

PHYSICAL SYSTEM AND THEORETICAL FRAMEWORK

The atomic systems of two-electrons may be described by the following Hamiltonian (in atomic units a.u.) :

$$H = h(1) + h(2) + \frac{1}{r_{12}}, \quad (1)$$

where $h(i) = -\frac{\nabla_i^2}{2} - \frac{Z}{r_i}$, with Z the nuclear charge. For the two-femions case the total wave function can be factorized in **orbital part** (symmetric or antisymmetric), and **spin part** (singlet or triplet, respectively)

$$|\Psi(1,2)\rangle = |\Phi_{S,A}(r_1, r_2)\rangle \otimes |\chi_{S,T}(\sigma_1, \sigma_2)\rangle. \quad (2)$$

We use a *configuration interaction* (CI) scheme to solve the Schrödinger equation by means of the following highly correlated function

$$|\psi; {}^{2S+1}L^{\pi}\rangle^{CI} = \sum_{n_1 l_1; n_2 l_2} C_{n_1 l_1; n_2 l_2} \left[P_{n_1 l_1}(r_1) P_{n_2 l_2}(r_2) \mathcal{Y}_{l_1 l_2}^{L, M_L}(\Omega_1, \Omega_2) \chi_S^M(1, 2) \right], \quad (3)$$

where we have used decoupled one-electron functions $|nlm^s\rangle = \frac{1}{r} P_{nl}(r) Y_{lm}^s(\theta, \phi) \chi_m^s$. We calculate the radial functions $P_{nl}(r)$ using a variational method with **B-splines bases**.

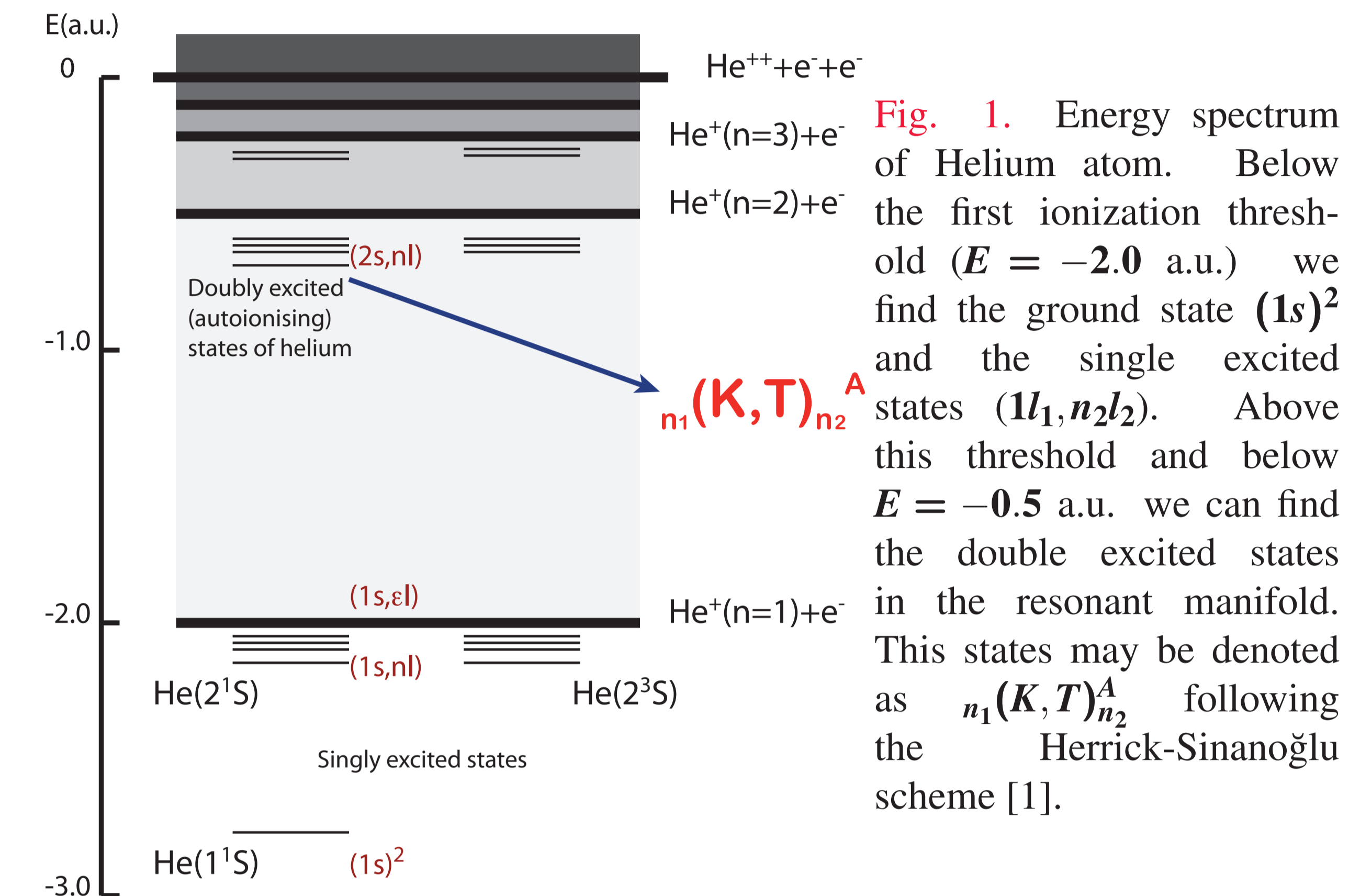


Fig. 1. Energy spectrum of Helium atom. Below the first ionization threshold ($E = -2.0$ a.u.) we find the ground state $(1s)^2$ and the single excited states $(1l_1, n_2 l_2)$. Above this threshold and below $E = -0.5$ a.u. we can find the double excited states in the resonant manifold. This states may be denoted as $n_1(K, T)n_2^A$ following the Herrick-Sinanoğlu scheme [1].

The **Feshbach formalism** is one of the most rigorous many-body theories to deal with doubly excited states immersed in an electronic continuum [2]. In Feshbach theory the wave function is splitted into two orthogonal spaces \mathcal{Q} **resonant**, and \mathcal{P} **non-resonant**:

$$\Psi = \mathcal{P}\Psi + \mathcal{Q}\Psi, \quad (4)$$

where \mathcal{P} and \mathcal{Q} are the projection operators associated with each subspace. The projectors obey the following properties $\mathcal{P} + \mathcal{Q} = 1$, $\mathcal{P}^2 = \mathcal{P}$, $\mathcal{Q}^2 = \mathcal{Q}$. By replacing the splitting form of the total wave function into the time independent Schrödinger equation $H\Psi = E\Psi$, it is straightforward to obtain the following equations for the bound-like and the *non-resonant* scattering-like parts [2]

$$(\mathcal{Q}H\mathcal{Q} - \mathcal{E}_n)\mathcal{Q}\Phi_n = 0 \quad (5a)$$

$$(\mathcal{P}H'\mathcal{P} - E)\mathcal{P}\Psi^0 = 0, \quad (5b)$$

where H' is the operator containing the atomic Hamiltonian plus an optical potential.

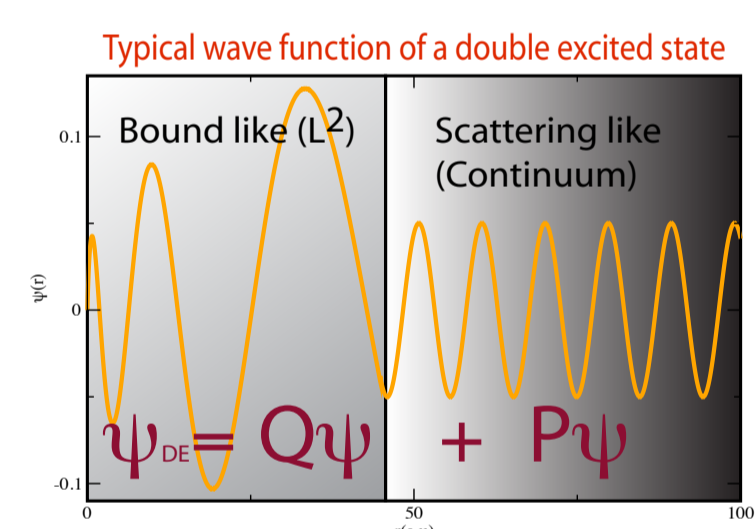


Fig. 2. This is a typical wave function of a resonance where the localized part carries most of the topological differential information about doubly excited states. Our goal is to analyze whether these topological differences discriminates the resonances in sets or series (K,T).

DENSITY FUNCTION

The two-electron density function or distribution function $\rho(r_1, r_2)$ is defined as the probability of finding one electron at point r_1 and the second electron at point r_2 . This density function carries almost all the information about quantum correlations of a compound system. The two-electron distribution function $\rho(r_1, r_2)$ is the expectation value of the operator $\hat{G}(r_1, r_2)$ which has the following form in the position representation for an atom or ion with N electrons [3]:

$$\hat{G}_2(r_1, r_2, \theta) = \sum_{j < i} \frac{1}{2} [\delta(u_i - r_1) \delta(u_j - r_2) + \delta(u_i - r_2) \delta(u_j - r_1)] \times \delta(\cos\theta_{ij} - \cos\theta). \quad (6)$$

$$\rho(r_1, r_2, \theta) = G_2(r_1, r_2, \theta) = \langle \Psi | \hat{G}_2(r_1, r_2, \theta) | \Psi \rangle. \quad (7)$$

$$\rho(r_1) = \int_0^\infty dr_2 \int_{-1}^1 r_2^2 d(\cos\theta) \rho(r_1, r_2, \theta). \quad (8)$$

In this form, we have rotational-invariant **two-electron** and **one-electron densities** that have no dependence on the magnetic quantum number m .

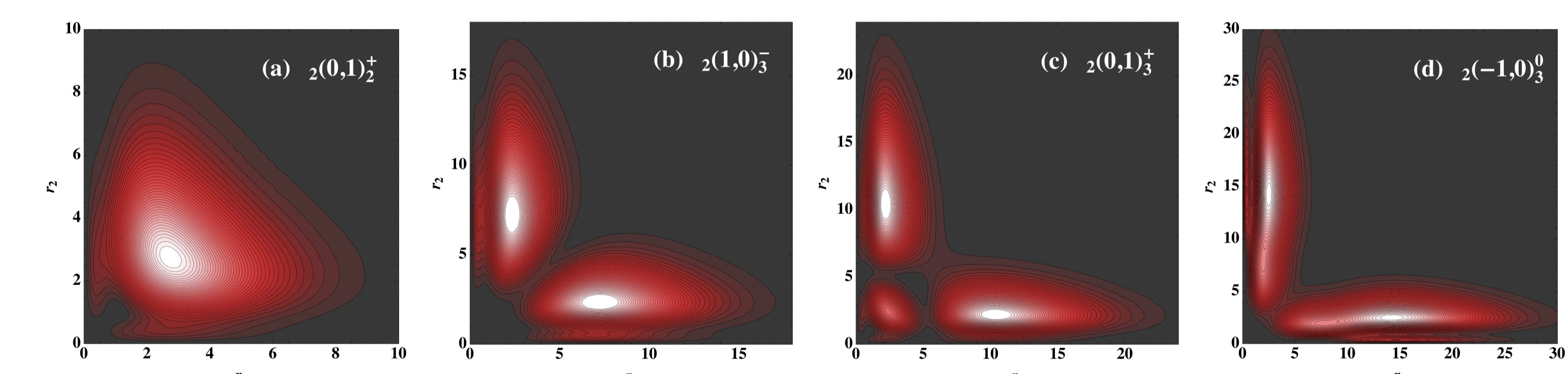


Fig. 3. Electronic density $\rho(r_1, r_2) r_1^2 r_2^2$ for a few resonances belonging to symmetry $1P^0$

MEASURES IN INFORMATION THEORY [4]

Shannon Entropy

$$S[\rho] = - \int_{\mathcal{S}} \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}. \quad (9)$$

It is a measure of the uncertainty of a probability distribution, i.e., it is a measure of how compact or spread is a probability distribution. The Shannon entropy is also a measure of information.

Fisher Information

$$I[\rho] = \int_{\mathcal{S}} \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r}. \quad (10)$$

The Fisher Information is a local measure, i.e., it does not have a global character. This measure is very sensitive to strong changes on the distribution over a small-sized region.

ENTANGLEMENT FOR SINGLY EXCITED STATES OF HELIUM: SYMMETRIES $1S^e$ AND $3S^e$

The entanglement information for a bipartite system can be found in the reduced density operator $\hat{\rho}_1 = \text{Tr}_2 \hat{\rho}$. This means that we must average over all relevant coordinates of subsystem **2**. Now, we can use the following two quantities to measure the amount of entanglement between the particles of a two-electron system:

Linear entropy S_L

$$S_L = 1 - \text{Tr}[\hat{\rho}(\vec{r}_1)]^2. \quad (11)$$

Von Neumann entropy S_{VN}

$$S_{VN} = -\text{Tr}[\hat{\rho}(\vec{r}_1) \text{Log}_2 \hat{\rho}(\vec{r}_1)]. \quad (12)$$

Since the expansion (3) is performed using an orthonormal set of symmetry-adapted two-electron configurations, the reduced density matrix can be straightforwardly calculated by using a partial trace over the second electron in the full density matrix

$$\hat{\rho}(\vec{r}_1) = \text{Tr}_2 \hat{\rho}(\vec{r}_1, \vec{r}_2), \quad (13)$$

Table: Linear Entropy and Von Neumann Entropy for bound states of Helium: Symmetries $1S^e$ and $3S^e$.

State	Dehesa <i>et al</i> [5]		Benenti <i>et al</i> [6]		Restrepo & Sanz	
	S_L	S_{VN}	S_L	S_{VN}	S_L	S_{VN}
$(1s)^2; {}^1S$	0.015914	0.01606	0.0785	0.011460	0.066475	0.066475
$ 1s2s; {}^1S\rangle$	0.48866	0.48871	0.991099	0.487222	0.988964	0.988964
$ 1s3s; {}^1S\rangle$	0.49857	0.49724	0.998513	0.497154	0.998530	0.998530
$ 1s4s; {}^1S\rangle$	0.49892	0.49892	0.999577	0.498909	0.999631	0.999631
$ 1s5s; {}^1S\rangle$	0.4993	0.499565	0.999838	0.499468	0.999881	0.999881
$ 1s2s; {}^3S\rangle$	0.47778	0.500378	1.00494	0.500375	1.004924	1.004924
$ 1s3s; {}^3S\rangle$	0.49342	0.5000736	1.00114	0.500073	1.001136	1.001136
$ 1s4s; {}^3S\rangle$	0.49746	0.5000267	1.000453	0.500026	1.000450	1.000450
$ 1s5s; {}^3S\rangle$	0.49955	0.5000125	1.000091	0.500012	1.000227	1.000227

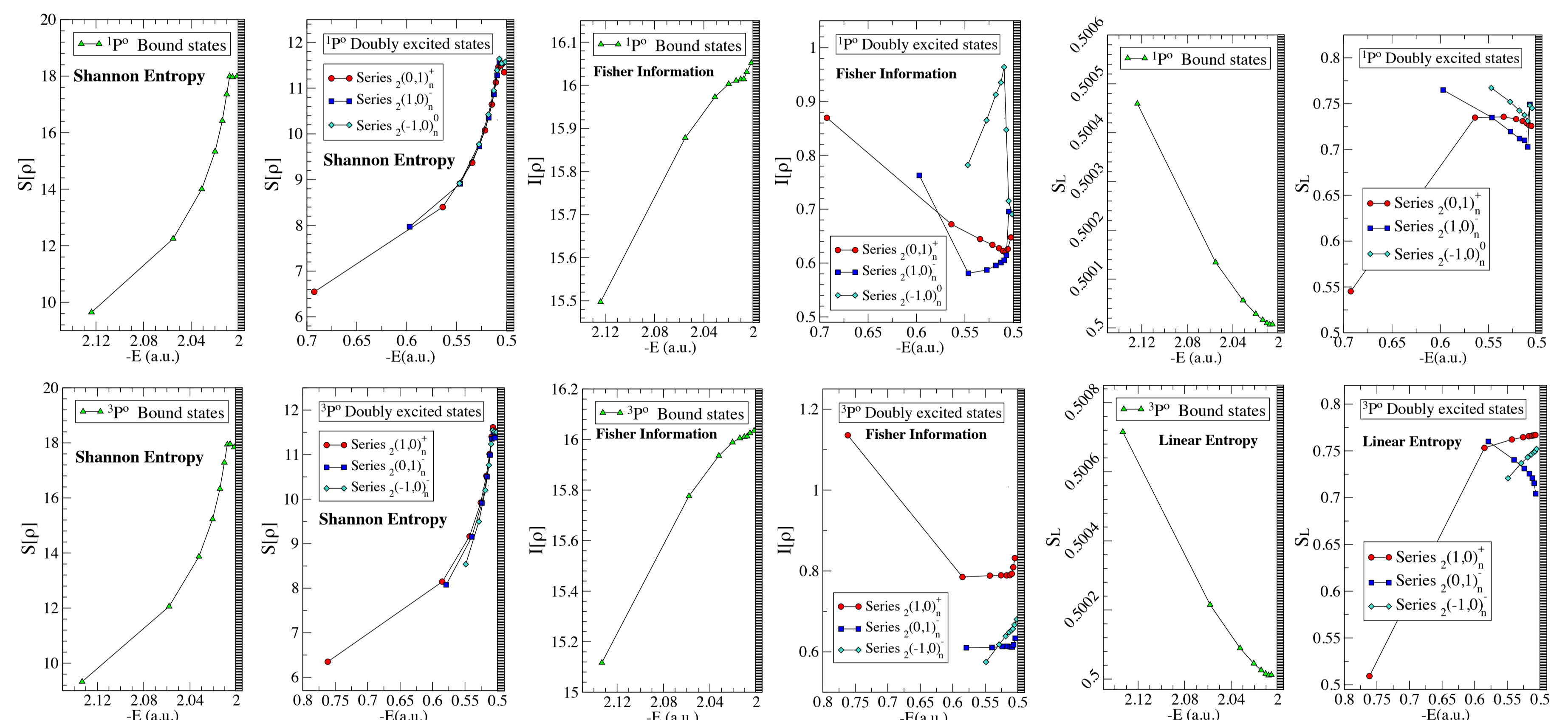
where

$$\hat{\rho}(\vec{r}_1, \vec{r}_2) = C_{n_1 l_1; n_2 l_2} C_{n_1' l_1'; n_2' l_2'}^*. \quad (14)$$

Thus the configuration interaction method enables us to calculate this trace in a simple algebraic way, then avoiding the very demanding numerical integration of multidimensional integrals of the density matrix [5]. Now, the partial trace takes the following form in terms of the configuration interaction coefficients

$$\hat{\rho}(\vec{r}_1)_{n_1 l_1; n_1' l_1'} = \sum_{n l} C_{n_1 l_1; n l} C_{n_1' l_1'; n l}^*. \quad (15)$$

SHANNON ENTROPY, FISHER INFORMATION AND LINEAR ENTROPY. SINGLY AND DOUBLY EXCITED STATES - SYMMETRIES $1P^o$ AND $3P^o$.



In numerical calculations for symmetries $1P^o$ and $3P^o$ we used the following scheme to obtain the wave function, the electronic density, and the density matrix.

- ▶ $1P^o$ Bound states: Number of configurations 2500
- ▶ $1P^o$ Resonances: Number of configurations 2475
- ▶ $3P^o$ Bound states: Number of configurations 2500
- ▶ $3P^o$ Resonances: Number of configurations 2475
- ▶ $1D^e$ Bound states: Number of configurations 3175

- ▶ $1D^e$ Resonances: Number of configurations 3150
- ▶ $3D^e$ Bound states: Number of configurations 3075
- ▶ $3D^e$ Resonances: Number of configurations 3050
- ▶ All calculations were made using configurations with $l_{max} = 4$ and $n_{max} = 25$.
- ▶ We used an exponential grid of knot points in B-splines set for both singly and doubly excited states.

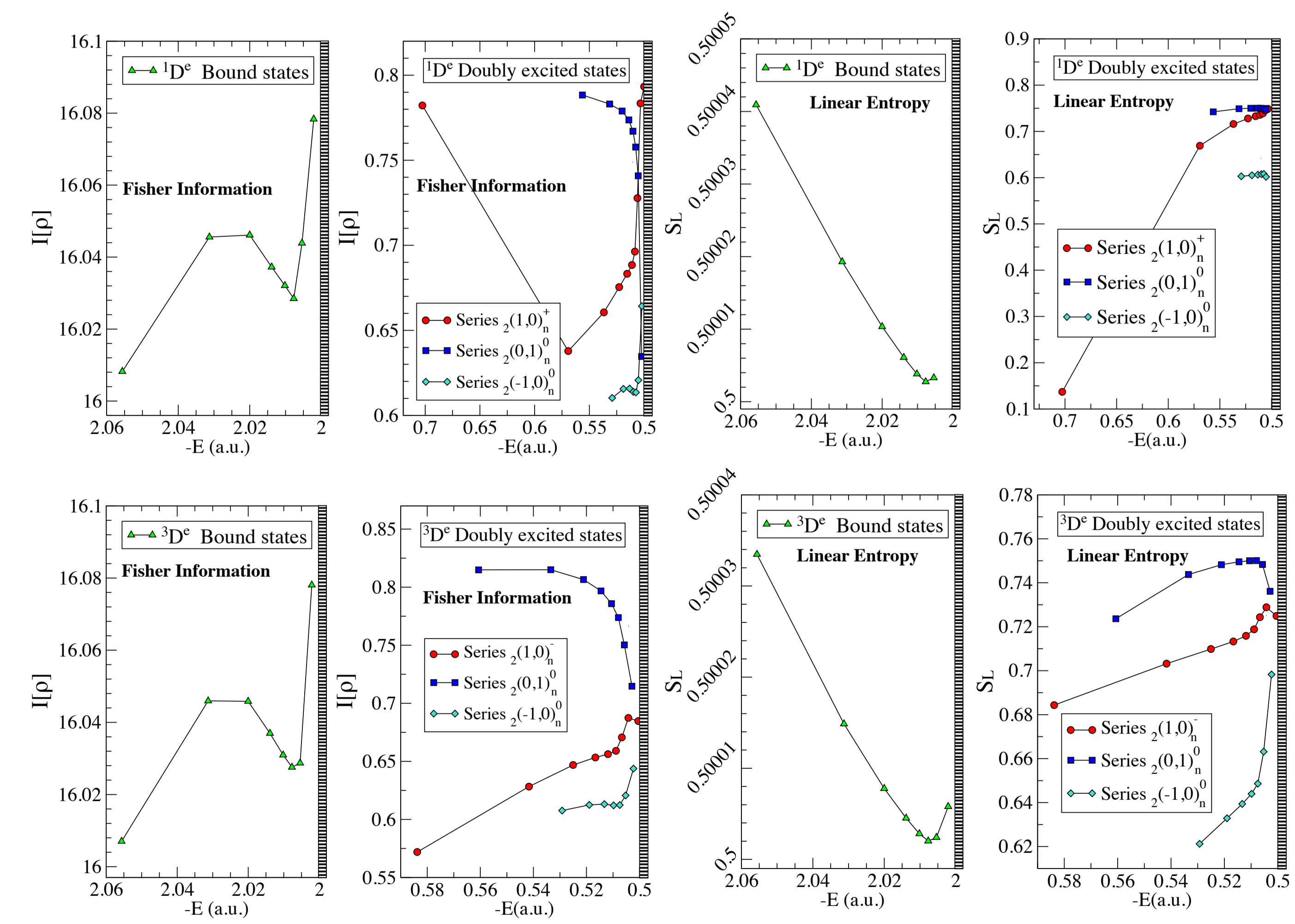
FISHER INFORMATION AND LINEAR ENTROPY. SINGLY AND DOUBLY EXCITED STATES - SYMMETRIES $1D^e$ AND $3D^e$.

1. The Shannon entropy increases monotonically for both bound states and resonances. This quantity is not able to separate the different (K,T) series in the resonant manifold. The global characteristics of the density function can not be used to classify the doubly excited states.

2. The Fisher information seems to have a trend towards a constant value in each case. Because this quantity is sensitive to strong changes on the density function over a small-sized region, these local strong variations allow to classify each resonance in each different (K,T) series by means of Fisher Information.

3. Linear entropy measures the amount of entanglement between the two electrons in our system. It is a measure of quantum correlations which exist in the system and these correlations can distinguish the resonances within the Rydberg series.

The Linear entropy reaches an almost constant value at the ionization threshold energy (different for bound states and resonances), precluding further distinctions due to the complexity that makes any classification useless.



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