XXIX International Conference on Photonic, Electronic, and Atomic Collisions (ICPEAC2015) IOP Publishing
Journal of Physics: Conference Series **635** (2015) 072026 doi:10.1088/1742-6596/635/7/072026

Plasma screening effects in molecular hydrogen: modified energies and lifetimes of doubly excited states.

Andrés F. Ordóñez-Lasso*[1], José L. Sanz-Vicario†[2], and Fernando Martín*[3]

* Departamento de Química,Módulo 13, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain
† Grupo de Física Atómica y Molecular, Instituto de Física, Universidad de Antioquia, Medellín, Colombia

Synopsis We perform a systematic study on the behaviour of energy positions and autoionization widths of metastable resonance states in the Hydrogen molecule subject to screened Coulomb interactions among all particles using an *ab initio* Feshbach configuration interaction method. We only focus on the $\mathcal{Q}_1$ series of doubly excited states lying between the first $H_2^+(1s\sigma_g)$ and the second $H_2^+(2p\sigma_u)$ ionization thresholds, for several spectroscopic molecular symmetries $^{1,3}\Sigma_{g\,u}$, $^{1,3}\Pi_{g,u}$ and $^{1,3}\Delta_{g,u}$. Special attention is given to the efficient and accurate method for the evaluation of screened Coulomb two-electron integrals in molecules when using configurations in terms of molecular orbitals described using a B-spline basis.

The electronic Hamiltonian describing two-electrons and two nuclei with charges Z_1 and Z_2 with pairwise screened Coulomb interactions is $\hat{H}{=}\hat{T}{+}\hat{V}$, where the kinetic term is (in a.u.) $\hat{T}{=}-\sum_{i=1}^{2}\nabla_i^2/2$ and the potential term is

$$\hat{V} = -\sum_{A=1}^{2}\sum_{i=1}^{2}\frac{Z_A e^{-\lambda r_{iA}}}{r_{iA}} + \frac{e^{-\lambda r_{12}}}{r_{12}} + \frac{Z_1 Z_2 e^{-\lambda R_{12}}}{R_{12}}$$

where λ is the screening parameter. In standard molecular structure calculations for bound states, the molecular orbitals are built as linear combinations of atomic orbitals expanded in terms of Gaussian basis functions (GTOs). In this particular case, all required molecular integrals involving screened Coulomb interactions and GTOs can be carried out analytically [1]. However, GTOs are not well suited basis functions to perform calculations to describe superexcited states (resonances) and electronic continuum states of H_2. Instead, screened molecular orbitals are obtained by diagonalizing the screened H_2^+ Hamiltonian using one-center expansions in terms of B-splines, i.e., $r^{-1}B_i^k(r)\mathcal{Y}_{lm}(\Omega)$ with the origin placed at the nuclear center of mass. The electron-nucleus and electron-electron molecular integrals are evaluated by expanding both screened interactions in partial waves

$$\frac{e^{-\lambda r_{mn}}}{r_{mn}} = -\lambda\sum_{\ell=0}^{\infty}[\ell]j_\ell(i\lambda r_<)h_\ell^{(1)}(i\lambda r_>)P_\ell(\cos\theta_{mn})$$

where $[\ell]{=}2\ell+1$, $P_\ell(x)$ is the Legendre polynomial, and $j_\ell(x)$ and $h_\ell^{(1)}(x)$ correspond to the spherical Bessel and Hankel functions, respectively.

Whereas the one-electron molecular integrals with screening can be readily computed with quadratures, the accurate computation of screened two-electron molecular integrals is more involved. For the latter, $\langle ab|e^{-\lambda r_{12}}/r_{12}|cd\rangle$, we first obtain and solve the corresponding screened Poisson equation, which is satisfied by the standard auxiliary function $Y^k(bd;r)$ within the electronic radial box $r\in[0,r_{max}]$ in which the B-splines are defined. We employ the Feshbach formalism to compute the resonance parameters, by first solving the $\mathcal{Q}$-projected eigenvalue problem $(\mathcal{Q}H\mathcal{Q}-\mathcal{E}_n)\phi_n{=}0$ for the autoionizing states and then widths are calculated using Fermi's golden rule, $\Gamma_n{=}2\pi\sum_\mu|\langle\phi_n|\mathcal{Q}H\mathcal{P}|\mathcal{P}\psi^{0-}_{\mu E=\mathcal{E}_n}\rangle|^2$, where $|\mathcal{P}\psi^{0-}_{\mu E=\mathcal{E}_n}\rangle$ is the non-resonant continuum state with appropriate incoming boundary conditions at the resonance energy [2]. The variation of energies and widths with the screening parameter λ has been successfully tested with our molecular code set at the internuclear distance $R\to 0$ (where $H_2\to$ He), for which accurate atomic values are available [3]. We show that the metastability properties of autoionizing states may change significantly when molecules are immersed in plasma environments.

References

[1] J. M. Ugalde and C. Sarasola 1997 *Int. J. Quantum Chem.* **62** 273

[2] I. Sánchez and F. Martín 1997 *J. Chem. Phys.* **106** 7720

[3] A. F. Ordóñez-Lasso, J. C. Cardona, and J. L. Sanz-Vicario 2013 *Phys. Rev. A* **88** 012702

[1] E-mail: andres.ordonez@estudiante.uam.es
[2] E-mail: jose.sanz@udea.edu.co
[3] E-mail: fernando.martin@uam.es