

Exchange and correlation effects in the strongly interacting He-Ps system

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Abstract. The density functional theory has been used to calculate the total energy of the system comprising a He and a positronium atom. The single particle orbitals have been used to calculate the non-interacting kinetic energy, while the electron and positron densities were used for the Hartree energy, the electron exchange-correlation energy and the external potential energies. The electron exchange-correlation energy has been calculated within the Local Density Approximation and the General Gradient Approximation (PBE). For the electron-positron correlation energy the formula by Boronski and Nieminen has been used. The results have been compared to many-body wavefunction calculations employing the exact diagonalization of an explicitly correlated gaussians basis. While the many-body value result predicts that HePs is not bound, the density functional approach predicts a bound state with mean nucleus-positron distance of ~ 9 a.u.. To discuss the origin of this discrepancy the exchange-correlation energy has been deduced from the many-body result and it has been compared to the density functional scheme.

1. Introduction

The ortho-positronium (o-Ps) atom is the bound state of an electron and a positron with the total spin $S = 1$. It is formed in molecular matter and in some insulators, such as SiO_2 , where the electron density is low in the interstitial region [1]. Its annihilation with an electron of the matter occurs typically through the two-gamma channel. The resulting pick-off annihilation rate depends on the overlap of the o-Ps with the electron density of the matter and it can reduce the positron lifetime remarkably [2]. The pick-off annihilation lifetime spectroscopy of o-Ps has a rather unique role as a method capable to study open volumes in polymers [3] and biostructures [4; 5].

The understanding of the experimental results would benefit from calculations of o-Ps states in molecular soft-matter. However both the electron and the positron in the Ps atom are light quantum-mechanical particles and the non-adiabatic correlation effects have to be properly taken into account; something that has inhibited progress in this field. For delocalized positrons in metals and semiconductors, where Ps is not formed and the density of positrons can be assumed to be low, the quantum-mechanical state of a single positron [6] can be represented within the two component density functional theory (DFT). Accurate lifetime values have been obtained, and even the lifetimes of positrons trapped at vacancies can be calculated with good accuracy [7]. Using a DFT approach for the simulation of the positronium atom would also be desirable but the description of the electron-positron bound state is challenging.



In this work, the many-body wavefunction and the interaction energy of the unbound HePs system has been calculated by using explicitly correlated gaussian and the stochastic variational method (ECG-SVM) [8; 9] for a set of configurations with the nucleus-positron mean distance ranging between 2.0 a.u. and 40 a.u.. The DFT exchange-correlation energy has been deduced using the electron and positron densities of the many-body calculation. The interaction and the exchange-correlation energies have been calculated using the Local Density Approximation (LDA) and the General Gradient Approximation implementation by Perdew et al. (PBE) for the electron-electron exchange correlation.

2. Computational methods

The many-body wavefunction is written as a linear combination of properly antisymmetrized ECG functions. The 5-particle system comprising the heavy nucleus (treated as a single particle), the electrons and the positron has been described by the non-relativistic Hamiltonian $\hat{H} = \sum_i \frac{\vec{p}_i^2}{2m_i} - T_{cm} + \sum_{i<j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$, where \vec{p}_i , m_i , and q_i , are the momenta, masses, and charges of the particles, respectively, r_{ij} is the distance between the i^{th} and j^{th} particles, and T_{cm} is the center-of-mass (CM) kinetic energy. More details about the calculations can be found in reference [9].

The energy of the HePs system under the two component DFT with electron density n_- and positron density n_+ is [10]:

$$E = F[n_-] + F[n_+] + Z \int d\mathbf{r} \frac{n_+(\mathbf{r}) - \mathbf{n}-(\mathbf{r})}{r} - \int d\mathbf{r} d\mathbf{r}' \frac{n_-(\mathbf{r})n_+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_c^{e-p}[n_+, n_-] \quad (1)$$

where E_c^{e-p} is the electron-positron correlation energy and $F[n]$ the hamiltonian for one component DFT ($F[n] = T[n] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$). The LDA [11] and PBE [12] functionals have been used for the exchange-correlation energy (E_{xc}) while for E_c^{e-p} the parametrization by Boronski and Nieminen (BN) [10] has been used. The non-interacting kinetic energies have been calculated from the single particle orbitals. The positron single particle orbital is the square root of the positron density. For the electrons, the orbitals are also approximated as the square root of the components of the electron density forming a singlet and a triplet with the positron, $\rho_i^e = \langle \Psi | \hat{P}_i^{e-p} \hat{\rho}^e | \Psi \rangle$. \hat{P}_i^{e-p} projects the singlet or triplet component of the electron density operator and Ψ is the ECG-SVM many-body wavefunction.

3. Results & Discussion

The values of the interaction energy $E_I = E_{HePs} - E_{He} - E_{Ps}$ of HePs are shown in table 1 ordered according to the increasing nucleus-positron mean distance $\langle r_p \rangle$. The ECG-SVM result, E_I^{ED} , is always positive and approaches zero for large $\langle r_p \rangle$ values. The energy values decrease from 0.4054 Ha in the strongest constrained system to 0.0017 Ha in the less constrained system and it further decreases going towards zero at larger separations [9]. The positron non-interacting kinetic energy E_{kin}^p agrees with the zero point energy of positronium E_{conf}^{sq} in an infinite square potential with $R=2\langle r_p \rangle$. E_{kin}^p is $\sim 37\%$ of the total interaction energy for the most confined system but for the system with the largest $\langle r_p \rangle$ it is $\sim 83\%$. The DFT interaction energy has been calculated using the density obtained from the ECG-SVM wavefunction and the LDA (E_I^{LDA}) and PBE (E_I^{PBE}) functionals for the indistinguishable particle exchange-correlation energy. The interaction energies are similar in LDA and PBE. At $\langle r_p \rangle$ larger than 2 a.u., the interaction energy is negative and it shows a minimum at $\langle r_p \rangle \sim 9$ a.u. (~ -0.031 Ha). At very long separations E_I^{LDA} and E_I^{PBE} increases towards zero. In the most confined system, the interaction energy obtained from the density is also lower than the ECG-SVM value.

In order to gain a deeper insight into the origin of the discrepancy between the ECG-SVM and the DFT results, the exchange-correlation energy has been calculated by subtracting from

Table 1. Values of the interaction energy from the ECG-SVM calculation (E_I^{ED}), DFT (E_I^{LDA} and E_I^{PBE}) and non-interacting kinetic energy of the positron in Hartrees. The zero-point energy inside an infinite square potential of $R=2\langle r_p \rangle$ is also shown. The values are ordered according to $\langle r_p \rangle$ (in a.u.).

| $\langle r_p \rangle$ | 2.07 | 5.00 | 10.11 | 14.55 | 19.41 |
|-----------------------|--------|---------|---------|---------|---------|
| E_I^{ED} | 0.4054 | 0.0492 | 0.0079 | 0.0033 | 0.0017 |
| E_I^{LDA} | 0.2422 | -0.0087 | -0.0307 | -0.0231 | -0.0129 |
| E_I^{PBE} | 0.2354 | -0.0110 | -0.0313 | -0.0232 | -0.0129 |
| E_{kin}^p | 0.1504 | 0.0267 | 0.0057 | 0.0026 | 0.0014 |
| E_{conf}^{Sq} | 0.1435 | 0.0246 | 0.0060 | 0.0029 | 0.0016 |

the many-body result the DFT single particle kinetic and potential (External and Hartree terms) energies. The values shown in figure 1 are compared to the corresponding DFT values. The ECG-SVM exchange-correlation energy has an almost constant value of -1.31 Ha for systems with $\langle r_p \rangle$ larger than 10 a.u. and it is lower ($E_{xc}^{ED} \sim -1.45$ Ha is lower, in the more confined systems. While the total PBE+BN exchange-correlation energies are lower than ECG-SVM values for all $\langle r_p \rangle$, the total LDA+BN exchange-correlation energies are larger than those from ECG-SVM when $\langle r_p \rangle$ is larger than 15 a.u.. It keeps on growing till $\langle r_p \rangle \sim 35$ a.u. and the increase is markedly stronger, -0.3 Ha, than in the ECG-SVM result, -0.14 Ha. The LDA results are ~ 0.06 Ha larger than the PBE values in all the calculated systems and the interaction energy is similar under both approximations. The PBE exchange-correlation energies are lower than the ECG-SVM values in all the systems but the LDA value are larger for $\langle r_p \rangle \geq 15$ a.u..

The difference between the ECG-SVM and the DFT total interaction energies come from the low values of the DFT exchange-correlation energy in the more confined systems, in which the electron-electron exchange-correlation energy is the dominating contribution. The exchange-correlation functionals are known to have severe difficulties in describing the energetics of closed-shell molecules and atoms with HOMO-LUMO gaps. DFT is also known to be unable to describe the attractive dispersion energy [13] so that the predicted interaction energies are typically too large. In addition, in the HePs system the attractive dispersion interaction is very weak, because the polarizability of He is low. The BN parametrization of the electron-positron correlation energy, obtained from many-body results for a single positron in an infinite homogeneous electron gas, is also a source of inaccuracy. It should be noted though that the electron-positron correlation energy for a finite positron density would be smaller and it cannot account for the observed difference [14].

4. Conclusions

The He-Ps interaction energy obtained from many-body ECG-SVM results and that arising from a DFT scheme have been compared. The interaction energies are similar in magnitude but show important differences in their behaviors as the confinement of the system is varied. While the ECG-SVM total energy decreases monotonically as the mean positron increases, the DFT results show a minimum at ~ 9 a.u. and it incorrectly predicts a bound state for the HePs system. In the most confined systems the ECG-SVM energies are more repulsive than the DFT energies. The origin of the weakened repulsive in DFT has been linked to the electron-electron exchange term which fails to account for the strong repulsion when the system is confined. The electron-positron correlation energy can also be a source of inaccuracy but it cannot explain the low values of the interaction energy in the DFT result.

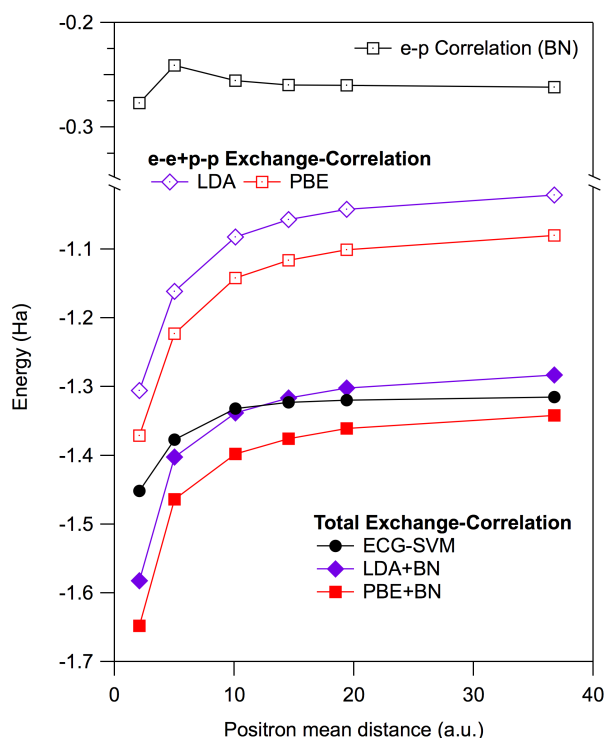


Figure 1. (Color online) The total exchange-correlation energy terms for the ECG-SVM (black full circles) and the DFT LDA (purple full diamonds) and PBE (red full squares) energies versus $\langle r_p \rangle$. See the text for the definition of the ECG-SVM exchange-correlation energy. Also the DFT electron-electron exchange correlation energies (purple dotted diamonds for LDA and red dotted square for PBE) and the BN electron-positron correlation energy (black dotted squares) are shown.

5. Acknowledgments

This work was supported by the Academy of Finland through individual fellowships and the centre of excellence program.

References

- [1] Stepanov S V and Byakov V M 2003 *Principles and application of positron & positronium chemistry* 5 (World Scientific)
- [2] Mogensen O E 1995 Springer series in chemical physics *Positron Annihilation in Chemistry* vol 58 ed Lotsch H (Springer-Verlag) chap Principles of Positron Annihilation in Molecular Solids, p 193
- [3] Uedono A, Suzuki R, Ohdaira T, Uozumi T, Ban M, Kyoto M, Tanigawa S and Mikado T 1998 *J. Polym. Sci. Part B* **36** 2597
- [4] Sane P, Salonen E, Falck E, Repakova J, Tuomisto F, Holopainen J and Vattulainen I 2009 *J. Phys. Chem. B Letters* **113** 1810
- [5] Dong A W, Pascual-Izarra C, Pas S J, Hill A J, Boyd B J and Drummond C J 2009 *J. Phys. Chem. B* **113** 84
- [6] Puska M J and Nieminen R M 1994 *Rev. Mod. Phys.* **66** 841
- [7] Makkonen I and Puska M J 2007 *Phys. Rev. B* **76** 054119

- [8] Varga K and Suzuki Y 1995 *Phys. Rev. C* **52** 2885
- [9] Zubiaga A, Tuomisto F and Puska M J 2012 *Phys. Rev. A* **85** 052707
- [10] Boroński E and Nieminen R M 1986 *Phys. Rev. B* **34** 3820
- [11] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- [12] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [13] Johnson E R, Mackie I D and DiLabio G A 2009 *J. Phys. Org. Chem.* **22** 1127
- [14] Lantto L J 1987 *Phys. Rev. B* **36** 5160