

Magnitude of static and dynamic polarizabilities of doubly excited states of negative ions: Application to the second bound state of H^-

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A many-electron, many-photon theory has been applied to the computation of static α and dynamic $\alpha(\omega)$ linear polarizability of the $H^- 2p^2\ ^3P$ state. The calculation involves the nonperturbative mixing of one bound ($2p^2\ ^3P$), and one autoionizing ($2s2p\ ^3P^\circ$) state with 13 continua. State-specific, compact, and accurate square-integrable wave functions have been employed. The magnitude of the polarizability is huge: $\alpha = 64\,000$ a.u.

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I. INTRODUCTION

Some of the interesting properties of atoms and molecules whose reliable *ab initio* computation offers a good challenge to theory, are the static and dynamic linear and nonlinear polarizabilities. For polyelectronic systems, the available quantitative information on the magnitude of these quantities refers to the ground state only, or, for the static, linear polarizability α , in a few cases [1,2], to low- n Rydberg states. Regarding the static α , their magnitude for neutral or ionic species are of the order of one or two digits in atomic units. Those of the negative ions (where available) are much larger, reaching in the cases of H^- and Li^- magnitudes such as [3,4] 206 and [5] 750 a.u., respectively. In fact, the Li^- linear polarizability appears to be the largest known yet for a ground state [6]. Of course, as the perturbation theory solutions of the hydrogenic excited states suggest, large magnitudes are expected for singly excited states, as for example with the Rydberg states of the alkalis [1,2].

What is the magnitude of static and dynamic polarizabilities for the class of states that is *valence doubly excited*? In particular, those of negative ions have large mean radii [7] and therefore one might expect their polarizability to be very large. In any case, this problem of electronic structure theory and calculation has remained open. In this paper, we present such results, taking the $2p^2\ ^3P$ doubly excited state (DES) of the prototype negative ion H^- as the test case. This state is the second member [8,9] of the discrete spectrum of H^- —the first one being the ground state $1s^2\ ^1S$.

II. THEORETICAL APPROACH

The calculation of polarizabilities is an old subject. A large number of theoretical methods and results has been published, but most of them refer to the ground state (for a recent list of references see Ref. [5]).

Work from this institute on such properties has emphasized the importance of formulating the theory around a state- and property-specific computation of the

unperturbed and perturbed correlated wave functions, whether ground or excited [4,5,10]. For example, relatively small-size wave functions yielded accurate results for the α of Be [10].

Recently [4,5], we presented a nonperturbative, all-orders many-electron, many-photon theory (MEMPT) for the calculation of static as well as dynamic linear and nonlinear polarizabilities. The formalism and its methodology is presented elsewhere [5,11,12], so for reasons of economy its presentation is omitted here. Its main features are the following. The dynamic polarizabilities $\alpha(\omega)$, $\gamma(\omega)$, etc. are obtained as averages over an optical cycle by fitting to a polynomial in the average of the oscillating external field the total energy shift $\Delta(\omega)$, whose calculation is carried out within the Floquet-theorem framework of atom-field interactions. When the external field is static, the Taylor series of Δ yields the well-known [13] expansion defining static polarizabilities. Thus, for an atom

$$\Delta(\text{static}) = -\frac{1}{2!}\alpha F^2 - \frac{1}{4!}\gamma F^4 - \dots \quad (1a)$$

and, according to the present theory,

$$\Delta(\omega) = -\frac{1}{2!}\alpha(\omega)\frac{1}{2}F^2 - \frac{1}{4!}\gamma(\omega)\frac{3}{8}F^4 - \dots \quad (1b)$$

The calculation of Δ and $\Delta(\omega)$ is carried out according to the MEMPT [11,12]. Suffice it to say here that the dressed, state-specific correlated wave functions include the separately optimized contribution from the discrete and the continuous spectrum.

III. APPLICATION TO $H^- 2p^2\ ^3P$

A. Field-free case

The $H^- 2p^2\ ^3P$ state is in the H $n=1$ continuum and just below the $n=2$ threshold. Drake [8] computed variationally an electron affinity (EA) of 0.0095 eV using a trial wave function with 50 terms and an r_{ij} -dependent basis. Aashamar [8] employed the variation-perturbation

method to 20th perturbation order, including relativistic corrections, using again Hylleraas bases and expansions up to 204 terms. The EA thus obtained is 0.008 8 eV. A state-specific Hartree-Fock (HF) plus variationally optimized 41-term expansion yielded [9] EA = 0.0093 eV. Results such as those of Ref. [9] and subsequent ones (e.g., see Ref. [7] and references therein) have demonstrated that for DES, the numerical state-specific HF or multiconfigurational Hartree-Fock (MCHF) wave function yields very good convergence, since it is forced to have accurate long-range behavior while accounting for dynamical screening much better than any fixed basis, including the Hylleraas type. Thus, once the correct zeroth-order correlation effects have been accounted for, the computation of a related property is economical as well as reliable. A case in point is the wave function of the $H^- 2p^2 3P$. Just the four-term expansion obtained from a numerical [14] MCHF calculation

$$\Psi_0(^3P) = 0.930(2p^2) - 0.342(3p^2) + 0.132(3d^2) + 0.011(4f^2) \quad (2)$$

yields $E_0 = -3.410$ eV which corresponds to EA = 0.0085 eV. This compact pair wave function, containing angular as well as radial correlation and accounting for the long-range behavior by satisfying the correct boundary conditions [15], is used in this work as input for the implementation of the MEMPT.

B. The field-dressed state

In the presence of the electric dipole external field, the 3P state becomes unbound by coupling via one or more photons to the adjacent continuum, $1s\epsilon l$, to the autoionizing state just below, $2s2p^3P^\circ$, and, depending on the frequency and on the field strength, to channels above the $n=2$ threshold. For the present calculation, we employed a three-term numerical MCHF $2s2p^3P^\circ$ square-integrable Ψ_0 [16],

$$\Psi_0(^3P^\circ) = 0.968(2s2p) - 0.210(2p3d) - 0.138(3s3p), \quad (3)$$

with $E_0 = -3.860$ eV. This is just 0.007 eV above the 84-term, r_{ij} -dependent optimized basis calculation of

TABLE I. Linear static and frequency-dependent polarizabilities of the discrete, doubly excited state, $H^- 2p^2 3P$, whose electron affinity with respect to the $H n=2$ threshold is just 0.0096 eV (0.00035 a.u.). The frequency 0.0165 a.u. corresponds approximately to the energy difference between the $2p^2 3P$ state and the H^- resonance $2s2p^3P^\circ$. The ensuing coupling causes a change of the sign of $\alpha(\omega)$.

ω (a.u.)	$\alpha(\omega)$ (a.u.)	ω (a.u.)	$\alpha(\omega)$ (a.u.)
0.0000	6.4×10^4	0.0070	-1.0×10^4
0.0007	18	0.0080	-0.92
0.0008	13	0.0090	-0.84
0.0009	11	0.0100	-0.80
0.0010	8.8	0.0105	-0.77
0.0020	-0.16	0.0120	-0.76
0.0030	-1.4	0.0135	-0.82
0.0040	-1.4	0.0150	-1.2
0.0050	-1.3	0.0165	1.6
0.0060	-1.1	0.0180	0.48
		0.0195	0.12

Bhatia and Temkin [17] with the continuum-interaction shift explicitly included.

As regards the open channels, for each one we employed a ten-term complex-coordinate Slater-type orbital (STO) representation [5,11]. Given that the frequencies considered ionize the 3P state with one photon, the following continua were included: $1s\epsilon s^3S$, $1s\epsilon p^3P^\circ$, $1s\epsilon d^3D$, $2s\epsilon s^3S$, $2s\epsilon p^3P^\circ$, $2s\epsilon d^3D$, $2p\epsilon s^3P^\circ$, $2p\epsilon p^3S$, 3P , 3D , $2p\epsilon d^3P^\circ$, $^3D^\circ$, $^3F^\circ$. Thus, the overall calculation [5,11,12] involved the simultaneous mixing of one discrete DES ($2p^2 3P$), one autoionizing DES ($2s2p^3P^\circ$), and 13 continua.

The results of our calculations are presented in Table I. A huge α is computed: 64 000 a.u. The values of the frequency go up to the range of the ($2p^2 3P - 2s2p^3P^\circ$) Bohr frequency (around 0.0165 a.u.), where a change of sign is observed. Such knowledge is of interest not only for testing new theories and furthering our understanding of electronic structure and properties of highly excited states, but also for using it in studies of other problems, such as collision phenomena.

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