

Electronic structure of heavy few-electron diatomic quasimolecules

Artem Kotov

Saint Petersburg State University

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Principal investigator Dr. Dmitry Glazov (St. Petersburg State University), Priv.-Doz. Dr. Günter Plunien (TU Dresden)

Summary

The solution of the Dirac equation for electron in two-center potentials of Xe(54+)-Xe(54+) and U(92+)-U(92+) is numerically calculated within the dual-kinetic-balanced finite-basis-set approach for axially symmetric systems (A-DKB). To account for interelectronic interaction energy, the so-called configuration interaction method (CI) is used. In total, the configuration space is constructed with 1 ground state and first 49 excited states which gives configuration space of the size 50. The higher-order contribution beyond the 1st order of the perturbation theory is found for the ground state and few lowest excited states.

1. Introduction

Few-electron diatomic quasimolecules represent the simplest molecular systems. One of the most interesting cases is the heavy quasimolecules which total nuclear charge is greater than 173. In such a system, as quantum electrodynamics (QED) predicts, the lowest-lying electronic state is close to dive into the Dirac negative-energy continuum at a small enough internuclear distance [1, 2]. In this case the parameter $\alpha Z \simeq 1$ (α is the fine-structure constant and Z is the total nuclear charge) so the calculation should be done to all orders in αZ , that is the so-called Furry picture of the bound-state QED.

While collisions of highly charged ions with neutral atoms are presently available for experimental investigations, in particular, at the GSI Helmholtz Center for Heavy Ion Research [3-5], the upcoming experiments at the GSI/FAIR [6], NICA [7], and HIAF [8] facilities might even allow observation of the heavy ion-ion (up to U92+-U92+) collisions. The relativistic dynamics of the heavy-ion collisions has been investigated for decades by various methods, see, e.g., Refs. [9-18] and references therein. Theoretical predictions of the quasimolecular spectra are also in demand for analysis of the experimental data in these collisions.

In our previous G-RISC projects, we performed calculations of the one-electron quasimolecular energies. The obtained results are published in the Ref. [19, 20]. In few-electron systems, electronic correlations play an important role also. One possible way to account for interelectronic interaction energy is the configuration interaction approach [21].

2. Methods

Firstly, we consider the Dirac problem for an electron in the two center potential generated by two bare nuclei.

$$[\vec{\alpha} \cdot \vec{p} + \beta + V(\vec{r})]\Psi = E\Psi,$$
$$V(\vec{r}) = V_{nucl_A}(|\vec{r} - \vec{R}_A|) + V_{nucl_B}(|\vec{r} - \vec{R}_B|),$$

here \vec{r} and $\vec{R}_{A,B}$ are the the coordinates of the electron and nuclei, respectively, $V_{nucl_{A,B}}$ is the nuclear potential at the distance r by the nucleus with the charge $Z_{A,B}$, $\vec{\alpha}$ and β are the standard 4×4 Dirac matrices.

In this project we consider Xe(54+) and U(92+) as the source of the potential. To solve the problem, we use the A-DKB approach in which the electronic wave function is expanded into the finite

series over a basis set [22]. In the case of axially symmetric potential, we can explicitly determine dependence of the wave functions on the azimuth angle φ in the spherical coordinate system (r, θ, φ) . The remaining unknown dependences on r and θ are numerically found with help of basis set of the B-splines over the radial variable and the Legendre polynomials over the θ variable. Unfortunately, for the Dirac equation one will face the so-called spurious-state problem. These non-physical states occur in the spectrum upon solving the Dirac equation using the finite basis set [23]. To solve this problem, the dual kinetic balance conditions are used [24]. As a result of such a procedure, we obtain the quasicomplete Dirac spectrum. In order to obtain interelectronic-interaction energy between two electrons, one could consider interelectronic-interaction operator $I(\omega) = \alpha(1 - \alpha_1 \cdot \alpha_2) \exp(i|\omega|r_{12})/r_{12}$. With the help of such an operator, we calculate the exchange energy between two-electron states. In the first order of the QED perturbation theory (QED PT), it gives the so-called one-photon-exchange contribution $E^{1ph} = \langle ab|I(0)|ab \rangle - \langle ba|I(E_a - E_b)|ab \rangle$.

In the CI approach, we build the following two-electron Hamiltonian matrix: $H_{ij} = \langle \psi_i | \sum_{i=1}^2 h_i + I | \psi_j \rangle$ where h_i is the one-electron Hamiltonian. Finally, after the diagonalization procedure, we obtain the two-electron energies with respect to the dimension of the configuration space.

3. Results and Discussion

Table 1: Interelectronic-interaction energies [eV] of the U(92+)-U(92+) quasimolecule at different internuclear distances. Here $E^{CI} = E_{e_1 e_2} - E_{e_1} - E_{e_2}$, i.e., the interelectronic contribution calculated within the CI method, and E^{1ph} is the corresponding value of the one-photon-exchange contribution.

$D, \text{ fm}$	$E_{(1s\sigma_g)^2}^{CI}$	$E_{(1s\sigma_g)^2}^{1ph}$	$E_{1s\sigma_g 2s\sigma_g}^{CI}$	$E_{1s\sigma_g 2s\sigma_g}^{1ph}$	$E_{1s\sigma_g 2p_{3/2}\pi_g}^{CI}$	$E_{1s\sigma_g 2p_{3/2}\pi_g}^{1ph}$
40	14 036	14 058	12 237	12 261	4 365	4 365
50	12 351	12 370	10 537	10 558	3 967	3 967
80	9 497	9 509	7 733	7 750	3 218	3 220
100	8 412	8 422	6 710	6 725	2 909	2 910
200	5 802	5 807	4 430	4 440	2 120	2 122
250	5 138	5 143	3 911	3 919	1 914	1 916
500	3 454	3 457	2 774	2 780	1 761	1 766
700	2 812	2 814	2 410	2 414	1 595	1 599
1 000	2 245	2 247	2 075	2 077	1 353	1 355

Table 2: Interelectronic-interaction energies [eV] of the Xe(54+)-Xe(54+) quasimolecule at different internuclear distances. The notations are the same as in Table 1.

D, fm	$E_{(1s\sigma_g)^2}^{\text{CI}}$	$E_{(1s\sigma_g)^2}^{\text{1ph}}$	$E_{1s\sigma_g 2s\sigma_g}^{\text{CI}}$	$E_{1s\sigma_g 2s\sigma_g}^{\text{1ph}}$	$E_{1s\sigma_g 2p_{3/2}\pi_g}^{\text{CI}}$	$E_{1s\sigma_g 2p_{3/2}\pi_g}^{\text{1ph}}$
40	3 042	3 046	1 228	1 235	964	965
50	3 009	3 012	1 223	1 229	955	956
80	2 909	2 912	1 208	1 214	930	931
100	2 845	2 848	1 197	1 203	914	916
200	2 563	2 566	1 148	1 153	846	847
250	2 444	2 446	1 126	1 131	818	819
500	1 999	2 001	1 045	1 049	780	782
700	1 758	1 759	1 015	1 018	766	768
1 000	1 500	1 502	1 000	1 002	725	726

From these tables one can see that the difference between the CI values and E^{1ph} decreases with increase in the internuclear distance. For the higher excited states this difference is particularly small due to the weakness of the interelectronic interaction for those states in comparison to the ground-state case. The CI method allows us to account for interelectronic interaction beyond the 1st order of the PT. Although the interelectronic-interaction contribution already in the 2nd order is smaller by a few orders of magnitude in comparison with the 1st order [19], it can play an important role in the two-electron transition energies. Here we see a great opportunity to compare the CI values with the corresponding interelectronic-interaction contribution including the higher-order terms in future works.

4. Conclusion

In this project, the two-electron energies are calculated within A-DKB approach via two schemes: 1) 1st order perturbation theory of the QED, i.e., the one-photon-exchange diagram and 2) configuration interaction method. In the latter case, the configuration space of 50 two-electron states is used. We found that the interelectronic-interaction contribution to the total two-electron energies obtained within the CI method is significant for the ground and few lowest excited states in comparison to the 1st order of the QED PT. The results will be published in a peer-reviewed journal. The results of the previous related projects are published [19, 20].

5. References

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6. Personal Impressions

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