

Calculations of Positron Binding to Polyatomic Molecules

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Our work provides the first quantitative explanation for positron binding to nonpolar molecules (alkanes, C_nH_{2n+2}), including the near-linear dependence on the size of the molecule and emergence of the 2nd bound state at $n = 12$.

Positron-molecule binding energies have been measured for over 70 molecules [1]. The majority (about 60) are nonpolar or weakly polar species, for which binding is made possible by polarisation of the electron cloud. In contrast, almost all existing calculations of positron-molecule binding deal with strongly polar species (see, e.g., Ref. [2]), using approaches such as configuration interaction and diffusion Monte Carlo. For these molecules, binding occurs even at the lowest (Hartree-Fock) level of the theory, but is greatly enhanced by electron-positron correlations, e.g., polarisation [3]. Only 6 molecules have been studied both experimentally and theoretically, and the best agreement for the binding energy is only at the level of 25% for acetonitrile [4].

We have developed a model-potential approach to calculating positron-molecule binding energies. We write the positron-molecule interaction potential as $V(\mathbf{r}) = V_{st}(\mathbf{r}) + V_{cor}(\mathbf{r})$, where $V_{st}(\mathbf{r})$ is the electrostatic potential of the ground-state molecule (described at the Hartree-Fock level), and $V_{cor}(\mathbf{r})$ is a model correlation potential, viz., $V_{cor}(\mathbf{r}) = -\frac{1}{2} \sum_A \alpha_A |\mathbf{r} - \mathbf{r}_A|^{-4} g_A(\mathbf{r})$, where the sum is over the molecule's constituent atoms A (whose nucleus is at position \mathbf{r}_A), α_A is the hybrid polarisability of atom A [5], and $g_A(\mathbf{r}) = 1 - \exp[-(|\mathbf{r} - \mathbf{r}_A|/\rho_A)^6]$ is a cutoff function that prevents $V_{cor}(\mathbf{r})$ from diverging near an atomic nucleus, with ρ_A a free parameter. In practice, a standard quantum-chemistry package [6] is used to compute $V_{st}(\mathbf{r})$ and has been modified to include $V_{cor}(\mathbf{r})$ for the positron. The figures below shows the results of the simplest calculation for several n -alkanes, taking $\rho_A = 2.2$ or 2.25 a.u. for all atoms, along with experimental data [7]. Our calculations correctly predict the existence of a second bound state for dodecane ($C_{12}H_{26}$) and larger alkanes.

Future work will entail adjusting values of ρ_C and ρ_H to obtain binding energies in closer agreement with experiment for the alkanes. We will also study aromatic hydrocarbons, alcohols, aldehydes, ketones, formates, acetates, nitriles and halogenated hydrocarbons. These calculations will provide insight into most of the molecules for which binding energies have been measured. The positron bound-state wavefunctions will be used to compute the electron-positron contact densities, positron annihilation rates and annihilation γ -ray spectra.

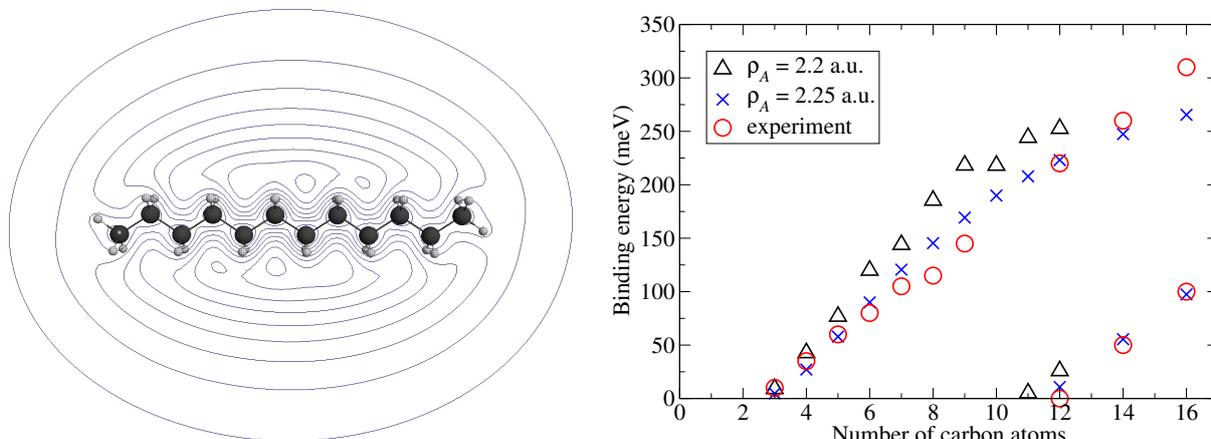


Fig. 1: Left: the positron bound state wavefunction in dodecane ($C_{12}H_{26}$) for $\rho = 2.25$ a.u. Right: comparison of the measured binding energies for n -alkanes C_nH_{2n+2} (circles) [7] with the calculated values that use the cutoff radius $\rho = 2.2$ a.u. and α_{mol} from [8] (triangles), or $\rho = 2.25$ a.u., with $\alpha_C = 7.096$ and $\alpha_H = 2.650$ a.u. obtained from a linear fit of the molecular polarisabilities from Ref. [5] (crosses).

References

- [1] J. R. Danielson, J. A. Young and C. M. Surko, *J. Phys. B* **85**, 022709 (2012); J. R. Danielson, J. J. Gosselin, and C. M. Surko, *Phys. Rev. Lett.* **104**, 233201 (2010); J. R. Danielson, A. C. L. Jones, J. J. Gosselin, M. R. Natisin, and C. M. Surko, *Phys. Rev. A* **85**, 022709 (2012).
- [2] G. F. Gribakin, J. A. Young, and C. M. Surko, *Rev. Mod. Phys.* **82**, 2557 (2010).
- [3] G. F. Gribakin and A. R. Swann, *J. Phys. B* **48**, 215101 (2015).
- [4] M. Tachikawa, *J. Phys. Conf. Ser.* **488**, 012053 (2014).
- [5] K. J. Miller, *J. Am. Chem. Soc.* **112**, 8533 (1990).
- [6] M. W. Schmidt et al., *J. Comput. Chem.* **14**, 1347 (1993); P. E. Adamson *et al.*, *J. Phys. Chem. A* **112**, 1346 (2008).
- [7] J. A. Young and C. M. Surko, *Phys. Rev. A* **77**, 052704 (2008).
- [8] *CRC Handbook of Chemistry and Physics*, 89th edition, Ed. D. R. Lide (Boca Raton, CRC Press, 2008–2009).

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