Positron binding and annihilation in molecules

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State of the art and motivations

The positron is the antiparticle of the electron. It was the first *antimatter* particle ever discovered, first theoretically by Paul Dirac in 1931, and then experimentally by Carl Anderson in 1932, both physicists awarded the Nobel Prize soon after. Positrons are also the simplest and most abundant form of antimatter. They come from β^+ radioactive decays, can be generated in accelerators, and are produced in large quantities (15×10^9 tonnes per second!) near the centre of our Galaxy. The ability of positrons to *annihilate* with electrons and emit characteristic annihilation gamma rays, underpins their use in various diagnostics, from positron lifetime spectroscopy of solids to positron emission tomography (PET) in medicine. When partnered with antiprotons, positrons can form *antihydrogen*, currently under intense investigation at CERN.

The electrons with which positrons annihilate are usually not free but packed in atoms or molecules. The process of annihilation is strongly affected by the positron interaction with the target. For example, positrons are repelled by atomic nuclei, so they usually annihilate only with the outermost, valence electrons. On the other hand, when a positron approaches an atom or molecule, it *polarises* it by pulling the electron cloud towards itself. This gives rise to an attractive polarisation potential acting on the positron. Another important effect is "hopping" of an atomic electron to the positron, temporarily forming an electron-positron "atom" called positronium (Ps). This increases the positron-atom attraction and strongly enhances the positron annihilation probability (see, e.g., detailed calculations for noble-gas atoms [1]).

For many atoms, the attraction is so strong that it overcomes the positron-nucleus repulsion and allows the creation of positron-atom *bound states* (predicted in [2] and proved variationally in [3]). To date, positron binding to about ten atoms has been predicted in state-of-the-art calculations. There are also firm expectations that many more atoms are capable of binding [4, 5], but there have not been any experimental conformation of this phenomenon yet [6].

What makes the problem of binding so important is the effect it has on positron annihilation in molecules [7]. When a positron collides with a molecule, it can be captured into the bound state by transferring its excess energy into molecular vibrations. This gives rise to *resonances* and orders-of-magnitude enhancement of the annihilation rates. Annihilation studies of resonances enabled measurements of positron binding energies for over 70 molecules (see [8] and references therein). In contrast, a significant theoretical effort towards computing positron-molecule bound states resulted in only a handful of predictions that could be compared with experiment, with the best agreement being at 25% level [9]. The reason for this was that positron-molecule attraction and binding are due to electron-positron *correlation effects*, such as polarisation and virtual Ps formation, which are difficult to describe theoretically.

In 2018 a new method was proposed to attack the problem. Based on the earlier extensive studies of positron-atom interactions [1], we constructed a model positron-molecule correlation

potential that was capable of describing positron binding to a wide range of molecules [10, 11], as well as positron scattering and annihilation from small molecules [12]. The relative simplicity of the method has enabled us to apply it to more difficult problems, such as the dependence of the positron binding on the molecular conformation (i.e., the shape of the molecule) for long alkane molecules with up to 16 carbon atoms [13].

Objectives & Methodology

The aim of the project is to explore positron binding to molecules and related problems by developing the new approach further. At the heart of the theory is the positron-molecule model correlation potential. While some of its parameters are based on the known molecular properties (such as the dipole polarisabilities), others are adjustable, e.g., by comparison with experimental data for positron binding. The potential also has some limitations, e.g., its long-range form is assumed to be spherical, which is an additional approximation.

Future work will involve introduction of non-spherical potentials, consideration of new molecular families and new processes, e.g., the interaction of the positron-molecule complexes with photons, or determination of the spectra of annihilation gamma rays, an area where large amounts of experimental data still await proper theoretical understanding.

On the technical side, calculations of positron binding and annihilation rates will be performed by using GAMESS [14], an advanced, free quantum-chemistry package. Its capabilities have been expanded by Dr Andrew Swann who introduced the model correlation potential for positron binding and implemented the calculations of the annihilation rate in the positron bound state. Studying new problems will require further development of the computer codes, analysis of the results, comparisons with experimental data (where available) and making predictions of new processes and properties.

Collaborations

Our group has a successful long-term collaboration with the experimentalist group of Prof. Cliff Surko (University of California, San Diego), whose famous positron trap is the workhorse of many positron experiments world over, and who pioneered measurements of positron-molecule resonant annihilation and binding energies. New links are emerging with the group of Dr. David Cassidy at UCL (London), who develop novel experiments with long-lived Rydberg-state positronium, with prospects of measuring positron binding to atoms and molecules [6].

Required skills

The candidate is expected to have good working knowledge of and interest in Quantum Mechanics. He/she will be expected to learn and master quantum-chemistry computational approaches. Running, modifying and developing computer codes will be an integral and substantial part of the project. In spite of the complexity of the codes, the underlying physics of positron-molecule binding and positron annihilation is relatively simple, and it is expected that many interesting insights into the problem will be obtained.

Further information

While focussed on the positron-molecule binding problem, the project will inroduce the candidate to the range of problems concerning antimatter and its applications, as well as to methods of quantum chemistry and its computational approaches. The experience of handling and writing computer codes, that will be acquired through the work on the project, will be useful in a wide range of future careers.

For further information, please contact Dr Gleb Gribakin.

References

[1] D. G. Green, J. A. Ludlow, and G. F. Gribakin, Phys. Rev. A **90**, 032712 (2014); D. G. Green and G. F. Gribakin, Phys. Rev. Lett. **114**, 093201 (2015).

[2] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A **52**, 4541 (1995).

[3] G. G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. **79**, 4124 (1997).

[4] J. Mitroy, M. W. J. Bromley and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).

[5] V. A. Dzuba, V. V. Flambaum, and G. F. Gribakin, Phys. Rev. Lett. **105**, 203401 (2010); V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati, Phys. Rev. A **86**, 032503 (2012); C. Harabati, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A **89**, 022517 (2014).

[6] A. R. Swann, D. B. Cassidy, A. Deller, and G. F. Gribakin, Phys. Rev. A **93**, 052712 (2016).

[7] G. F. Gribakin, J. A. Young and C. M. Surko, Rev. Mod. Phys. **82**, 2557 (2010).

[8] J. R. Danielson, A. C. L. and Jones, J. J. Gosselin, M. R. Natisin, and C. M. Surko, Phys. Rev. A **85**, 022709 (2012).

[9] M. Tachikawa, Y. Kita, and R. J. Buenker, Phys. Chem. Chem. Phys. **13**, 2701 (2011); M. Tachikawa, J. Phys. Conf. Ser. **488**, 012053 (2014).

[10] A. R. Swann and G. F. Gribakin, *Calculations of positron binding and annihilation in polyatomic molecules*, J. Chem. Phys. **149**, 244305 (2018).

[11] A. R. Swann and G. F. Gribakin, *Positron binding and annihilation in alkane molecules*, Phys. Rev. Lett **123**, 113402 (2019).

[12] A. R. Swann and G. F. Gribakin, *Model-potential calculations of positron binding, scattering, and annihilation for atoms and small molecules using a Gaussian basis*, Phys. Rev. A **101**, 022702 (2020).

[13] A. R. Swann and G. F. Gribakin, J. Chem. Phys. **153**, *Effect of molecular constitution and conformation on positron binding and annihilation in alkanes*, 184311 (2020).

[14] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993); M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: the first forty years*, edited by C. E. Dykstra *et al.* (Elsevier, Amsterdam, 2005) pp. 1167–1189.