Positron and positronium affinities in the Work Formalism Hartree-Fock Approximation

Rajendra R. Zope

Center of Advanced Studies in Materials Science and Solid State Physics,
Department of Physics, University of Pune, Pune-411007, India

(March 31, 2022)

Positron binding to anions is investigated within the work formalism proposed by Harbola and Sahni (HS) for the halide anions and the systems \(\text{Li}^-\) through \(\text{O}^-\) excluding \(\text{Be}^-\) and \(\text{N}^-\). The total ground state energies of the anion-positron bound systems are empirically found to be an upper bound to the Hartree-Fock (HF) energies. The computed expectation values as well as positron and positronium affinities are in good agreement with their restricted Hartree-Fock counterparts. Binding of a positron to neutral atomic species is also investigated using an iterative method.

PACS numbers: 36.10Dr, 71.60.+z

I. INTRODUCTION

Despite extensive studies [1-11] the problem of a positron forming a transient bound state with a neutral atom has not yet been decisively settled. It is known that a negatively charged ion always binds a positron; in fact it turns out that there is an infinite number of bound states. The classical Coulomb interaction between an anion and a positron is sufficient to bind a positron while in case of neutral atoms the polarization of electron charge distribution is found to be vital for binding [2]. Schrader et al. [13,14] have calculated the positronium affinities for halogen atoms using a diffusion quantum Monte Carlo technique in which the core region is represented by a model potential. Accurate calculations on the positronium hydride, positronium helium and positronium lithium systems using the all particle diffusion Monte Carlo method have been recently reported by Yoshida et al. [8,9]. Very recently, Bressanini et al. [15] have investigated the positron-anion bound states for the anionic species \(\text{Li}^-\), \(\text{B}^-\), \(\text{C}^-\), \(\text{O}^-\) and \(\text{F}^-\) using variational and diffusion quantum Monte Carlo techniques. They found that except \(\text{B}^-\) all these systems are stable against dissociation into the corresponding neutral atom and positronium. Such methods are computationally very demanding thereby restricting their applicability to systems with fewer particles. The independent particle approximation methods such as the Hartree-Fock or density functional theories enable one to compute with ease the anionic-positron interactions for all the anions in the periodic table. Calculations within the restricted HF theory have been reported by Cade and Farazdel [16,17] and Patrick and Cade [2] for the systems \(\text{Li}^-\) through \(\text{O}^-\) as well as for halogen anions. They have also examined the stability of anion-positron bound systems with respect to their dissociation into the corresponding atom and positronium. For the description of many electron-positron bound system within the density functional theory (DFT), Chakraborty [18] has proposed a two component density functional theory wherein the electron and the positron densities play the role of basic variables. This was subsequently extended by Harrison [19] to incorporate self-interaction correction [20] wherein the calculated positron and positronium affinities are in close agreement with their HF counterparts. By invoking the Slater transition state concept Baruah et al. [21] have obtained decent estimates of positron affinities to negative ions. Earlier, density functional calculations of the positron-anion bound state had also been carried out by Kanhere et al. [22].

Recently, an attractive alternative to the Hartree-Fock theory was proposed by Harbola and Sahni [23]. The exchange-correlation potential in the so-called work formalism of Harbola-Sahni (HS) is obtained as the work done in bringing an electron in the electric field of its Fermi-Coulomb hole charge distribution. The work formalism HF
approximation essentially emerges if one ignores Coulomb correlations and the correlation contribution to the kinetic energy in the Kohn-Sham theory [24]. Recently, Holas and March [25] have shown that the HS potential can be obtained from the full second order density matrix. The total atomic energies and various one electron properties of work formalism are practically equivalent to those of HF theory [26]. Unlike other local exchange-only density functionals, the work formalism of HS selectively gives convergent orbitals and eigenvalues for negative ions that are comparable to the HF accuracy [30]. In the present communication, we address the problem of positron binding to anions and atoms within the exchange-only work formalism. The purpose of the present work is two-fold: 1) To compute the positron affinities and binding energies using local orbital-independent density functional theory. 2) To test the work formalism of the Harbola-Sahni for the description of many electron-positron system. The computed positron affinities, binding energies and $< r^n >$ moments ($n = -1$ through 2) within the work formalism are compared against their restricted Hartree-Fock (RHF) counterparts. For the neutral atom-positron bound states we use an iterative method similar to the one used by Patrick and Cade [12]. The plan on the presentation is as follows: In section II we outline the theory of work formalism for the description of electron-positron system while section III deals with the results and discussion which will be followed by conclusions in section IV.

II. THEORY

The non-relativistic Hamiltonian $H$ for an $N$-electron and one positron system is the sum of the electronic part $H_e$ (atomic units are used throughout),

$$H_e = \sum_i^N \left( -\frac{\nabla_i^2}{2} \right) - \sum_i^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

(1)

consisting of the kinetic energy of electrons, the electron-nuclear interaction, the electron-electron repulsion, and the Hamiltonian $H_p$ for a positron,

$$H_p = -\frac{\nabla_p^2}{2} + \frac{Z}{r_p} - \sum_{i=1}^N \frac{1}{|\vec{r}_i - \vec{r}_p|}$$

(2)

containing the positron kinetic energy, the nucleus-positron repulsion and the positron-electron attractive interaction.

Within the exchange-only work formalism of Harbola-Sahni the local exchange potential is obtained as the work done in moving an electron in the electric field $\vec{E}$ of its Fermi hole $\rho_x(\vec{r}, \vec{r}')$ charge distribution, that is,

$$W_x(\vec{r}) = -\int_{\infty}^{\vec{r}} \vec{E}_x(\vec{r}') \cdot d\vec{r}'$$

(3)

with

$$\vec{E}_x(\vec{r}) = \int \frac{\rho_x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} (\vec{r} - \vec{r}') d^3 r'$$

(4)

and

$$\rho_x(\vec{r}, \vec{r}') = -\frac{\sum_i \phi_i^*(\vec{r}) \phi_i(\vec{r}') \phi_j^*(\vec{r}') \phi_j(\vec{r})}{\sum_k \phi_k^*(\vec{r}) \phi_k(\vec{r})}$$

(5)

Now, in order that the effective potential experienced by electron is well defined the curl of the “exchange electric field” represented by Eq. (4) should vanish. This is the case for the closed shell atoms and open shell atoms in the central field approximation in which the present calculations have been carried out (see references [24], [26] for details). It is to be noted that HS exchange potential obtained this way differ from the exact Kohn-Sham potential only by the kinetic correlation contribution [27, 24]. The orbitals, $\phi_i$, in Eq. (1) are the solutions of the (Kohn-Sham like) HS equation.
\[
\left\{-\frac{\nabla^2}{2} - \frac{Z}{r} + \int \frac{n^-(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \mathcal{W}_x(\vec{r}) - \int \frac{n^+(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' \right\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}). \tag{6}
\]

Here, \( n^-(\vec{r}) = \sum_i^N | \psi_i(\vec{r}) |^2 \) is the electron density, \( n^+(\vec{r}) = | \psi^+(\vec{r}) |^2 \) is the positron density with \( \psi^+ \) being the solution of the corresponding differential equation for the positron

\[
\left\{-\frac{\nabla^2}{2} + \frac{Z}{r} - \int \frac{n^-(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' \right\} \psi^+(\vec{r}) = \epsilon^+ \psi^+(\vec{r}). \tag{7}
\]

The effective potential seen by the positron in the exchange-only formalism also has the interpretation as the work done in moving the positron in the field of the electronic and nuclear charge distribution. Eqs. (6) and (7) are solved self consistently to obtain the ground state energy of the electron-positron combined system which is expressed as

\[
E = T_e + T_p - Z \int \frac{n^-(\vec{r})}{r} d^3r + Z \int \frac{n^+(\vec{r})}{r} d^3r + E_x - \int \frac{n^-(\vec{r})n^+(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + \frac{1}{2} \int \frac{n^-(\vec{r})n^+(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'. \tag{8}
\]

The first two terms, \( T_e \) and \( T_p \) denote respectively, the kinetic energy of electrons and the positron, the next two terms represent the attractive and the repulsive interaction energies of the electrons and a positron with the nuclear charge, \( E_x \) is the exchange energy while the last two terms signify the electron-electron and electron-positron interaction energies respectively. The expressions for the calculation of exchange energy and electron-electron interaction energies can be found in the appendix of Ref. [28]. The electron-positron energy can be obtained by following the steps exactly similar to the electron-electron case and emerges as

\[
E = -\sum_{nlm} \sum_{n'l'm'} N_{nlm} \int r^2 dr r^2 d\theta d\phi R_{nl}(r) R_{n'l'm'}(r) \frac{r_{l''}^0}{r_{l''+1}^0} \times (2l + 1) (2l' + 1) \begin{pmatrix} l & l' & l'' \ m & 0 & -m \ m' & 0 & -m' \end{pmatrix} \begin{pmatrix} l & l'' & l' \ 0 & 0 & 0 \ m & 0 & -m' \end{pmatrix}. \tag{9}
\]

Here, \( R_{nl} \) and \( R_{n'l'm'} \) are respectively the radial parts of the electron orbitals and the positron orbitals, and \( N_{nlm} \) is the orbital occupancy. The \( 3j \) symbols in Eq. (9) arise due to integration over the solid angle \( \Omega \equiv \Omega(\theta, \phi) \).

The Herman-Skillman code [29], modified for the Harbola-Sahni potential has been further modified in order to incorporate the positron. The calculations are carried out in the central-field approximation for the systems \( Li^- \) through \( F^- \) except for \( Be^- \) and \( N^- \) and the halide ions. In order to obtain the ground state of an anion \( A^- \), we start with converged potential of the neutral atom \( A \) and perform self-consistent calculation. The converged potential of the anionic system \( A^- \) was then taken as a starting potential for the anion-positron self-consistent calculation. This was done in order to achieve fast convergence. In the following section we present our main results.

### III. RESULTS

The total energies of the anion-positron bound states calculated in the present formalism and the corresponding restricted HF (RHF) energies for the positron in different states are displayed in Table I. The RHF numbers for total energies, positron and positronium affinities against which we compare our results are due to Patrick and Cade [12] and Cade and Farazdel [16]. The present total energies are in good agreement with the HF energies. The differences in parts per million between the energies of the present work and those of the HF theory are given in Table II for the anion-positron bound state (the positron is in the 1s orbital). The differences diminish with the size of the anion. It is also evident from the table that the calculated total energies are slightly higher than the HF energies. This is expected since the HS orbitals differ from the HF orbitals which variationally minimize the total energy.
The positron affinity is defined as

\[ P.A. = E(A^-) + E(e^+) - E([A^-; e^+]), \tag{10} \]

where \( E([A^-; e^+]) \) denotes the energy of the anion-positron bound system. Positive value of the P.A. indicates that \( E[\text{A}^-; e^+] \) is a bound state, that is, the system \( A^- \) will bind a positron. The calculated positron affinities and the negative of the positron eigenvalue are given Table in \( \text{II} \), also given are the corresponding HF values given for comparison. For all the systems, the PA is positive indicating their stability with respect to dissociation into an anion and a positron. The present values of the positron energy eigenvalues are in general higher in magnitude than the corresponding HF values and lie between the PA calculated from Eq. (10) and the recent diffusion quantum Monte Carlo (QMC) values \( \text{[3]} \). The available diffusion Monte Carlo values \( \text{[3]} \) for the positron affinities for different systems (in ground state) are 6.507(\( Li^- \)), 6.015(\( B^- \)), 5.941(\( C^- \)), 5.862(\( O^- \)) and 6.170(\( F^- \)) in \( \text{eV} \).

Another binding energy of importance is the \emph{positronium} affinity, a positive value of which means the system \([\text{A}^-; e^+]\) is stable with respect to break up into the positronium (\( Ps \)) and a neutral atom \( A \). The binding energies or positronium affinities can be computed in various ways \( \text{[3]} \). We compute the positronium affinities using the following two definitions:

\[ PsA = E(A) + E(Ps) - E([A^-; e^+]) \tag{11} \]

and

\[ PsA = E.A. + P.A. + E(Ps). \tag{12} \]

Positronium affinities computed from Eq. (11) are compared against the restricted Hartree-Fock (RHF) positronium affinities \( \text{[12,16]} \) in Table \( \text{II} \). While for all the systems investigated the present and the RHF values of positronium affinities (calculated using Eq. (11)) are in good agreement, no system is stable with respect to dissociation into a neutral atom and positronium: the positronium affinities for all systems are negative.

In order to calculate the positronium affinity using Eq. (12), we choose \(-\epsilon_{max}\) of anionic system for the electron affinity (EA) as it is empirically found \( \text{[3]} \) that in the exchange-only work formalism and the HF theory, the \(-\epsilon_{max}\) of the anionic system is, in general, a better estimate of EA than those obtained from the difference of self-consistent total energies of the atom and the corresponding anion. Further, it is observed that such estimates of EA within the present formalism are closer to the experimental EA \( \text{[12]} \) than those obtained in HF theory by means of Koopmans’ theorem \( \text{[8]} \). For positron affinity we employ \(-\epsilon^+\) (third column in Table \( \text{II} \)) since this quantity is, in general, in better agreement with the accurate QMC positron affinity than the one obtained by taking difference of self-consistent energies (using Eq. (11)). The positronium affinities thus calculated are also given in the last column of the Table \( \text{II} \). These values of \( PsA \) are less negative than the \( PsA \) computed as the difference of the self-consistent energies (Eq. (11)) leading in some cases to the binding. The systems \([O^-; e_{1s}^+], [F^-; e_{1s}^+], [F^-; e_{2p}^+], [Cl^-; e_{1s}^+]\) and \([Br^-; e_{1s}^+]\) are found to be stable against the dissociation into the positronium and an atom. This binding may be attributed to the accurate asymptotic structure of the work formalism HF approximation.

We finally present the one electron properties such as \(<r^m>\) expectation values for halide anions in the Table \( \text{IV} \). The one electron expectation values are in good agreement with their HF counterparts. The computed \(<1/r>\) values are slightly larger than the HF values, implying the slight increase in the positron density towards the nucleus which therefore, should be compensated by small reduction in the long-range of the positron density leading to smaller \(<r>\) and \(<r^2>\). This is indeed the case as can be seen from the Table \( \text{IV} \).

We have also investigated the binding of positron to neutral atoms in the spirit of Patrick and Cade, by starting with the anion-positron bound state and reducing the ionicity of the system to obtain desired neutral system. It was found that the neutral-atom positron bound state does not exist in the exchange-only work formalism. This, however, is not surprising as the present treatment lacks the electron-positron and electron-electron correlation effects which
are crucial to permit such a binding [21]. Further, it has been rigorously shown by Pathak [35] that the deviation from the spherical symmetry is a necessary condition in order that the positron binding to neutral atom would occur. The present treatment can be extended to include the correlations effects, namely the electron-electron Coulomb correlations, correlation contribution to the kinetic energy and the electron-positron correlation. The first one can be incorporated by modeling the correlation second-order density matrix as suggested by Levy and Perdew [27] while the second one can be derived in terms of density matrices via virial theorem [22]. The electron-positron correlation potential [36] can be added in an *ad hoc* manner to the effective potential.

IV. CONCLUSIONS

In the present work, the positron binding to negative ions is investigated within the exchange-only work formalism. The work formalism of Harbola-Sahni seems to provide the Hartree-Fock level description of the electron-positron system as can be seen from the agreement between the present values of positron and positronium affinities and their restricted Hartree-Fock counterpart. The advantage of the work formalism is that its effective potential is local, orbital independent and therefore computationally cheaper. The systems \([O^-; e_1^+]\), \([F^-; e_1^+]\), \([F^-; e_2^+]\), \([Cl^-; e_1^+]\) and \([Br^-; e_1^+]\) are found to be stable against the dissociation into the positronium and the corresponding atom.
TABLE I. Negative total energies (in Hartree a.u.) of $[A^-; e^+]$ bound system calculated in central field approximation within the work formalism. Also given are the total energies in HF theory.

| System | Work formalism $-E$ | HF $-E$ | System | Work formalism $-E$ | HF $-E$ |
|--------|----------------------|---------|--------|----------------------|---------|
| $Li^-\ 1s^2\ 2s^2$ | 7.4270 | 7.4282 | $F^-\ 1s^22s^22p^6$ | 99.4543 | 99.4594 |
| $Li^- : 1s$ | 7.5286 | 7.5299 | $F^- : 1s$ | 99.6383 | 99.6434 |
| $Li^- : 2s$ | 7.4748 | 7.4760 | $F^- : 2s$ | 99.5253 | 99.5305 |
| $Li^- : 3s$ | 7.4528 | - | $F^- : 2p$ | 99.5641 | 99.5692 |
| $Li^- : 2p$ | 7.5017 | 7.5030 | $F^- : 3s$ | 99.4917 | - |
| $Li^- : 3p$ | 7.4653 | - | $F^- : 3p$ | 99.5048 | - |
| $Li^- : 3d$ | 7.4752 | 7.4765 | $F^- : 3d$ | 99.5095 | 99.5147 |
| $Li\ 1s^2\ 2s^1$ | 7.4316 | 7.4328 | $F\ 1s^22s^22p^5$ | 99.4046 | 99.4095 |
| $B^-\ 1s^22s^22p^2$ | 24.5156 | 24.5192 | $Cl^- [Ne]3s^23p^6$ | 459.5640 | 459.5769 |
| $B^- : 1s$ | 24.6495 | 24.6531 | $Cl^- : 1s$ | 459.7071 | 459.7189 |
| $B^- : 2s$ | 24.5733 | 24.5769 | $Cl^- : 2s$ | 459.6243 | 459.6373 |
| $B^- : 2p$ | 24.6108 | 24.6202 | $Cl^- : 2p$ | 459.6625 | 459.6754 |
| $B^- : 3s$ | 24.5477 | - | $Cl^- : 3s$ | 459.5972 | - |
| $B^- : 3p$ | 24.5610 | - | $Cl^- : 3p$ | 459.6107 | - |
| $B^- : 3d$ | 24.5694 | 24.5757 | $Cl\ [Ne]3s^23p^5$ | 459.4697 | 459.4830 |
| $B\ 1s^22s^22p^1$ | 24.5261 | 24.5292 | $Br^- [Ar]4s^23d^104p^6$ | 2572.523 | 2572.5363 |
| $C^-\ 1s^22s^22p^3$ | 37.7041 | 37.7088 | $Br^- : 1s$ | 2572.656 | 2572.6695 |
| $C^- : 1s$ | 37.8563 | 37.8610 | $Br^- : 2s$ | 2572.5803 | - |
| $C^- : 2s$ | 37.7671 | 37.7718 | $Br^- : 2p$ | 2572.6177 | 2572.6311 |
| $C^- : 3s$ | 37.8040 | 37.8087 | $Br\ [Ar]4s^23d^104p^5$ | 2572.229 | - |
| $C^- : 3p$ | 37.7384 | - | $C^- : 3p$ | - | - |
| $C^- : 3d$ | 37.7513 | - | $C^- : 3d$ | - | - |
| $C\ 1s^22s^22p^2$ | 37.6847 | 37.6887 | $O^-\ 1s^22s^22p^7$ | 74.7849 | 74.7897 |
| $O^-\ 1s^22s^22p^5$ | 74.7849 | 74.7897 | $O^- : 1s$ | 74.9583 | 74.9630 |
| $O^- : 2s$ | 74.8534 | 74.8582 | $O^- : 2p$ | 74.8940 | 74.9026 |
| $O^- : 3s$ | 74.8214 | - | $O^- : 3p$ | 74.8350 | - |
| $O^- : 3d$ | 74.8403 | 74.8461 | $O^- : 3d$ | - | - |
| $O\ 1s^22s^22p^4$ | 74.8050 | 74.8095 | $O\ 1s^22s^22p^4$ | - | - |
TABLE II. The total ground state energy differences between the present work and the HF theory in parts per million for anion-positron bound states (the positron is in the 1s orbital).

| system            | differences (ppm) |
|-------------------|-------------------|
| $[\text{Li}^-, e_1^+]$ | 173               |
| $[\text{B}^-, e_1^+]$  | 146               |
| $[\text{C}^-, e_1^+]$  | 124               |
| $[\text{O}^-, e_1^+]$  | 59                |
| $[\text{F}^-, e_1^+]$  | 51                |
| $[\text{Cl}^-, e_1^+]$ | 26                |
| $[\text{Br}^-, e_1^+]$ | 5                 |
| system | \( n + l \) | \(-\epsilon^+\) | PA | PsA | PsA† |
|--------|-----------|---------|-----|------|------|
|        | HS | RHF | HS | RHF | HS | RHF |
| \( Li^- \) | : 1s | 3.049 | 2.996 | 2.765 | 2.766 | -4.161 | -4.159 | -3.341 |
| \( Li^- \) | : 2s | 1.347 | 1.329 | 1.306 | 1.301 | -5.625 | -5.624 | -5.0427 |
| \( Li^- \) | : 3s | 0.770 | - | 0.770 | - | -6.169 | - | -5.620 |
| \( Li^- \) | : 3p | 1.064 | - | 1.042 | - | -5.883 | - | -5.326 |
| \( Li^- \) | : 3d | 1.339 | 1.331 | 1.312 | 1.312 | -5.614 | -5.613 | -5.051 |
| \( B^- \) | : 1s | 3.785 | 3.778 | 3.644 | 3.642 | -3.422 | -3.428 | -2.395 |
| \( B^- \) | : 2s | 1.584 | 1.582 | 1.714 | 1.569 | -5.372 | -5.502 | -4.506 |
| \( B^- \) | : 2p | 2.557 | 2.799 | 2.590 | 2.748 | -4.240 | -4.323 | -3.623 |
| \( B^- \) | : 3s | 0.876 | - | 0.875 | - | -4.988 | - | -5.304 |
| \( B^- \) | : 3p | 1.212 | - | 1.235 | - | - | - | -4.968 |
| \( B^- \) | : 3d | 1.442 | 1.540 | 1.464 | 1.536 | -5.450 | -5.535 | -4.738 |
| \( C^- \) | : 1s | 4.204 | 4.218 | 4.142 | 4.141 | -2.131 | -2.21 | -0.854 |
| \( C^- \) | : 2s | 1.712 | 1.718 | 1.714 | 1.713 | -4.558 | -4.540 | -3.346 |
| \( C^- \) | : 2p | 2.712 | 2.135 | 2.718 | 2.718 | -3.554 | -3.535 | -2.346 |
| \( C^- \) | : 3s | 0.931 | - | 0.933 | - | -5.339 | - | -4.127 |
| \( C^- \) | : 3p | 1.282 | - | 1.284 | - | -4.988 | - | -3.776 |
| \( C^- \) | : 3d | 1.478 | 1.480 | 1.478 | 1.480 | -4.795 | -4.773 | -3.580 |
| \( O^- \) | : 1s | 4.784 | 4.769 | 4.718 | 4.716 | -2.628 | -2.662 | 1.443 |
| \( O^- \) | : 2s | 1.869 | 1.865 | 1.864 | 1.862 | -5.483 | -5.475 | -1.472 |
| \( O^- \) | : 2p | 2.917 | 3.079 | 2.969 | 3.070 | -4.378 | -4.268 | -0.424 |
| \( O^- \) | : 3s | 0.993 | - | 0.993 | - | -6.354 | - | -2.348 |
| \( O^- \) | : 3p | 1.350 | - | 1.363 | - | -5.984 | - | -1.991 |
| \( O^- \) | : 3d | 1.498 | 1.532 | 1.508 | 1.532 | -5.839 | -5.805 | -1.843 |
| \( F^- \) | : 1s | 5.061 | 5.048 | 5.007 | 5.006 | -0.441 | -0.434 | 3.126 |
| \( F^- \) | : 2s | 1.932 | 1.936 | 1.932 | 1.933 | -3.516 | -3.506 | 0.003 |
| \( F^- \) | : 2p | 2.993 | 2.992 | 2.998 | 2.987 | -2.460 | -2.452 | 1.058 |
| \( F^- \) | : 3s | 1.020 | - | 1.018 | - | -4.430 | - | -0.015 |
| \( F^- \) | : 3p | 1.377 | - | 1.374 | - | -4.073 | - | -0.598 |
| \( F^- \) | : 3d | 1.503 | 1.502 | 1.503 | 1.503 | -3.946 | -3.937 | -0.432 |
| \( Cl^- \) | : 1s | 3.928 | 3.922 | 3.948 | 3.894 | -0.340 | -0.350 | 1.052 |
| \( Cl^- \) | : 2s | 1.645 | 1.644 | 1.641 | 1.642 | -2.590 | -2.600 | -1.231 |
| \( Cl^- \) | : 2p | 2.687 | 2.687 | 2.680 | 2.680 | -1.554 | -1.560 | -0.189 |
| \( Br^- \) | : 1s | 3.655 | 3.653 | 3.619 | 3.626 | -0.620 | -0.690 | 0.409 |
| \( Br^- \) | : 2s | 1.568 | - | 1.559 | - | -2.680 | - | -1.678 |
| \( Br^- \) | : 2p | 2.585 | 2.588 | 2.577 | 2.577 | -1.670 | -1.740 | -0.661 |

† Calculated using Eq. (12) (see text for details).
TABLE IV. The radial expectation values $<\frac{1}{r}>, <r>$ and $<r^2>$ for the 1s positron orbital in halide ions calculated within the work formalism and the corresponding Hartree-Fock values (the values are in Hartree atomic units).

| system    | $<\frac{1}{r}>$ | $<r>$   | $<r^2>$  |
|-----------|-----------------|---------|----------|
| $[F^-; e^+]$ | 0.2959          | 4.067   | 19.454   |
|           | 0.2948          | 4.080   | 19.572   |
| $[Cl^-; e^+]$ | 0.2194          | 5.2987  | 32.2031  |
|           | 0.2189          | 5.3085  | 32.3131  |
| $[Br^-; e^+]$ | 0.2018          | 5.7178  | 37.1800  |
|           | 0.2015          | 5.7198  | 37.2715  |

ACKNOWLEDGMENTS

The author gratefully acknowledges the help of Dr. M. K. Harbola for providing him with a Herman-Skillman work formalism code. The author would also like to thank Dr. R K. Pathak, Dr. A. Kshirsagar and Ms. Tonna Baruah for the helpful discussions and encouragement, and further acknowledge the Council of Scientific and Industrial Research, New Delhi, India for the assistance for this work in the form of senior research fellowship.
[1] F. H. Gertler, H. B. Snodgrass and L. Spruch, Phys. Rev. 172, 110(1968).
[2] I. Aronson, C. J. Kleinman and L. Spruch, Phys. Rev. A 4, 841(1971).
[3] D. C. Clary, J. Phys. B: Atom, Molec. Phys. 9, 3115(1976).
[4] S. Golden and I. R. Epstein, Phys. Rev. A 10, 761(1974).
[5] D. M. Schrader, in Positron Annihilation ed. P.G. Coleman, S.C. Sharma and L.M. Diana (North-Holland Publishing Company, 1982).
[6] A. Harju, B. Barbiellini and R.M. Nieminen, Phys. Rev. A 54, 4849(1996).
[7] G.G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. 79, 4124(1997).
[8] T. Yoshida and G. Miyako, Phys. Rev. A 54, 4571(1996).
[9] T. Yoshida and G. Miyako, J. Chem. Phys. 107, 3864(1997).
[10] T. Baruah, R. K. Pathak and A. Kshirsagar, Phys. Rev. A 55, 1518(1997).
[11] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A 52, 4541(1995).
[12] A. J. Patrick and P. E. Cade, J. Chem. Phys. 75, 1903(1981).
[13] D. M. Schrader, T. Yoshida and K. Iguchi, Phys. Rev. Lett. 86, 3281(1992).
[14] D. M. Schrader, T. Yoshida and K. Iguchi, J. Chem. Phys. 98, 7185(1993).
[15] D. Bressanin, M. Mella and G. Morosi, J. Chem. Phys. A 108, 4756(1998).
[16] P. E. Cade and A. Farazdel, J. Chem. Phys. 66, 2598(1977).
[17] P. E. Cade and A. Farazdel, Solid. State. Commn. 14, 807(1974).
[18] B. Chakraborty, Phys. Rev. B 24, 7423(1981).
[19] J. G. Harrison, J. Chem. Phys. 84, 1659(1986).
[20] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048(1981).
[21] T. Baruah, R. R. Zope, A. Kshirsagar and R. K. Pathak, Phys. Rev. A 50, 2191(1994).
[22] D.G. Kanhere, A. Kshirsagar and V. Bhamre, Chem. Phys. Lett., 160, 526(1989).
[23] M. K. Harbola and V. Sahni, Phys. Rev. Lett. 62, 89(1989); V. Sahni and M. K. Harbola, Int. J. Quant. Chem. Symp. Pro. 24, 569(1990).
[24] V. Sahni, Phys. Rev. A 55, 1846 (1997); V. Sahni, in Density Functional Theory I, Top. Curr. Chem. 180 , edited by R. Nalewajski(Springer-Verlag, Heidelberg, 1996).
[25] A. Holas and N. H. March, Phys. Rev. A 51, 2040(1995).
[26] V. Sahni, Y. Li and M. K. Harbola, Phys. Rev. A 45, 1434(1992).
[27] M. Levy and N. H. March, Phys. Rev. A 55, 1885(1997).

[28] M. K. Harbola, R. R. Zope and R. K. Pathak, Phys. Rev. A 53, 3652(1996).

[29] F. Herman and S. Skillman Atomic Structure Calculations (Englewood Cliffs, NJ: Prentice-Hall, 1963).

[30] K.D. Sen and M. K. Harbola, Chem. Phys. Lett. 178, 347(1991).

[31] Y. Li, J.B. Kriger and G.J. Iafrate, Chem. Phys. Lett. 191, 38(1992).

[32] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4 539(1975).

[33] J. P. Perdew, R.G. Parr, M. Levy and J.L.Balduz Jr., Phys. Rev. Lett. 49, 1691(1982).

[34] J. P. Perdew and M. Levy, Phys. Rev. A 56, 16021(1997) and references therein.

[35] R. K. Pathak, Phys. Rev. A 49, 5100(1994).

[36] M. J. Puska, A. P. Seitsonen and R. M. Nieminen, Phys. Rev. B 52, 10947(1995).