work the nonrelativistic Schrödinger equation for three-particle molecular systems \( \{a_1^+ a_2^+ a_3^-\} \) is solved using a Laguerre-based wave function with two nonlinear variational parameters when \( a_1 = a_2 \) and three when \( a_1 \neq a_2 \), and includes the quantum effects of nuclear motion directly \([3]\). No a priori assumptions as to the structure of the systems are made.

The effects of nuclear motion are investigated using intracule densities and center-of-mass particle densities. Intracule densities measure the radial correlation between the two nuclei and provide information on the dynamical behavior of the two particles and the equilibrium bond distance. The particle densities relative to the center of mass characterize the spatial distribution of each nucleus with respect to the center of mass and provide information on the extent of localization or delocalization of the particles. Previous work using density distributions focused on symmetric systems \( (a_1 = a_2) \).

Arias de Saavedra et al. \([4]\) reported intracule densities for electronic and muonic three-particle molecular systems using the Laguerre-based wave function. Mátýus et al. \([5]\) calculated the particle density at the center of mass to study the transition from atomic \( \{e^- e^- p^+\} \) to molecular \( \{p^+ p^+ e^-\} \) systems using explicitly correlated Gaussian functions and translationally invariant Cartesian coordinates. In the present work, intracule densities and center-of-mass particle densities are reported for both homonuclear \( (a_1 = a_2) \) and heteronuclear \( (a_1 \neq a_2) \) electronic and muonic diatomics. For the electronic systems the data are compared with the results of a standard Born-Oppenheimer computational chemistry calculation. A Laguerre-based wave function in perimetric coordinates (linear combinations of the interparticle coordinates) is used to calculate intracule densities. To calculate the center-of-mass particle densities a different approach is used, which combines the interparticle coordinates with barycentric mass ratios, to construct a set of coordinates that allows the particle density at the center of mass to be calculated for any three-particle system based on the interparticle distances. This coordinate system is used to determine the effects of mass and nuclear motion on the particle density distributions of homonuclear and heteronuclear three-particle molecular ions.

II. METHOD

The nonrelativistic Schrödinger equation is solved for the ground state of \( \{a_1^+ a_2^+ a_3^-\} \) three-particle molecular systems with two heavy like-charged particles \( a_1 \) and \( a_2 \) using the series solution method described in detail previously \([3,6]\). The most effective way to describe the correlation between particles in a Coulombic system is to use basis functions that explicitly depend on their interparticle distances \([7]\). Interparticle coordinates are, however, restricted by the triangular condition, Fig. 1(a), resulting in dependent integration domains. To overcome this difficulty, the problem is recast in perimetric coordinates \([8]\): linear combinations of \( r_i \) which have the advantage of being independent over the range \( 0 \rightarrow \infty \) and take the form \( z_i = r_j + r_k - r_j \). The wave function in
perimetric coordinates has the form
\[ \psi(z_1, z_2, z_3) = e^{-\frac{1}{2}(\alpha z_1^2 + \beta z_2^2 + \gamma z_3^2)} \sum_{l,m,n=0}^{\infty} A(l,m,n)L_l(\alpha z_1)L_m(\beta z_2)L_n(\gamma z_3), \]
(1)
where \( L_n(x) \) is a Laguerre polynomial of degree \( n \), and \( \alpha \), \( \beta \), and \( \gamma \) are nonlinear parameters. Substitution into the Schrödinger equation results in a 57-term recursion relation between the coefficients, which is used to form a sparse secular determinant that is solved in truncated form to give the relation between the coefficients, which is used to form a sparse algorithm [11], with all optimizations being performed in quadruple precision (32 digits) to ensure a higher level of accuracy. Both algorithms were used simultaneously to ensure the global energy minimum was found since there is the potential for multiple minima on the \((\alpha, \beta, \gamma)\) energy surface. All particle masses used in this work were taken from the 2014 CODATA recommended values [12]; \( m_e = 1 \) a.u., \( m_p = 1836.152\,673 \) a.u., \( m_d = 3670.482\,967 \) a.u., \( m_t = 5496.921\,535 \) a.u., and \( m_\mu = 206.768\,282 \) a.u. Atomic units (\( m_e = \hbar = 1, e = 1 \)) are used for electronic systems and muon-atomic units (\( m_\mu = \hbar = 1, e = 1 \)) are used for muonic systems throughout.

### III. Intracule and Center-of-Mass Particle Densities

The probability density function
\[ D_{p,a_l}^{(1)}(\mathbf{R}) = \langle \psi | \delta(\mathbf{x}_{a_l} - \mathbf{x}_P - \mathbf{R}) | \psi \rangle \]
(4)
characterizes the spatial distribution of particle \( a_l \) with respect to some body-fixed point \( P \) [13,14], which is chosen here to be either \( a_2 \) or the center of mass (denoted by \( c \)). For states with angular momentum \( L = 0 \) and parity \( p = +1 \) the wave function, and thus the particle densities, are spherically symmetric. Therefore \( D_{p,a_l}^{(1)}(\mathbf{R}) \), \( P = a_2 \) or \( c \), are spherically symmetric and their values depend only on the length of \( \mathbf{R} \). Following [13], we can introduce
\[ \rho_{p,a_l}(r) = D_{p,a_l}^{(1)}(\mathbf{R}), \]
(5)
with \( \mathbf{R} = (0,0,r) \) and \( r = \| \mathbf{r} \|, r \in \mathbb{R}_0^+ \). When \( P \) is chosen to be \( a_2 \) this gives rise to the intracule density which in the interparticle coordinates defined in Fig. 1(a) is given by
\[ h(r) \equiv \rho_{p,a_l}(r) = \langle \psi | \delta(r_3 - r) | \psi \rangle \]
(6)
The intracule density measures the radial correlation between the two heavy like-charged particles \( a_1 \) and \( a_2 \), where \( r_3 \) is the distance between them. It is a two-particle pair density and evaluates the relative motion of these particles, and is normalized to unity such that \( 4\pi \int_0^{\infty} r^2\rho_{p,a_l}(r) \, dr = 1 \). Throughout the text, \( 4\pi r^2 h(r) \) will be referred to as the radial intracule distribution and \( h(r) \) as the intracule density.

The second reference point used is the center of mass. Mátys et al. [5] measured the particle density of the like-charged particles from the center of mass using translationally invariant Cartesian coordinates. In this work a different approach is used which combines the interparticle coordinate system \( r_1, r_2, \) and \( r_3 \) and barycentric mass ratios \( \lambda_1, \lambda_2, \) and \( \lambda_3 \), to construct a coordinate system. This allows the particle density to be calculated from the center of mass to any of the three particles, and thus is suitable for the high-accuracy wave function in perimetric coordinates given by Eq. (1).

A three-particle system \((a_1^- a_2^- a_3^-)\) forms a triangle, with the masses located at the vertices and sides labeled by the interparticle distances \( r_{12}, r_{23}, \) and \( r_3 \) [Fig. 1(a)]. Barycentric coordinates are a natural framework for this problem, because the barycenter is defined as the center of mass of a triangle where masses have been placed at its vertices [15]. The coordinate system \((r_1, r_2, r_3)\) is transformed into \((r_{12}, s_1, i)\), \( i = 1 \) or \( 2 \), Fig. 1(b), by a coordinate transformation.
TABLE I. Electronic energy $E$ (a.u.), dissociation energy $D_0$ (cm$^{-1}$), and bond length $r$ (a.u.) for the nonadiabatic and Born-Oppenheimer electronic hydrogen molecule isotopologues ($m_2 = 1, \tilde{h} = 1, e = 1$), and the muonic energy (m.a.u.), dissociation energy (cm$^{-1}$), and bond-length (m.a.u.) for muonic hydrogen molecule isotopologues ($m_\mu = 1, \tilde{h} = 1, e = 1$). A wave function corresponding to $\omega = 30$ (see text for details) was used to obtain the nonadiabatic data.

<table>
<thead>
<tr>
<th>Energy $^a$</th>
<th>Born-Oppenheimer</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^+\mu^-e^-$</td>
<td>$E_{BO} +$ZPE $^b$, $r_{BO}$, $D_0$(BO)</td>
<td>$r_{expt}^c$, $D_0$(expt.)</td>
</tr>
<tr>
<td>$p^+p^-e^-$</td>
<td>$-0.585 126 098 25$</td>
<td>$2.205 215 237$</td>
</tr>
<tr>
<td>$d^+d^-e^-$</td>
<td>$-0.597 139 063 07$</td>
<td>$2.063 913 867$</td>
</tr>
<tr>
<td>$t^+t^-e^-$</td>
<td>$-0.599 506$</td>
<td>$2.044 070 029$</td>
</tr>
<tr>
<td>$p^+d^-e^-$</td>
<td>$-0.599 879 968 60$</td>
<td>$2.054 803 238$</td>
</tr>
<tr>
<td>$p^+t^-e^-$</td>
<td>$-0.598 788 784$</td>
<td>$2.051 456 621$</td>
</tr>
<tr>
<td>$d^+t^-e^-$</td>
<td>$-0.599 130 661$</td>
<td>$2.039 939 515$</td>
</tr>
<tr>
<td>$\mu^+\mu^-e^-$</td>
<td>$-0.262 005 070 23$</td>
<td>$8.548 580 655$</td>
</tr>
<tr>
<td>$p^+p^-\mu^-$</td>
<td>$-0.494 386 812 860$</td>
<td>$3.299 486$</td>
</tr>
<tr>
<td>$d^+d^-\mu^-$</td>
<td>$-0.531 111 130 611$</td>
<td>$2.834 451$</td>
</tr>
<tr>
<td>$t^+t^-\mu^-$</td>
<td>$-0.546 374 222 033$</td>
<td>$2.652 824$</td>
</tr>
<tr>
<td>$p^+d^-\mu^-$</td>
<td>$-0.512 711 790 563$</td>
<td>$3.100 710$</td>
</tr>
<tr>
<td>$p^+t^-\mu^-$</td>
<td>$-0.519 880 084 536$</td>
<td>$3.036 524$</td>
</tr>
<tr>
<td>$d^+t^-\mu^-$</td>
<td>$-0.538 594 970 881$</td>
<td>$2.747 914$</td>
</tr>
</tbody>
</table>

$^a$All digits presented are converged. Bold digits in agreement with [17] for electronic systems and [32] for muonic systems. Note, older mass data are used by [17] and [32].

$^b$Bold digits in agreement with [17] for electronic systems (except for $\mu^+\mu^-e^-$ which was taken from [18]). Muonic systems were compared to data in the papers of Frolov [18,20,33,34].

$^c[35]$

$^d[36,37]$

$^e[36,38]$

$^f[39]$

The center of mass is the barycenter of the three masses and it will have a position vector relative to either particle $a_1$ or $a_2$ given by

$$s_i = \lambda_1 r_3 + \lambda_2 r_1, \quad i, j = 1 \text{ or } 2, \quad i \neq j.$$  \hspace{1cm} (7)

The $\lambda_i$ are normalized barycentric coordinates given by $\lambda_i = m_i/(m_1 + m_2 + m_3)$, where $\lambda_1 + \lambda_2 + \lambda_3 = 1$ and $(i,j,k) = (1,2,3)$ by cyclic permutation. The length $s_i = |s_i|$ obtained using simple trigonometry is

$$s_i = |s_i| = \sqrt{(\lambda_i r_i - \lambda_j r_j)^2 + \lambda_j \lambda_3 (r_i + r_j)^2 - r_j^2},$$  \hspace{1cm} (8)

$$i, j = 1 \text{ or } 2, \quad i \neq j.$$  

Because unsymmetric systems are considered in this work, the particle densities measured from each of the like-charged

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FIG. 2. Intracule densities $h(r)$ for (a) electronic systems (in atomic units) and (b) muonic systems (in muon-atomic units, where 1 m.a.u. = $\frac{1}{368.582}$ a.u.). The inset corresponds to $[\mu^+\mu^-\mu^-]$.  

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particles $a_1$ and $a_2$ are treated separately. The particle density measured from $a_1$ is denoted as $ρ_{c,a_1}(s)$ and the particle density measured from $a_2$ is denoted as $ρ_{c,a_2}(s)$ and they are calculated using the form

$$ρ_{c,a}(s) = \langle ψ|δ(x_a - x_c - s)|ψ⟩ = \langle ψ|δ(s_i - s)|ψ⟩,$$

$i = 1$ or $2$. (9)

The center-of-mass particle density is normalized according to $4π \int_0^∞ s^2ρ_{c,a}(s)ds = 1$. For homonuclear diatomics, $ρ_{c,a_1}(s) = ρ_{c,a_2}(s)$, and the density distribution of the heavy particles will be symmetric about the center of mass. This is not the case for heteronuclear diatomics with $a_1 \neq a_2$, as $ρ_{c,a_1}(s) \neq ρ_{c,a_2}(s)$. To facilitate comparison between heteronuclear systems the radial (spherically averaged) center-of-mass distribution, $4πs^2ρ_{c,a}(s)$, will also be presented.

IV. RESULTS AND DISCUSSION

A. Energy and wave function

The energy as a function of wave-function (matrix) size and various expectation values such as interparticle distances and their powers, the two- and three-particle Dirac δ functions, two-particle cusps, and interparticle cosine functions used to determine the convergence of the energy and the quality of the wave function are provided in the Supplemental Material (SM) [16]. All values are converged to at least six significant figures, determined by comparison with highly accurate literature values [17–20] and by comparison with exact values (such as the Kato cusp condition [21] and the Virial condition). The exception is the nuclear-nuclear cusp for the electronic hydrogen molecule isotopologues (a known problem discussed by [19]).

A major advantage of treating a molecule nonadiabatically is that the kinematic effects of rotation and vibration are automatically included in the solution. Table I provides the nonadiabatic (fully correlated) ground-state energy and the expectation value of the internuclear distance ($r_3$) for the electronic and muonic hydrogen molecule isotopologues. Also provided is the zero-point energy (ZPE) corrected Born-Oppenheimer (BO) energy, and the bond length obtained from a standard computational chemistry calculation using the Gaussian09 software package [22] at the Hartree-Fock (HF) level of theory with a very large aug-cc-pV6Z basis set. (For a one-electron system a fully correlated method such as the configuration interaction (CI) or coupled-cluster method is redundant because CI/aug-cc-pV6Z, etc., is equivalent to HF/aug-cc-pV6Z at the minimum on the potential energy surface.) As the masses of the nuclei increase, the kinetic energy (which is always positive) becomes smaller, which in the limit of infinite nuclear mass (BO approximation) becomes zero. This is reflected in the ZPE corrections provided by a frequency calculation at the minimum of the BO potential energy surface (as $E_{BO} = -0.6026329$ a.u. for all isotopologues). This energy stabilization as the nuclear masses increase is also true for the muonic hydrogen molecule isotopologues.

Table I also compares experimental dissociation energies and equilibrium bond distances (where available) with those calculated from the current work and the ZPE-corrected BO values. The expectation values are in excellent agreement with those of [17]. These authors have attributed the shortening of the bond length ($r_3$) as the nuclear masses become heavier, which cannot be explained in the BO approximation, to the fact that the electrons tend to be more attracted to the heavier nucleus because it has less motion [17]. However, the internuclear distance determined by the maximum in the intracule density (below) follows the trend in the experimental bond length. Table I demonstrates that for very accurate dissociation energies, and to explain variations in structural data of the isotopologues, it is important to include the coupling of the electronic and nuclear motions. Also included are the data for muonic systems which are in good agreement with the work of Bhatia and Drachman [23]. The dissociation energies are nearly two orders of magnitude greater than those of the electronic systems, demonstrating the much stronger binding due to the greater mass of the muon.

Furthermore, the energy difference between eigenvalues, obtained from a single diagonalization of the secular determinant, provides the vibrational frequency. The frequency for $H_2^+$ between the ground and first excited vibration state ($ν = 0$ and 1) is 2191.099 52 cm$^{-1}$ which is in excellent agreement with experiment (2191.2 ± 0.2 cm$^{-1}$, [24] and the very high

<table>
<thead>
<tr>
<th>$r_{max}$</th>
<th>$h(r_{max})$</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$μ^+μ^+e^-$</td>
<td>1.977 798</td>
<td>0.018 245</td>
</tr>
<tr>
<td>$p^+p^+e^-$</td>
<td>2.136 628</td>
<td>0.970 123</td>
</tr>
<tr>
<td>$d^+d^+e^-$</td>
<td>1.989 685</td>
<td>0.033 910</td>
</tr>
<tr>
<td>$t^+t^+e^-$</td>
<td>2.041 771</td>
<td>1.731 407</td>
</tr>
<tr>
<td>$p^+d^+e^-$</td>
<td>1.991 768</td>
<td>0.040 740</td>
</tr>
<tr>
<td>$p^+t^+e^-$</td>
<td>2.026 677</td>
<td>2.068 576</td>
</tr>
<tr>
<td>$d^+t^+e^-$</td>
<td>2.022 506</td>
<td>2.291 297</td>
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<td>$d^+d^+e^-$</td>
<td>1.990 635</td>
<td>0.036 610</td>
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<td>2.035 674</td>
<td>1.864 502</td>
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<td>2.032 119</td>
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<td>1.992 169</td>
<td>0.042 725</td>
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<td>2.166 764</td>
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<tr>
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<td>0.000 459</td>
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<td>6.263 763</td>
<td>0.111 155</td>
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<td>1.984 563</td>
<td>0.004 779</td>
</tr>
<tr>
<td>$p^+p^+μ^-$</td>
<td>2.867 104</td>
<td>0.351 625</td>
</tr>
<tr>
<td>$d^+d^+μ^-$</td>
<td>1.967 179</td>
<td>0.007 125</td>
</tr>
<tr>
<td>$d^+d^+μ^-$</td>
<td>2.559 161</td>
<td>0.457 461</td>
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<td>$t^+t^+μ^-$</td>
<td>1.965 083</td>
<td>0.008 645</td>
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<td>2.437 699</td>
<td>0.525 613</td>
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<td>$p^+d^+μ^-$</td>
<td>1.977 355</td>
<td>0.003 610</td>
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<td>$p^+t^+μ^-$</td>
<td>2.728 007</td>
<td>0.389 979</td>
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<tr>
<td>$p^+t^+μ^-$</td>
<td>1.976 818</td>
<td>0.005 966</td>
</tr>
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<td>$d^+t^+μ^-$</td>
<td>2.679 483</td>
<td>0.405 077</td>
</tr>
<tr>
<td>$d^+t^+μ^-$</td>
<td>1.966 082</td>
<td>0.007 787</td>
</tr>
<tr>
<td>$2.500 945$</td>
<td>$0.487 131$</td>
<td>$1.912 104$</td>
</tr>
</tbody>
</table>
corresponds to the center of mass. (Note scale, 1 m.a.u.

Within the BO approximation, the vibrational frequencies are calculated from the potential energy curve, but their values are approximate because the coupling of the electronic and nuclear motions is completely neglected.

B. Intracule densities

The intracule densities $h(r)$ for both the electronic and muonic homonuclear and heteronuclear molecular systems are shown in Fig. 2. The intracule densities for the symmetric systems are in excellent agreement with those available in the literature [4]. (Arias et al. [25] also studied nonsymmetric systems in a later paper but did not present intracule densities.)

The key features of the intracules [the maximum in the distribution $r_{\text{max}}$, the density at that point $h(r_{\text{max}})$, and the FWHM for each spatial distribution] are provided in Table II. Also provided (in italics) are the data for the radial intracule distributions which have a very similar profile to those shown in Fig. 2 but $r_{\text{max}}$, which corresponds to the most probable internuclear distance, is shifted slightly to greater distance.

The maximum in the density occurs at $r_{\text{max}} \approx 2$ a.u. for the electronic systems, i.e., close to the Born-Opffenheimer result, and $r_{\text{max}} = 2/m_p \approx 9.672 \times 10^{-3}$ a.u. for the muonic.
systems, with the exception of \( \{ \mu^+ \mu^+ \mu^- \} \) which peaks at a much greater distance (Table II). In line with the principles of muon catalyzed fusion [26] [27], the nucleus-nucleus bond length decreases significantly when the electron is replaced by the heavier muon. The mass ratio \( a_i/a_3 \), \( i = 1 \) or 2, controls the localization of the intracule densities; and as \( a_i/a_3 \) gets smaller, e.g., \( a_1 \to t^+ \to d^+ \to p^+ \to \mu^+ \), the intracule densities become more diffuse for both the electronic and muonic systems. This “uncertainty” in the internuclear distance (Fig. 2) is a manifestation of the vibrational motion in the BO picture. The distribution is approximately symmetric about the maximum in the distribution (cf. the vibrational wave function of the harmonic oscillator on the BO potential curve), but is not completely symmetric since the present work contains the non-BO coupling of the electronic and nuclear motions and the inherent anharmonicity of the vibrational motion.

C. Center-of-mass densities

Figure 3 shows density plots of \( \rho_{c,a}(s) \) along the plane given by resolving \( s \) into \( x \) and \( y \) components. The center of mass is at the center of each plot. The shell-like density plots indicate that the like-charged particles are most likely found in a shell, of finite width, at a given distance from the center of mass. For the homonuclear ions a single shell arises and the width of the shell increases as the masses of the heavy particles decrease to the point at which the zero density at the center of mass disappears in the \( \{ \mu^+ \mu^+ \mu^- \} \) system. For the heteronuclear systems, the distance of the shell from the center of mass and the width of the shell are dependent on the relative masses of the particles. In the case of the muonic systems, these shells appear to merge.

Figures 4 and 5 show cuts of the three-dimensional spherically symmetric particle density relative to the center of mass, in homonuclear and heteronuclear ions, respectively.
FIG. 5. Center-of-mass particle densities for heteronuclear diatomic ions for (a) electronic systems and (b) muonic systems, and radial center-of-mass particle density distributions for (c) electronic systems and (d) muonic systems. For (c) and (d) the area under each peak is equal to 1. The center of mass coincides with the origin and the left peak corresponds to $\rho_{c,a_1}(s)$ and the right peak $\rho_{c,a_2}(s)$ where in each case $m_{a_1} \leq m_{a_2}$. (Note scale, 1 m.a.u. = $\frac{1}{206.768.282.6}$ a.u.)

The key features of radial center-of-mass densities are provided in Table III. For the homonuclear systems in Fig. 4, the center-of-mass position is situated adjacent to the midpoint of $r_3$. Due to the negligible effect of the electron on the center-of-mass position, the peak-to-peak distances are in excellent agreement with the $r_{max}$ positions from the radial intracule distribution plots (Table II) and therefore give an indication of the internuclear distance. However, the peak-to-peak separation ($s_{1max} + s_{2max}$, Table III) and $r_{max}$ in the radial intracule distribution (Table II) are not in quite such good agreement for muonic systems where the mass ratio $m_i/m_3$, $i = 1,2$ is smaller, the BO separation is less appropriate, and the spatial distributions are more diffuse.

The localization of the particle density is governed by the mass of the particles, as $a_1 = a_2 \rightarrow t^+ \rightarrow d^+ \rightarrow p^+ \rightarrow \mu^+$ the FWHM increases. The FWHM for each peak in $\{t^+t^+e^-\}$ is 0.205 a.u. and for $\{\mu^+\mu^+e^-\}$ it is 0.483 a.u., which corresponds to an increasing mass ratio $a_3/a_i$, $i = 1,2$. The finite width of the center-of-mass particle densities in homonuclear diatomics has been attributed to the zero-point vibration of the nuclei in the Born-Oppenheimer treatment [5]. The center-of-mass particle densities $\rho_{c,a_i}(s)$ show that the distribution of the like-charged particles is essentially zero at the center of mass in the electronic systems, but as the mass of the uniquely charged particle $a_3$ increases, a minimum in the particle density at the center of mass appears. The inset of Fig. 4(b) shows that when all the particles have the same mass, a nonzero minimum in the particle density is apparent. Due to the mass-scale similarity and the charge-inversion invariance of the Coulomb Hamiltonian, this is indicative of the onset of the molecular to atomic transition, observed previously for the positronium negative ion [5].

The heteronuclear ions, $\{p^+d^+e^-\}$, $\{p^+t^+e^-\}$, $\{d^+t^+e^-\}$, and $\{p^+t^+\mu^-\}$, $\{p^+\mu^+e^-\}$, $\{d^+t^+\mu^-\}$, display a very different
TABLE III. Key features of the radial center-of-mass particle density distributions provided in Figs. 4 and 5, where \( s_i \) corresponds to the lighter particle and \( s_i \) the heavier particle in the heteronuclear diatomic ions \( \{a_i^+ a_i^+ a_j^-\} \). Values in atomic units (electronic systems) and muon-atomic units (muonic systems).

<table>
<thead>
<tr>
<th>( m_i^+ m_j^- e^- )</th>
<th>( s_{i_{\text{max}}} )</th>
<th>( \rho(s_{i_{\text{max}}}) )</th>
<th>( \text{FWHM} (s_1) )</th>
<th>( s_{j_{\text{max}}} )</th>
<th>( \rho(s_{j_{\text{max}}}) )</th>
<th>( \text{FWHM} (s_2) )</th>
<th>( s_{i_{\text{max}}} + s_{j_{\text{max}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p^+ p^- e^- )</td>
<td>1.068 309</td>
<td>1.940 095</td>
<td>0.483 222</td>
<td>1.068 309</td>
<td>1.940 095</td>
<td>0.483 222</td>
<td>2.136 618</td>
</tr>
<tr>
<td>( d^+ d^- e^- )</td>
<td>1.020 850</td>
<td>3.462 470</td>
<td>0.271 140</td>
<td>1.020 650</td>
<td>3.462 470</td>
<td>0.271 140</td>
<td>2.041 706</td>
</tr>
<tr>
<td>( t^+ t^- e^- )</td>
<td>1.013 338</td>
<td>4.109 394</td>
<td>0.228 804</td>
<td>1.013 338</td>
<td>4.109 394</td>
<td>0.228 804</td>
<td>2.026 676</td>
</tr>
<tr>
<td>( p^+ d^- e^- )</td>
<td>0.5003</td>
<td>3.4890</td>
<td>0.205 031</td>
<td>0.5003</td>
<td>3.4890</td>
<td>0.205 031</td>
<td>2.022 506</td>
</tr>
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<td>0.5003</td>
<td>3.4890</td>
<td>0.205 031</td>
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<td>3.4890</td>
<td>0.205 031</td>
<td>2.022 506</td>
</tr>
</tbody>
</table>

In the BO picture the mass-weighted coordinate displacement of the like-charged particles relative to the center of mass is inversely proportional to their mass ratio \( m_i/m_j \). For example, for \( H_2^+ \) or \( D_2^+ \) the ratio of these peak heights is \( 0.5003 \), which is in excellent agreement with \( m_p/m_d = 0.5002 \). For \( d^+ t^- e^- \), the ratio of these peak heights is \( 0.5003 \), which is in excellent agreement with \( m_d/m_t = 0.5002 \). The ratio of these peak heights is \( 0.5003 \), which is in excellent agreement with \( m_d/m_t = 0.5002 \).

Also revealed in Fig. 5 is that the relative masses of the nuclei further control the localization of the particle density, rather than just their absolute mass. The heavier particle is always more localized and, the lighter the partner mass, the greater the localization.

In the BO picture the mass-weighted coordinate displacements along the internuclear axis (normal mode of vibration) result in a similar feature. For example, the vibrational displacements for \( H_2^+ \) or \( D_2^+ \) are approximately \( \pm 0.71 \), and for HD\(^+\) are 0.89 for the proton and \(-0.45\) for the deuteron (i.e., the ratio of the displacements is inversely proportional to their mass ratio). In the nonadiabatic radial center-of-mass distributions a similar relation arises naturally from the fully correlated treatment. The ratio of \( s_{i_{\text{max}}} \) to \( s_{j_{\text{max}}} \) is inversely proportional to their mass ratio. Furthermore, the ratio of the FWHM of the distribution for each nucleus is inversely proportional to the mass ratio \( m_i/m_j \). For example, for \( d^+ t^- e^- \), the ratio of these peak heights is \( 1.4975 \) and \( 0.9990 \), which is in excellent agreement with \( m_d/m_t = 0.9990 \). Additional information provided by this nonadiabatic treatment reveals that the relative peak heights of the radial center-of-mass particle density distribution of the heavy particles, Fig. 5(c) and Table III, are directly proportional to their mass ratios. For example, a comparison of \( \{p^+ d^- e^-\} \) and \( \{d^+ t^- e^-\} \) shows that the heavier particle in \( \{p^+ d^- e^-\} \) has a greater localization in position than the deuteron in \( \{d^+ t^- e^-\} \). To quantify, in \( \{p^+ d^- e^-\} \), \( \rho_{c,d^+}(s_{\text{max}}) = 2.6749 \) and \( \rho_{c,d^+}(s_{\text{max}}) = 5.3465 \) (Table III), and the ratio of these peak heights is \( 0.5003 \), which is in excellent agreement with \( m_d/m_t = 0.5002 \). For \( d^+ t^- e^- \), the ratio of these peak heights is \( 0.5003 \), which is in excellent agreement with \( m_d/m_t = 0.5002 \). This is also true for the muonic systems shown in Fig. 5(d) and with agreement to just two significant figures, due to a greater coupling between the nuclear and muonic motions.

This demonstrates not only that the quantum effects of nuclear motion are correlated but also that the nature of the distribution is dependent on the other particle. Furthermore, molecular structural features are emerging from a method originally designed and applied with great success for atomic systems [9,28,29] that makes no a priori assumptions about the nature of the system.

V. CONCLUSION

A high-accuracy, nonrelativistic wave function is used to study nuclear motion in the ground state of three-particle \( \{a_1^+ a_2^- a_3^-\} \) electronic and muonic molecular systems. All particles were treated on an equal footing. Intracule densities were calculated for a variety of molecular systems and as the mass ratio \( a_i/a_3 \), \( i = 1 \) or 2 becomes smaller, the localization of the like-charged particles \( a_1 \) and \( a_2 \) is seen to decrease, which is characterized by the intracule density becoming more delocalized. A coordinate system is used to calculate center-of-mass particle densities for systems where \( a_1 \neq a_2 \). The center-of-mass particle density shows that there is significant nuclear correlation: the spatial distribution of a given nucleus is dependent on the mass of the other nucleus in the diatomic ion. Recently [30,31], it was shown that molecular systems are quite stable to breaking of the mass symmetry of the like-charged particles, contrary to the situation found for atomic systems. In the present work, it is shown that it is this difference in the heavy masses that characterizes the particle density distribution of the like-charged particles relative to the center of mass. The spatial localization of each nucleus is...
quantified in terms of $\rho_{c,a}(s_{\text{max}})$ and the FWHM. It is found that $\rho_{c,a}(s_{\text{max}})/\rho_{c,a}(s_{\text{max}})$ is directly proportional to $m_{c,a}/m_{a}$ and that the ratio of the FWHM is directly proportional to $m_{c,a}/m_{a}$. The results presented in this paper quantify the quantum effects of nuclear motion.

ACKNOWLEDGMENTS

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[35] Taken from NIST: http://webbook.nist.gov/chemistry/ and converted from Å to a.u. using the conversion 1 a.u. (Bohr) $= 0.529 177 210 67 Å; NIST values: H$_2$: 1.052 Å, D$_2$: 1.0559 Å, T$_2$: 1.0566 Å. .