Level of Positron Bound States in Atoms

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Abstract.   Positron annihilation from positron bound states in atomic systems has been investigated by using density functional theory. Positron lifetime shifts have been analyzed in terms of competing influences of correlation potentials. The results suggest that inclusion of electron-positron correlation is crucial in assignment of positron orbitals to lifetime components in density-functional investigations of bound states of the positron in negative and neutral atomic systems. The extracted experimental averages from alkali halides show the relatively good agreements to the calculated positron lifetimes.

1   Introduction

Positron annihilation (PA) is a widely-used tool in condensed-matter systems, because positron lifetimes often hold key information about the electronic states. The positron can preferentially annihilate on the special sites where electron density is concentrated. Unlike other probes where final-state effects can often be neglected, in the case of PA, the annihilation event can take place from a bound state which represents a significant perturbation of the original electronic states. The goal of first-principles theories is to adequately account for the perturbation of the electronic states, including electron-positron correlation effects which directly relate to the observed annihilation rates[1, 2].

A first-principles methods for the self-consistent calculation of the positron states in electronic systems have been implemented at the Hartree-Fock (HF) level[3, 4] for smaller atoms or ions and at the post-HF level in terms of configuration-interaction and Hylleraas-type calculations[5, 6, 7]. Correlation effects are crucial for addressing the issue of bound states of

positrons in neutral atoms. Therefore, another method is preferable for including correlation that is more tractable in larger systems. In general, one can expect positron annihilation in condensed matter to occur via channels involving localized, as well as delocalized, electronic states. The full range of such states may be analyzed within density functional theory (DFT) which includes in the energy functional both electron-electron and electron-positron correlation effects.

Bound states of positrons in negative ions have been dealt with in the context of the exchange-only (X-O) calculation, which shows that the positron binding energy is strong enough to form positron bound states in negative atoms[8]. The issue of electron-electron and electron-positron correlation is taken up in these systems. Moreover, the delicate problem of positron bound states in neutral atoms[6, 9, 10] has yet to be addressed and should provide a good test of the correlation functional to be employed. The positron can finally annihilate via either the single positron channel or the positronium channel in negatively charged atoms. However, the issue of the preferential channel is still controversial. This topic might be intensively studied on another work in future. In this work, we consider the 2γ annihilation from the positron bound states in atoms and assign positron orbitals from the computed annihilation lifetimes.

2 Density Functional Formalism for the positron annihilation

Total energy functional for an inhomogeneous system of electrons and a positron can be written by the density functional formalism in terms of the electron energy E_e, the positron energy E_p, and the cross terms between electron and positron such as the Coulomb potential energy V_{ep} and the correlation energy E_c^{ep}:

$$E[\rho_\uparrow, \rho_\downarrow, \rho_+] = E_e + E_p + V_{ep} + E_c^{ep}, \qquad (2.1)$$

$$E_e = T_0^e + V_{ext} + U_C + E_{xc} + U^{SIC}, \qquad (2.2)$$

$$E_p = T_0^p - V_{ext}, \qquad (2.3)$$

and

$$U^{SIC} = -\sum_\sigma \sum_{i=1}^{N_\sigma} (U_C[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}]). \qquad (2.4)$$

In the above equations, the part of electron energy is for the kinetic energy T_0^e, the nuclear-electron interaction V_{ext}, Coulomb energy U_c, the exchange-correlation energy E_{xc}. The part of positron energy includes the kinetic (T_0^p) and nuclear-positron ($-V_{ext}$) energies, and the interaction part comes from the electron-positron Coulomb potential (V_{ep}) and the electron-positron correlation (E_c^{ep}) energies. The self-interaction correction energy U^{SIC} comes from the orbital-by-orbital subtraction for the electron-electron Coulomb, exchange, and correlation energies.

In an inhomogeneous system of N electrons and a single positron densities are denoted by $\rho_\uparrow, \rho_\downarrow (\rho_- = \rho_\uparrow + \rho_\downarrow)$ for electrons and by ρ_+ for the positron. They can be written in terms of a set of orthonormal orbitals and occupation numbers,

$$\rho_\sigma = \sum_{i=1}^{N_\sigma} f_{i\sigma} |\Psi_{i\sigma}(\mathbf{r})|^2, \sigma = \uparrow, \downarrow, \tag{2.5}$$

$$\rho_+ = |\Psi_+(\mathbf{r})|^2, \tag{2.6}$$

where occupation numbers $f_{i\sigma}$ are located on the interval $0 \le f_{i\sigma} \le 1$.

>From the self-interaction corrected local spin density approximation (SIC-LSDA) of DFT[8], the self-consistent densities for the electron and the positron are obtained from solutions of self-consistent one-particle Kohn-Sham equations for orbitals as the following:

$$H_{i\sigma}\Psi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}\Psi_{i\sigma}(\mathbf{r}), i = 1, 2, ..., N_\sigma, \tag{2.7}$$

$$H_+\Psi_+(\mathbf{r}) = \varepsilon_+\Psi_+(\mathbf{r}), \tag{2.8}$$

with

$$H_{i\sigma} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + V_{Coul}^- + V_c^{ep-e} + \Delta V_e^{SIC}, \tag{2.9}$$

$$H_+ = -\frac{1}{2}\nabla^2 + \frac{Z}{r} + V_{Coul}^+ + V_c^{ep-p}, \tag{2.10}$$

and

$$\Delta V_e^{SIC} = V_{Coul} + V_{xc} - (V_{Coul}[\rho_{i\sigma}] + V_{xc}[\rho_{i\sigma}]), \tag{2.11}$$

$$V_{Coul}^-(\mathbf{r}) = -\int \frac{\rho_+(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \tag{2.12}$$

$$V_{Coul}^+(\mathbf{r}) = -\int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \tag{2.13}$$

where $H_{i\sigma}$, H_+, V_{Coul}^-, and V_{Coul}^+ are denoted for Hamiltonians and Coulomb potentials for electron and positron, respectively, and Z is the atomic number. The exchange-correlation potential between electron and electron is denoted by $V_{xc}[\rho_\sigma] = \frac{\delta E_{xc}[\rho_\sigma]}{\delta \rho_\sigma}$, the electron correlation potential of the electron-positron correlation is denoted by $V_c^{ep-e}[\rho_\sigma, \rho_+] = \frac{\delta E_c^{ep}[\rho_\sigma, \rho_+]}{\delta \rho_\sigma}$, and the positron correlation potential is denoted by $V_c^{ep-p}[\rho_\sigma, \rho_+] = \frac{\delta E_c^{ep}[\rho_\sigma, \rho_+]}{\delta \rho_+}$. The electron-electron correlation energy has been implemented from the Perdew-Zunger parametrization of the Ceperley-Alder results[11, 12].

It should be noted that unlike the case of the electron correlation, unfortunately, the *ab initio* calculation for the electron-positron correlation, such as quantum Monte Carlo simulation is not available until now due to the complex behavior of the positron annihilation with the electron. However, the electron-positron correlation energy per unit volume (E_c^{ep}) has been quantum-field theoretically calculated for certain relative values of the uniform electron and the positron densities by Arponen and Pajanne[13] ($\rho_+ \to 0$) and Lantto[14] ($\rho_+ = \rho_-, \rho_+ = \rho_-/2$). Boronski and Nieminen have devised an interpolation scheme to use

these data to fill in values of E_c^{ep} throughout the (ρ_+, ρ_-) plane [2]. >From this scheme of the electron-positron correlation, the minimization of the above total energy functional gives the self-consistent electron and positron densities which are the main ingredient for the evaluation of the positron annihilation. The Herman-Skillman code[8, 15] has been implemented and modified to solve these Kohn-Sham equations for the SIC-LSDA calculations of atoms interacting with a positron.

A positron annihilates with an electron in material and the emitted annihilation radiation is observed. If the spins of the electron and the positron are anti-parallel, i.e., a singlet state $^1S_0$ of the electron and the positron spins, two photons are emitted into opposite directions. For the spin parallel case, three photons are observed as a result of the spin interaction in the triplet state $^3S_1$. The distribution of the angle between the three photons and the annihilation energy of 1.02MeV are more complicated than that of the two photon mode. In this work, our main concern is focused on the two photon annihilation from the bound states of the positron in atoms.

The probability of pair-annihilation increases with increasing probability of the electron at a positron position. A key observable signal is the annihilation rate (inverse lifetime τ) proportional to the overlap of the electron and the positron densities that are self-consistently determined from Eqs. (2.5) and (2.6). This rate is written by

$$\lambda = \frac{1}{\tau} = \pi r_0^2 c \sum_\sigma \int d\mathbf{r} \rho_\sigma(\mathbf{r}) \rho_+(\mathbf{r}) g(0; \rho_\sigma, \rho_+, \zeta), \tag{2.14}$$

where r_0 is the classical electron radius, c the speed of light and $g(0; \rho_\sigma, \rho_+, \zeta)$ the pair-correlation function of the contact density at the origin of the positron in any polarization mode, ζ indicating the annihilation mode. The pair correlation function providing the measure of the enhancement effect in the positron-electron correlation has been implemented from the Boronski and Nieminen's interpolation[2, 14].

3   Results

The self-consistent electron and positron densities and the positron annihilation rates have been calculated for three levels of theory: 1) no correlation included(X-O), 2) electron-electron correlation included(EC-O), and 3) electron-electron and electron-positron correlation included(EP-O and EPC). The calculated theoretical lifetimes are compared with experimental data[16], which extracted from the averages of alkali halides crystals, and other theoretical calculations[3, 4, 5, 6, 7, 17] in Tables 1 and 2 for the negative ionic systems H^-:e^+, F^-:e^+, and Cl^-:e^+ and the neutral atomic systems Li:e^+, Na:e^+.

It has been noted that in HF calculations of negative ions[17], the result for the fully relaxed orbitals of both the electron and positron is only 10 percent smaller than that for the frozen core orbitals. This implies that the electron neutral inner orbit only contributes a small portion to the positron lifetime. Therefore, in both HF and X-O calculations, the

Atom	nl	X-O	EC-O	EP-O	EPC	Exp. The experimental averages referred from Bussolati et al[16]
F^-	1s	1.767	1.722	0.614	0.225	0.161
	2s	7.102	6.944	3.417	1.225	0.894
	2p	9.825	9.627	2.396	0.649	0.354
Cl^-	1s	4.324	4.180	1.192	0.326	0.245
	2s	15.207	14.768	5.708	1.514	1.105
	2p	13.253	12.864	2.552	0.565	0.531

Table 1: Positron lifetimes(10^{-9}sec) from the electron-positron pair annihilation in negative ion systems: F^-:e^+(nl) and Cl^-:e^+(nl) for nl=1s, 2s, and 2p states of the positron. X-O denotes exchange-only LSDA calculation, EC-O denotes inclusion of electron-electron exchange-correlation functional; EP-O denotes inclusion of the electron-electron exchange-correlation and electron-positron correlation with no enhancement effects; and finally the EPC denotes the full calculation.

Atom	nl	EP-O	EPC	HF	HTW
H^-	1s	0.576	2.403	0.300 Farazdel and Cade[17]	2.220 Navin et al[5]
				0.437 Clary[6]	2.459 Ho[7]
Li	1s	0.352	0.554	0.030 Clary[6]	0.880 Clary[6]
Na	1s	0.066	0.653	-	-

Table 2: Positron annihilation rates(GHz) for negative hydrogen and neutral lithium and sodium atoms. Comparison of SIC-LSDA (EP-O and EPC), Hartree-Fock(HF), and the extensive Hylleraas-type wavefunction (HTW) methods. Note that HTW method was used the 392 term wavefunction.

positron could not be well localized by the electron. The many-body interaction among electrons such as the electron-electron correlation also gives a negligibly small contribution to reducing the positron lifetime as can be seen in the EC-O values in Table 1. This also indicates that the density of the positron could not be distorted by this electron-electron correlation of the electron density. The order of bound states of the positron is not consistent with that of the annihilation lifetimes in the HF[17], the X-O, and the EC-O calculations. The annihilation order on these calculations is same with that of hydrogen-like electron orbitals.

>From the EP-O calculations, in which both densities of electron and positron are restricted to be quantum statistically independent, the positron correlation potential in the vicinity of the nucleus site strongly attracts positron density inward, as shown in Fig. 1.

Furthermore, the inclusion of the pair-correlation function as the annihilation enhancement factor g in the EPC calculation strongly reduces positron lifetimes. The increased
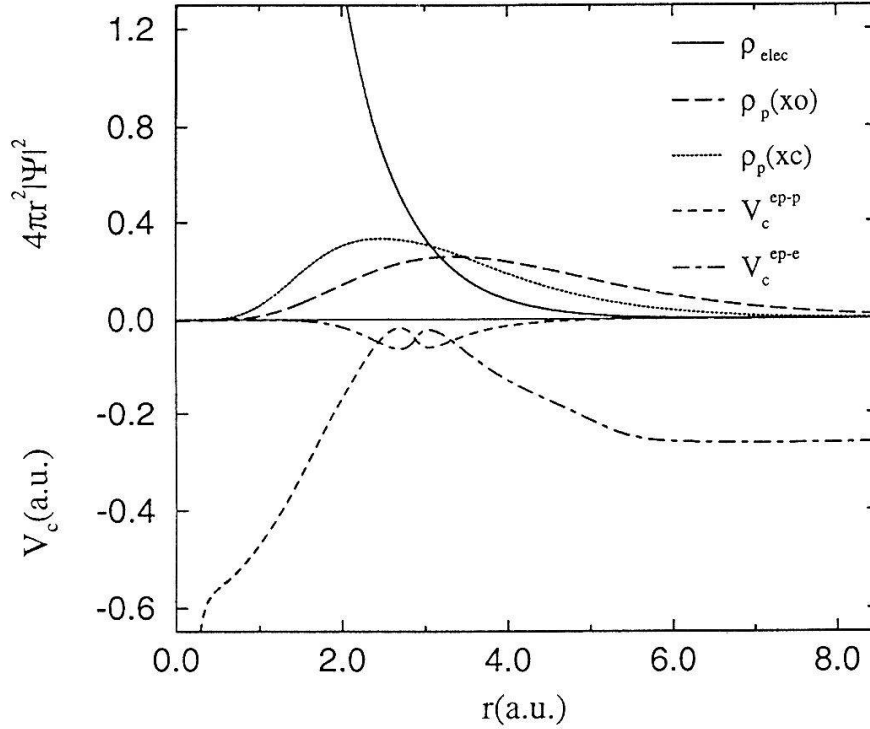
Figure 1: The positron bound state and correlation potentials for F^-:e^+(1s). Note the large positron potential of electron-positron correlation near the nucleus of negative ion F^-, which attracts the positron density toward the center of the ion (XC).

electronic charge density at the position of the positron increases the probability of the pair-annihilation rate. This correspondingly decreases the positron lifetimes, which agree relatively well with experiments.[16] This quantum correlation effect is associated with the density fluctuation at the position of the localized positron and strongly perturbs final states of both electron and positron for the positron bound atomic system.

>From these results, the fundamental positron orbital in the atomic system can be assigned accordingly. It is supposed that the experimental averages can be resolved into the components corresponding to the ground state and then to the first excited and the second excited states. The order of annihilation rates for the positron (inverse of positron lifetimes) would be dramatically changed from the hydrogen-like electron orbitals into the proper positron orbitals ($1s, 2p$, and $2s$), as shown in Table 1. The eigenvalues of positron bound states consistently correspond to the positron lifetimes of both calculation and experiment with the order $[(1s), (2p, 2s)$, and $(3d, 3p, 3s)]$, as shown in Fig. 2 and Table 3. This reflects that the annihilation of the positron is a very complicated process ·due to the quantum correlation effect. The principal quantum number of the positron has the same order with electron orbitals, but the higher angular quantum state of the positron has the lower eigenvalue.

The larger negative ions usually provide the longer lifetime to the 1s state of positron because the total positron potential becomes shallow due to the competing interactions be-
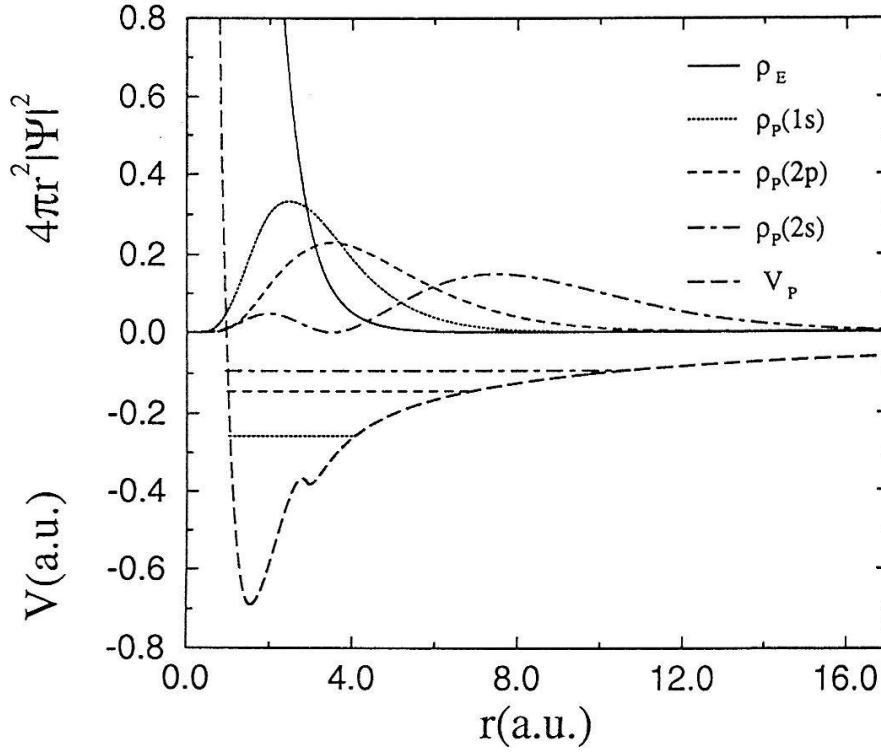
Figure 2: Positron bound state levels and radial densities for F^-:e^+(nl=1s, 2p, and 2s).

tween the repulsive nucleus potential and both electron-positron Coulomb potential and electron-positron correlation potential. It is interesting to compare the annihilation rate of the negative hydrogen from various calculational methods. This density functional calculation of the annihilation rate for the H^- gives the value 2.403 GHz, as shown in Table 2. This is comparable to 2.220 GHz[5] and 2.459 GHz[7] provided from the laborious method of the extensive Hylleraas-type wavefunctions. It is valuable to note that the above method has been used the 392 term wavefunction. Further discrepancy between the present results for negative ions and experiment may be attributed to the crystal field effect.

In Table 2, density functional calculations show that even though there is a strong nuclear repulsion to the positron from the core of the neutral atoms, the electron-positron correlation would make stable bound states of the positron in neutral alkali atoms such as Li and Na with lifetimes of 1.805 nsec and 1.531 nsec, respectively. The EP-O calculation directly provides that the Na atom has much shallower and wider positron potential well than that of the Li atom. However, in the EPC calculation which includes the pair-correlation function, the Na atom has a larger annihilation rate than that of the Li atom. Therefore, the positron correlation effect is crucial in obtaining positron bound states of large neutral atoms. This result is consistent with the viewpoint of Clary[6] that the positron bound state is stable with respect to the single positron dissociation from the neutral atom but not stable with respect to the dissociation of positronium.

Atom	nl	X-OHarrison[8]	RHF Cade and Farazdel[3], Patrick and Cade[4]	EC-O	EPC
F⁻	1s	4.959	5.048	4.976	6.948
	2s	1.913	1.936	1.914	2.508
	2p	2.965	2.992	2.965	3.874
	3s	1.011	-	1.010	1.252
	3p	1.365	-	1.363	1.809
	3d	1.501	-	1.496	1.684
Cl⁻	1s	3.845	3.922	3.867	5.943
	2s	1.621	1.644	1.626	2.236
	2p	2.651	2.687	2.658	3.887
	3s	-	-	0.895	1.177
	3p	1.258	-	1.259	1.739
	3d	1.478	-	1.476	1.842

Table 3: Positron eigenvalues (-eV) for various approximations. Note close correspondence of SIC-LSD X-O results to restricted Hartree-Fock (RHF).

4   Summary

In summary, we have presented density functional calculations of positron lifetimes for alkali and halide atoms in the SIC-LSDA scheme. >From this, we have examined the role of the electron-positron correlation which strongly perturbs the final states of electrons and the positron. Our results provide the fundamental concept of positron orbitals ($[(1s), (2p, 2s),$ and $(3d, 3p, 3s)]$) in the atomic system. This concept of positron orbitals in atomic systems may shed a piece of light on understanding the positron annihilation phenomenon in condensed matters.

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