Time-Dependent Multi-Component Density Functional Theory for Coupled Electron-Positron Dynamics

Yasumitsu Suzuki, Satoshi Hagiwara, and Kazuyuki Watanabe

1Department of Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

(Dated: June 13, 2018)

Electron-positron interactions have been utilized in various fields of science. Here we develop time-dependent multi-component density functional theory to study the coupled electron-positron dynamics from first principles. We prove that there are coupled time-dependent single-particle equations that can provide the electron and positron density dynamics, and derive the formally exact expression for their effective potentials. Introducing the adiabatic local density approximation to time-dependent electron-positron correlation, we apply the theory to the dynamics of a positronic lithium hydride molecule under a laser field. We demonstrate the significance of electron-positron dynamical correlation by revealing the complex positron detachment mechanism and the suppression of electronic resonant excitation by the screening effect of the positron.

When a low-energy positron beam is directed to a material, the incident positron diffuses inside the bulk and is finally annihilated with atomic electrons and γ rays are emitted [1]. Analysis of these γ rays provides various information related with the surface structures, lattice defects, and electronic structures of the materials [1–3]. The analysis of positron-annihilation γ rays has been utilized in many applications, such as positron annihilation spectroscopy [4] and positron emission tomography [5]. The positron-material interaction plays a key role in these experiments [6]. The interaction between positron and atom or molecule has also been widely studied to better understand how positrons interact with atomic electrons and are bound to them [7–8]. An experiment that measured positron-atom binding energies through the study of positron-atom recombination under a laser field was recently reported [9].

Theoretical approaches to study these positron physics have been extensively developed [10]. Among them, two-component density functional theory (2C-DFT) [2, 11], which is an extension of DFT [12] to the coupled electron-positron system, has been a powerful first-principles tool to calculate the ground-state electron and positron densities and their properties. 2C-DFT has been successfully applied to studies of positron interaction with atoms, solids and surfaces to determine the electron-positron momentum distributions [13], positron annihilation lifetimes [14], and positron binding energies [15], to name a few. Another powerful method is the wavefunction-based approach, such as the multi-component molecular orbital method [16] and quantum Monte Carlo method [17, 18], which have also revealed much positron physics with high accuracy. However, the dynamical interaction mechanism between positrons and electrons, especially under a laser field [7–9], has not yet been clarified, because there has been no first-principles method that can simulate the correlated dynamics of positrons and electrons for realistic systems.

In this study, we develop time-dependent multi-component density functional theory (TDMCDFT) [19, 20] toward an understanding of the mechanism of coupled electron-positron dynamics. Time-dependent density functional theory (TDDFT) [21–23] has enabled us to simulate real-time many-electron dynamics, by mapping it to the dynamics of the non-interacting Kohn-Sham (KS) system evolving in a single-particle potential by virtue of the Runge-Gross [21] and van Leeuwen [24] theorems. TDMCDFT is an extension of TDDFT to a multi-component (MC) system, and it has been expected to provide a first-principles simulation tool to elucidate the dynamics of a system that consists of different types of quantum particles. Li and Tong proved that one-to-one mapping between external potentials and time-dependent (TD) densities is established also in MC systems [19]. Gross et al. then applied the Li-Tong theorem to coupled electron-nuclear systems and developed TDMCKS equations for a one-dimensional model of the H$_2^+$ molecule [20]. However, there are some difficulties to apply their method to real (three-dimensional) systems that consist of many electrons and nuclei. To define electron and nuclear densities that are not constant in space, a body-fixed frame transformation [25], which makes electron density reflect the internal symmetry of the system, must be conducted. Only a Hartree approximation has been tested for a TD electron-nuclear correlation potential, and it did not give satisfactory results [20]. It has been a challenging issue to develop electron-nuclear correlation potential functionals, and there have been ongoing studies [26] including those based on the exact factorization approach [27].

Here, our purpose is to develop TDMCDFT for electron-positron dynamics. For this, we can circumvent the problem of the body-fixed frame transformation by treating nuclei as classical particles, because classical nuclei serve as external potentials for electrons and positrons and the Hamiltonian of the system is no longer translationally and rotationally invar-
ant \cite{28}. We define TD density and current density both for electrons and positrons, and prove non-interacting $v$-representability \cite{24} for these quantities. The formally exact expression for the TD electron-positron correlation functional is then derived by extending the TDDFT action principle \cite{29} to a MC system. Furthermore, we introduce the adiabatic local density approximation (ALDA) to the TD electron-positron correlation, and adopt the ground-state electron-positron correlation energy functional within the LDA \cite{15}. Finally, the TDMCDFT method is applied to the dynamics of a positronic lithium hydride ($e^-\cdot\cdot\cdot LiH$) molecule under a laser field and elucidate the significant role of TD electron-positron correlation in their coupled dynamics.

We begin by considering the full Hamiltonian of a system that consists of $N^-$ electrons and $N^+$ positrons:

$$H = \hat{T}(\mathbf{r}^-_i, \mathbf{r}^+_i) + W(\mathbf{r}^-_i, \mathbf{r}^+_i) + \hat{V}(\mathbf{r}^-_i, \mathbf{r}^+_i, t),$$

where the kinetic energy operator $\hat{T} = -\sum_{i=1}^{N^-} \frac{1}{2} \nabla_{\mathbf{r}^-_i}^2 - \sum_{i<j}^{N^-} \frac{1}{|\mathbf{r}^-_i - \mathbf{r}^-_j|} + \sum_{\alpha=1}^{N^+} \frac{1}{|\mathbf{r}^+_\alpha|}$, the interaction operator $\hat{W} = \sum_{\alpha<\beta}^{N^+} \frac{1}{|\mathbf{r}^+_\alpha - \mathbf{r}^+_\beta|}$, the potential operator due to the interaction with classical nuclei and TD external field $\hat{V} = \sum_{i=1}^{N^-} v_{\text{ext}}(\mathbf{r}^-_i, t) + \sum_{\alpha=1}^{N^+} v_{\text{ext}}(\mathbf{r}^+_\alpha, t)$, and $\mathbf{r}^-_i$ and $\mathbf{r}^+_i$ are the sets of electronic and positronic laboratory coordinates, respectively (i.e., $\mathbf{r}^-_i \equiv \{\mathbf{r}^-_1, \mathbf{r}^-_2, \cdots, \mathbf{r}^-_{N^-}\}$ and $\mathbf{r}^+_i \equiv \{\mathbf{r}^+_1, \mathbf{r}^+_2, \cdots, \mathbf{r}^+_{N^+}\}$). Throughout this letter, the sign $(-)$ indicates an electron (positron), and atomic units are used unless stated otherwise. The TD electron-positron wavefunction $\Psi(\mathbf{r}^-, \mathbf{r}^+, t)$ obeys the full TD Schrödinger equation $i\partial_t \Psi = \hat{H} \Psi$. By treating nuclei as classical charges that determine the laboratory coordinate system, the TD electron (positron) density $n^-(t)$ and current density $j^-(t)$ can be defined as follows:

$$n^+(\mathbf{r}^+, t) = N^+ \int d\mathbf{r}^+ \int d\mathbf{r}^+ \cdot |\Psi|^2,$$

$$j^+(\mathbf{r}^+, t) = \Re \left[ N^+ \int d\mathbf{r}^+ \int d\mathbf{r}^+ \cdot \Psi^* (-i \nabla_{\mathbf{r}^+} \Psi) \right].$$

The equations of motions for these quantities are:

$$\frac{\partial}{\partial t} n^\pm = -\nabla \cdot j^\pm,$$

$$\frac{\partial}{\partial t} j^\pm = -n^\pm (\nabla \cdot v_{\text{ext}}) - i \langle \Psi | [\hat{j}^\pm, \hat{T} + \hat{W}] | \Psi \rangle,$$

where $j^\pm = \frac{1}{2} \sum_{\alpha=1}^{N^\pm} \left( \nabla_{\mathbf{r}^\pm_\alpha} \delta (\mathbf{r}^\pm - \mathbf{r}^\pm_\alpha) + \delta (\mathbf{r}^\pm_\alpha - \mathbf{r}^\pm) \nabla_{\mathbf{r}^\pm_\alpha} \right)$.

Now we prove that, under some restrictions on the initial state, there are effective potentials $v_{\text{KS}}^\pm$ in a non-interacting (KS) system that reproduce the TD electron density $n^- (\mathbf{r}^+, t)$ and positron density $n^+ (\mathbf{r}^+, t)$ in an interacting system, i.e., TDMC non-interacting $v$-representability, by extending the van Leeuwen theorem \cite{24} to the MC system. Taking the divergence of Eqs. (5) and using the continuity Eqs. (4) gives:

$$\frac{\partial^2}{\partial t^2} n^\pm = \nabla \cdot \left( n^\pm (\nabla \cdot v_{\text{ext}}) \right) + i \nabla \cdot \langle \Psi | [\hat{j}^\pm, \hat{T} + \hat{W}] | \Psi \rangle,$$

which is valid for both the interacting system and the KS system. Now we impose the condition that the potentials in both the interacting system and the KS system are Taylor-expandable around the initial time $t_0$, i.e., $v_{\text{ext/KS}}^\pm (\mathbf{r}^\pm, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_{\text{ext/KS},k}^\pm (\mathbf{r}^\pm, t - t_0)^k$. Furthermore, we impose the initial conditions, i.e., that the initial state in the interacting system $\Psi_0$, and that in KS system $\Phi_0$, yield the same densities and their time-derivatives, i.e.,

$$n^+(\mathbf{r}^+, t_0) = n_{\text{KS}}^+(\mathbf{r}^+, t_0),$$

$$\left. \frac{\partial}{\partial t} n^\pm (\mathbf{r}^+, t) \right|_{t=t_0} = \left. \frac{\partial}{\partial t} n_{\text{KS}}^\pm (\mathbf{r}^+, t) \right|_{t=t_0}.$$

These initial conditions uniquely determine the solutions of the second-order differential Eqs. (5). If $n^\pm (\mathbf{r}^+, t_0) = n_{\text{KS}}^+(\mathbf{r}^+, t_0)$ at all times, then subtracting Eqs. (5) for the interacting system and the KS system gives:

$$\nabla \cdot \left( n^\pm (\nabla \cdot v_{\text{ext}}) - n_{\text{KS}}^\pm (\nabla \cdot v_{\text{ext}}^\pm) \right)$$

$$= i \nabla \cdot \langle \Psi | [\hat{j}^\pm, \hat{T} + \hat{W}] | \Phi \rangle - i \nabla \cdot \langle \Psi | [\hat{j}^\pm, \hat{T} + \hat{W}] | \Psi \rangle,$$

where $\Phi$ is the full wavefunction of the KS system. Under the boundary condition that $v_{\text{ext}} - v_{\text{KS}}^\pm = 0$ at infinity, Eqs. (5) have unique solutions for $v_{\text{KS}}^\pm (\mathbf{r}^+, t)$ when $n^\pm (\mathbf{r}^+, t)$, $\Psi_0 (\mathbf{r}^+, \mathbf{r}^+)$, $\Phi_0 (\mathbf{r}^+, \mathbf{r}^+)$, and $v_{\text{ext}}^\pm (\mathbf{r}^+, t)$ are given, similar to the procedure described in Ref. \cite{24}.

By virtue of the TDMC non-interacting $v$-representability proved above, the following coupled TDMCKS equations exist that produce $n^\pm (\mathbf{r}^+, t)$:

$$i \frac{\partial}{\partial t} \psi_{\text{KS}}^\pm (\mathbf{r}^+, t) = \left( \frac{-\nabla_{\mathbf{r}^+}^2 + v_{\text{KS}}^\pm (\mathbf{r}^+, t)}{2} \right) \psi_{\text{KS}}^\pm (\mathbf{r}^+, t),$$

where $\sum_{\alpha=1}^{N^\pm} |\psi_{\text{KS}}^\pm (\mathbf{r}^+, t)|^2 = n^\pm (\mathbf{r}^+, t)$.

Next, we derive the expressions of $v_{\text{KS}}^\pm (\mathbf{r}^+, t)$ from an action principle. Action principles in TDMCDFT can be formulated using the Keldysh time-contour technique \cite{20,30}, however, here we instead extend that in TDDFT formulated by Vignale \cite{22} to the electron-positron system. According to the Li-Tong theorem and TDMC non-interacting $v$-representability, the full wavefunction is a functional of the TD densities, and thus the
quantum mechanical action is also a density functional:

\[ A[n^-, n^+] = \int_{t_0}^{t_1} dt \langle \Psi[n^-, n^+] | i\partial_t - \hat{H} | \Psi[n^-, n^+] \rangle \]

\[ = A_0[n^-, n^+] - \int_{t_0}^{t_1} dt \int dr^- n^- (r^-, t)v_{\text{ext}}^- (r^-, t) 
- \int_{t_0}^{t_1} dt \int dr^+ n^+ (r^+, t)v_{\text{ext}}^+ (r^+, t), \]

(11)

where we define \( A_0[n^-, n^+] = \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{T} - \hat{W} | \Psi \rangle. \)

As in Ref. [29], we consider the variations of the densities such that \( \delta \Psi[n^-, n^+](t_0) = 0, \) and the variational principle \( \delta A[n^-, n^+] = i \langle \Psi(t_1) | \delta \Psi(t_1) \rangle \) leads to:

\[ \frac{\delta A_0[n^-, n^+]}{\delta n^\mp} - v_{\text{ext}}^\pm (r^\mp, t) = i \left\langle \Phi(t_1) \left| \frac{\delta \Phi(t_1)}{\delta n^\mp} \right\rangle. \]

(12)

Similarly, the variational principle for KS systems leads to

\[ \frac{\delta A_{\text{KS}}^0[n^-, n^+]}{\delta n^\mp} - v_{\text{KS}}^\mp (r^\mp, t) = i \left\langle \Phi(t_1) \left| \frac{\delta \Phi(t_1)}{\delta n^\mp} \right\rangle, \]

where \( A_{\text{KS}}^0[n^-, n^+] = \int_{t_0}^{t_1} dt \langle \Psi | i\partial_t - \hat{T} | \Psi \rangle. \) Now we define the exchange-correlation (xc) action functional for the electron-positron system as:

\[ A_{\text{xc}}^+ (n^-, n^+) = A_{\text{KS}}^0[n^-, n^+] - A_0[n^-, n^+] - A_{\text{H}}[n^-, n^+], \]

(14)

where \( A_{\text{H}} = \int dt dr^- dr^+ n^- (r^-, t)n^+ (r^+, t) + \int dt dr^- dr^+ n^- (r^-, t)n^+ (r^+, t) + \int dt dr^- dr^+ n^- (r^-, t)n^+ (r^+, t) \) is the Hartree action functional. With these definitions of \( A_{\text{xc}}^+, \) and Eqs. (12) and (13), we find the expression of the TDMC potentials:

\[ v_{\text{H}}^\pm (r^\mp, t) = v_{\text{ext}}^\pm (r^\mp, t) + v_{\text{xc}}^\pm (r^\mp, t), \]

(15)

where \( v_{\text{H}} = \frac{\delta A_{\text{H}}}{\delta n^\mp} \) are the Hartree potentials and

\[ v_{\text{xc}}^\pm = \frac{\delta A_{\text{xc}}^+}{\delta n^\mp} + i \left\langle \Phi(t_1) \left| \frac{\delta \Phi(t_1)}{\delta n^\mp} \right\rangle - i \left\langle \Phi(t_1) \left| \frac{\delta \Phi(t_1)}{\delta n^\mp} \right\rangle \right) \]

(16)

are the exchange-correlation potentials, which incorporate all TDMC many-body effects in TDMCDFT. Note that these expressions are causal because \( t_1 \) can be replaced by a time infinitesimally later than \( t \) [22,29].

Now the success of the theory is dependent on how to approximate \( v_{\text{xc}}^\pm \) so that they can be calculated practically. One promising way to develop the approximations of \( v_{\text{xc}}^\pm \) will be analysis based on the exact factorization approach [27]. Here we introduce the adiabatic approximation, i.e., neglecting the boundary terms and approximating \( A_{\text{xc}}^{+} \) as:

\[ A_{\text{xc}}^{+} = \int_{t_0}^{t_1} dt \left( E_{\text{xc}}^ [n_0^{0}] + E_{\text{xc}}^{+[n_0^{0}] [n_0^{+}]} \right) |_{n_0^{0} \rightarrow n^+ (t)}, \]

(17)

where \( E_{\text{xc}}^- \) is the electron-electron xc energy functional in DFT, and \( E_{\text{xc}}^+ \) is the electron-positron correlation energy functional in 2C-DFT. Note that in Eq. (17) and hereafter, we omit the positron-positron interaction term because in many cases a system that consists of one positron and many electrons is in interest. The adiabatic approximation to the xc term has been successfully used in many TDDFT studies [22,31], while its validity and limitations have also been extensively discussed [23,32].

Here, as the first application of TDMCDFT to a realistic molecular system, we use the adiabatic approximation. Specifically, the LDA [33] is used for \( E_{\text{xc}}^- \). For \( E_{\text{xc}}^+ \), we also use the LDA parameterized by Puska et al., which has been reported to be suitable for the ground state of positronic atoms [15].

We now show the application of TDMCDFT presented here to the dynamics of an \( \text{e}^+\text{-LiH} \) molecule under a laser field. The LiH molecule has been the target of many previous theoretical studies on positron-molecule interactions [7,18,34], and recent experimental studies [7,9] focused on the response of a positron-molecule compound to a laser field. Here we reveal the dynamical correlation between a positron and electrons and its importance in positron detachment from LiH and electronic excitation. One LiH molecule is placed in the center of a \( 30 \times 30 \times 30 \) Å\(^3\) cubic unit cell so that the molecular axis is along the \( x \)-axis. The bond length is set to the experimental value of 1.60 Å [35]. One positron is then added to the LiH molecule, and the ground-state electron and positron densities are determined by the self-consistent 2C-DFT calculation [2,11] using LDA both for

**FIG. 1.** (a) Snapshots of \( n^- (x, t) \) (black) and \( n^+ (x, t) \) (red) at \( t = 0 \) (dotted) and \( t = 4.36 \) fs (solid) in the dynamics of \( \text{e}^+\text{-LiH} \) under a laser field \( (\omega = 1.5 \text{ eV}) \), and (b) corresponding \( v_{\text{KS}} (x, y, z, t) \). The inset shows the isosurfaces of the ground-state densities (see text).
$E_{\infty}$ [33] and $E_{\infty}^+$ [15] and the plane wave basis set with norm conserving pseudopotentials [36] (cut off energy of 816 eV).

The inset of Fig. 1(a) shows plots of the isosurfaces of the ground-state electron (blue, 0.89 e$^-$/Å$^3$) and positron (red, 0.22 e$^+$/Å$^3$) densities, where Li and H nuclei are plotted as green and gray spheres, respectively. The electron density is localized around the H atom, and the positron density is loosely bound to the electron density. The densities integrated over the $yz$-plane, $n^\pm(x) = \int dy \int dz n^\pm(r)$, are plotted in Fig. 1(a) as black ($n^-$) and red ($n^+$) dotted lines. The Li (H) nucleus is located at $x = -0.8$ (0.8) Å. These distributions of the ground-state densities and the calculated positron binding energy of 0.81 eV are in good agreement with those calculated by the wavefunction-based approach [7, 18, 34].

![Figure 2](image)

**FIG. 2.** (a) Time evolution of positron detachment probability for three different laser fields, and (b) corresponding $E(t)$.

Now we propagate these densities under the laser fields by solving the TDMCKS equations [10] with the adiabatic approximation described above. The laser field is applied along the $x$-axis, described within the dipole approximation and length gauge as $v^\pm_{\text{Laser}}(r, t) = \mp E(t)x$ and $E(t) = E_0 \sin(\omega t) \exp\left[\frac{(t-t_0)^2}{\sigma^2}\right]$, where $E_0 = 0.2$ V/Å, $\sigma = 2$ fs, $t_0 = 4$ fs, and we compare the results from three different energies of $\omega = 0.5$, 1.5, and 3.0 eV ($E(t)$ are shown in Fig. 2(b)). In Fig. 1(a), the snapshot of $n^-(x,t)$ ($n^+(x,t)$) at $t = 4.36$ fs for $\omega = 1.5$ eV is plotted as a black (red) solid line [37]. Figure 1(b) shows the corresponding $v_{\text{KS}}^\pm(x, y_c, z_c, t)$ [37] ($y_c$ ($z_c$) is the midpoint of $y$ ($z$) side of the unit cell) [38]. It is evident from this figure and the movies in the Supplemental Material [37] that considerable positron density moves toward the positive $x$ direction at $t = 4.36$ fs, which indicates the increase of positron detachment probability. This laser energy of $\omega = 1.5$ eV gives the largest positron detachment probability, which is calculated by the integration of $n^-(x,t)$ over the region outside the bound region ($-3.4 < x < 7.2$ Å) [39], among the three energies as shown in Fig. 1(a). The 3.0 eV laser field leads to the lowest detachment probability. Furthermore, the positron dynamics are not synchronized to $E(t)$ (Fig. 2(b)), but there are retardation or even more complex response to the laser field [37]. Electrons and positrons respond to the laser field in the opposite way while attracting each other. This is the cause of the complex dynamics that appeared in Fig. 2. Only the TDMCDFT calculation can reveal the mechanism as to how the coupled positron and electron respond to the laser field by providing the dynamics of $v_{\text{KS}}^\pm$. The movies [37] show that in the case of $\omega = 1.5$ eV, $v_{\text{KS}}^+$ bends effectively for positron detachment at around $t = 4$ fs, while in the case of $\omega = 3.0$ eV, $v_{\text{KS}}^+$ changes the direction of its gradient before the positron starts to depart.

![Figure 3](image)

**FIG. 3.** (a) Time-dependent dipole moment of LiH without positronic contribution $d_x(t)$ of $e^+\cdot$LiH (red) and LiH (black) under the laser field ($\omega = 3.0$ eV), and (b) corresponding $E(t)$.

We present another intriguing result that shows the importance of the electron-positron dynamical correlation in Fig. 3. We compare the TD dipole moment of LiH without positronic contribution $d_x(t)$ [40] between the system of $e^+\cdot$LiH (red) and LiH (black) under the laser field with $\omega = 3.0$ eV. The linear-response TDDFT calculation [41] for LiH (not shown here) shows that the 3.0 eV energy laser elevates the electrons to the first excited state. It is evident in Fig. 3 that a charge density oscillation, which arises from the resonant excitation and remains after the laser field fades [42], is produced in LiH (black). The center of the dipole oscillation shifts to around −4.85 Debye from its ground-state value of −5.67 Debye, which indicates the occurrence of charge transfer excitation [43]. Now turning to the $e^+\cdot$LiH case (red), we see that such a charge oscillation is not induced, which indicates that no resonant excitation occurred. Thus, the positron suppresses the electronic excitation, as the result of dynamical electron-
was applied to positron dynamics quantum mechanically. TDMCDFT couples electron-positron systems, which is a first-principles method that treats both the electron and positron dynamics quantum mechanically. TDMCDFT was applied to electron-LiH under a laser field. There was no simple correlation between the laser energy and the positron detachment probability, which indicates a complex dynamical correlation between a positron and electrons. Only the TDMCDFT simulation can predict the positron detachment dynamics and reveal its mechanism by showing the TDMCKS potentials $v_{KS}$. Furthermore, it was elucidated that the attached positron significantly suppresses laser-induced electronic excitations, which suggests the possibility that the absorption spectrum and excited-state nuclear dynamics may also change. There are many other promising applications of the theory, such as application to the positron migration in the bulk of the material to reveal how it is trapped in a defect or surface, and positron scattering by materials. These are key events in slow positron beam experiments, and the TDMCDFT methodology developed here will be valuable for the study of fundamental positron physics.

YS and KW were supported by a Kakenhi Grants-in-Aid (No. JP16K17768 and No. JP16K05483) from the Japan Society for the Promotion of Science (JSPS). Part of the computations were performed on the supercomputers of the Institute for Solid State Physics, The University of Tokyo.

[1] C. Hugenschmidt, Surf. Sci. Rep 71, 547 (2016).
[2] M. J. Puska and R. M. Nieminen, Rev. Mod. Phys. 66, 841 (1994).
[3] S. W. H. Eijt, A. van Veen, H. Schut, P. E. Mijnarends, A. B. Denison, B. Barbiellini, and A. Bansil, Nat. Mater. 5, 23 (2006); F. Tuomisto and I. Makkonen, Rev. Mod. Phys. 85, 1583 (2013).
[4] D. W. Gidley, H.-G. Peng, and R. S. Vallyere, Ann. Rev. Mater. Res. 36, 49 (2006).
[5] R. L. Wahl, Principles and Practice of Positron Emission Tomography (Lippincott, Williams and Wilkins, Philadelphia, 2002).
[6] A. C. L. Jones, H. J. Rutbeck-Goldman, T. H. Hisakado, A. M. Piñeiro, H. W. K. Tom, A. P. Mills, Jr., B. Barbiellini, and J. Kurilpich, Phys. Rev. Lett. 117, 216402 (2016); T. Tachibana, T. Yamashita, M. Nagira, H. Yamashita, and Y. Nagashima, Sci. Rep. 8, 7197 (2018); M. Ichishio, T. Tachibana, H. Terabe, A. Igarashi, K. Wada, T. Kuga, A. Yagisita, T. Hyodo, and Y. Nagashima, Phys. Rev. Lett. 106, 153401 (2011).
[7] G. F. Gribakin, J. A. Young, and C. M. Surko, Rev. Mod. Phys. 82, 2557 (2010).
[8] J. R. Danielson, A. C. L. Jones, R. M. Natisin, and C. M. Surko, Phys. Rev. Lett. 109, 113201 (2012); J. R. Danielson, J. J. Gosselin, and C. M. Surko, ibid. 104, 233201 (2010).
[9] C. M. Surko, J. R. Danielson, G. F. Gribakin, and R. E. Continetti, New J. Phys. 14, 065004 (2012).
[10] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B 35, R81 (2002); D. G. Green, Phys. Rev. Lett. 119, 203404 (2017); S. Bubin and L. Adamowicz, Phys. Rev. A 74, 052502 (2006); M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, J. Phys. Chem. A 113, 4004 (2009); J. Usukura, K. Varga, and Y. Suzuki, Phys. Rev. A 58, 1918 (1998); A. Zubiaga, F. Tuomisto, and M. J. Puska, J. Phys. Chem. B 119, 1747 (2014).
[11] E. Borotinski and R. M. Nieminen, Phys. Rev. B 34, 3820 (1986); M. J. Puska, A. P. Seitsonen, and R. M. Nieminen, ibid. 52, 10947 (1995); B. Barbiellini and J. Kurilpich, Phys. Rev. Lett. 114, 147401 (2015).
[12] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, ibid. 140, A1133 (1965).
[13] A. Uedono, S. Ishibashi, K. Tenjinbayashi, T. Tsutsui, K. Nakahara, D. Takamizu, and S. F. Chichibu, J. Appl. Phys. 111, 014508 (2012).
[14] S. Hagiwara, C. Hu, and K. Watanabe, Phys. Rev. B 91, 115409 (2015); J. Lin, T. Yamasaki, and M. Saito, Jpn. J. Appl. Phys. 53, 053002 (2014); S. Hagiwara, Y. Suzuki, and K. Watanabe, Appl. Phys. Express 10, 045101 (2017).
[15] A. Zubiaga, F. Tuomisto, and M. J. Puska, Phys. Rev. A 89, 052707 (2014).
[16] H. A. Kurtz and K. D. Jordan, J. Chem. Phys. 75, 1876 (1981); M. Tachikawa, Y. Kita, and R. J. Buenker, Phys. Chem. Chem. Phys. 13, 2701 (2011).
[17] D. M. Schrader, T. Yoshida, and K. Iguchi, Phys. Rev. Lett. 68, 3281 (1992); D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. 108, 4756 (1998).
[18] Y. Kita, R. Mazzon, M. Tachikawa, M. Towler, and R. J. Needs, J. Chem. Phys. 131, 134310 (2009).
[19] T.-C. Li and P.-Q. Tong, Phys. Rev. A 34, 529 (1986).
[20] O. Butriy, H. Ebadi, P. L. de Boeij, R. van Leeuwen, and E. K. U. Gross, Phys. Rev. A 76, 052514 (2007).
[21] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
[22] C. A. Ullrich, Time-Dependent Density-Functional Theory: Concepts and Applications (Oxford University Press, 2012).
[23] N. T. Maitroy, M. J. Puska, and R. M. Nieminen, Rev. Mod. Phys. 86, 841 (1994).
[24] S. W. H. Eijt, A. van Veen, H. Schut, P. E. Mijnarends, A. B. Denison, B. Barbiellini, and A. Bansil, Nat. Mater. 5, 23 (2006); F. Tuomisto and I. Makkonen, Rev. Mod. Phys. 85, 1583 (2013).
[25] D. W. Gidley, H.-G. Peng, and R. S. Vallyere, Ann. Rev. Mater. Res. 36, 49 (2006).
[26] R. L. Wahl, Principles and Practice of Positron Emission Tomography (Lippincott, Williams and Wilkins, Philadelphia, 2002).
T. Udagawa, T. Tsuneda, and M. Tachikawa, Phys. Rev. A 89, 052519 (2014).

[27] A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. 105, 123002 (2010); Y. Suzuki, A. Abedi, N. T. Maitra, K. Yamashita, and E. K. U. Gross, Phys. Rev. A 89, 040501 (2014); E. Boström, A. Mikkelsen, and C. Verdozzi, Phys. Rev. B 93, 195416 (2016); R. Requist and E. K. U. Gross, Phys. Rev. Lett. 117, 193001 (2016).

[28] Note that it would also be possible to treat nuclei quantum mechanically by developing three-component density functional theory. In that case the body-fixed frame transformation would again need to be carried out.

[29] G. Vignale, Phys. Rev. A 77, 062511 (2008).

[30] R. van Leeuwen, Phys. Rev. Lett. 80, 1280 (1998).

[31] Y. Li and C. A. Ullrich, J. Chem. Theory Comput. 11, 5838 (2015); M. Dauth, M. Graus, I. Schelter, M. Wießner, A. Schöll, F. Reinert, and S. Kümmel, Phys. Rev. Lett. 117, 183001 (2016); U. D. Giovanni, H. Hübener, and A. Rubio, J. Chem. Theory Comput. 13, 265 (2017); K. Yabana, T. Sugiyama, Y. Shinozaka, T. Otobe, and G. F. Bertsch, Phys. Rev. B 85, 045134 (2012); Y. Miyamoto and A. Rubio, J. Phys. Soc. Jpn. 87, 041016 (2018); Y. Ueda, Y. Suzuki, and K. Watanabe, Phys. Rev. B 97, 075406 (2018).

[32] N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. 89, 023002 (2002); H. O. Wijewardane and C. A. Ullrich, ibid. 95, 086401 (2005); M. Thiele, E. K. U. Gross, and S. Kümmel, ibid. 100, 153004 (2008); D. Hofmann, T. Körzdörfer, and S. Kümmel, ibid. 108, 146401 (2012); J. D. Ramsden and R. W. Godby, ibid. 109, 036402 (2012); N. Helbig, J. I. Fuks, M. Casula, M. J. Verstraete, M. A. L. Marques, I. V. Tokatly, and A. Rubio, Phys. Rev. A 83, 032503 (2011); Y. Suzuki, L. Lacombe, K. Watanabe, and N. T. Maitra, Phys. Rev. Lett. 119, 263401 (2017).

[33] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[34] F. A. Gianturco, J. Franz, R. J. Buenker, H.-P. Liebemann, L. Pichl, J.-M. Rost, M. Tachikawa, and M. Kimura, Phys. Rev. A 73, 022705 (2006); Y. Kita, R. Maezono, M. Tachikawa, M. D. Toeler, and R. J. Needs, J. Chem. Phys. 135, 054108 (2011); A. Sirjoosingsh, M. V. Pak, C. Swalina, and S. Hammers-Schiffer, ibid. 139, 034103 (2013).

[35] NIST Computational Chemistry Comparison and Benchmark Database (2018), https://cccbdb.nist.gov/.

[36] K. Kobayashi, Comput. Mater. Sci. 14, 72 (1999).

[37] Movies of the dynamics are given in the Supplemental Material.

[38] Note that steps appeared in $v_{KS}$ around $x = 5$ Å are due to the LDA electron-positron correlation energy functional parameterized in Ref. [15].

[39] The bound region is defined as the region where considerable ground-state positron density exists (the region where $n^+(x, t = 0) > 0.001$).

[40] Time-dependent dipole moment of LiH without positronic contribution $d^-_{x}(t)$ is given by $d^-_{x}(t) = -\int dr^{-} x n^{-}(r^{-}, t)$.

[41] M. E. Casida, in Recent Advances in Density Functional Methods (World Scientific, Singapore, 1995) pp. 155–192.

[42] C. A. Ullrich, P.-G. Reinhard, and E. Suraud, J. Phys. B 30, 5043 (1997); J. Ma, Z. Wang, and L.-W. Wang, Nat. Commun. 6, 10107 (2015).

[43] J. I. Fuks, A. Rubio, and N. T. Maitra, Phys. Rev. A 83, 042501 (2011); N. T. Maitra, J. Phys.: Condens. Matter 29, 423001 (2017).