

STATE-SPECIFIC THEORY OF ELECTRON CORRELATION IN EXCITED STATES

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An approach to the many-electron problem is reviewed which, apart from being practical and general, essentially addresses the "basis set problem". It puts emphasis on the separate and appropriate choice and optimization of the function spaces describing the zeroth order and the remaining part of the N-electron wavefunction, especially in excited states. The calculated wavefunctions are compact and physically transparent while the results for properties which are obtained from them are reliable. The characteristic numerical examples which are given cover a wide spectrum: the importance of higher than pair subshell correlation clusters in certain excited states, (triple excitations in Cl KL3s3p⁶ 2s), positions of resonances and autoionizing states in He⁻ and He, the "sudden polarization effect" in ethylene, the transition probabilities to the valence-Rydberg 2s series of boron, the second-order perturbation theory calculation of electron correlation in CH₄, the 1s binding energies in atomic as well as in metallic Be, and the Hartree-Fock calculation of transition probabilities to multiply excited states and of the binding of the first excited state of the noble gas dihydrides, HeH₂, NeH₂ and ArH₂.

I. INTRODUCTION

Advances in the quantum theory of electronic matter and of physico-chemical processes have been made possible by a combination of physical intuition and related models (e.g. the independent particle model, IPM), efficient analysis of and practical approaches to the many-body problem, and the revolution in

The State-Specific Approach to the Solution of Problems of Electronic Structure and Dynamics Involving Excited States

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ABSTRACT

If, in conjunction with suitable computational methods, attention is given to the state-specific choice and optimization of function spaces, especially when studying excited states, the accuracy of the description of electronic structure and of the results of computation of properties increases, while the complexity of the many-electron problem is reduced significantly. These facts allow the consistent understanding of the interplay between major features of electronic structure and properties or processes, as well as the practical numerical solution of computationally very demanding problems (e.g., solution of the multielectron time-dependent Schrödinger equation). This is the conclusion from a number of applications of the state-specific approach (SSA) to the analysis and calculation of stationary and nonstationary states, in the absence or presence of external electromagnetic fields. A review is given of the basic features of the various formalisms that have been employed within the SSA for the solution of problems of electronic structure and dynamics. In addition, I comment, via specific examples, on the computation of the Fermi–Sea wavefunctions for strongly mixed states and of valence–Rydberg–continuum interactions. © 1996 John Wiley & Sons, Inc.

Introduction

An important and challenging goal of atomic, molecular, and chemical physics is the possibility of obtaining quantitative information about

the electronic structure and properties of excited states and about their role in a variety of spectroscopies and dynamic phenomena. The purpose of the present contribution was to review briefly certain basic elements of work carried out in our institute on different types of polyelectronic problems connected to the above goal and to comment

Regular and chaotic multiphoton dissociation

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The rate of multiphoton dissociation of the BeH^{2+} molecule in its ground and first two excited vibrational levels has been computed via classical mechanics as a function of laser frequency. There is agreement with earlier quantum-mechanical results as regards the existence and magnitude of an optimal frequency, ω^* , for which the dissociation rate is maximized. This fact has been analyzed and understood via the application of the theory of chaotic scattering. Indeed, we find fractal singularities in the function $T_d(x)$ of the duration of photodissociation, and we compute their dimension to be equal to 1, in agreement with the conjecture of Lau, Finn, and Ott [Phys. Rev. Lett. **66**, 978 (1991)] that this must be a characteristic of systems exhibiting nonhyberbolic scattering. Turning to the problem of interpreting the appearance of an optimal ω^* , we propose the following two mechanisms for the reduction of the multiphoton dissociation rate. First is the increase of fractal singularities when the frequency ω attains values larger than ω^* . Second is the gradually increasing overlap of the classical initial state with the region of Kolmogorov-Arnold-Moser tori when $\omega < \omega^*$. Finally, as the intensity is increased there is a transition from chaotic to regular photodissociation, where the singularities in $T_d(x)$ are finite. It is conjectured that this reflects the emergence of the quantum-mechanical phenomenon of above-threshold dissociation. [S1050-2947(97)08302-9]

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I. INTRODUCTION

Given the rapid growth of the field of nonlinear classical dynamics (e.g., Ref. [1]), and the strong interest in making connections to results and features of quantum mechanics, it is important and challenging to adopt as objects of investigation real quantal systems and processes. One such case is the multiphoton dissociation (MPD) of diatomic molecules induced by strong infrared lasers, which has been studied by applying advanced quantal and classical methods and interpretations to the parametrized Morse oscillator [2–14]. These classical methods have their basis in the progress that has been made in the nonlinear dynamics of *bound* systems.

On the other hand, during the past decade, significant progress has been made in the understanding of the chaotic behavior of *unbound*, i.e., scattering, systems, where the interaction time is small [15–24]. Now, rather than emphasizing and analyzing phase-space characteristics, the basic theme is to achieve mappings of properties of final scattering states with details of initial conditions. One general result is that classical scattering is divided into regular and chaotic. The criteria for this division are the singularities that appear in the scattering functions. If their number is finite, then we have regular scattering, while chaotic scattering is associated with the appearance of fractal structure. By scattering function is meant “a plot of an output variable characterizing the trajectory after scattering versus an input variable characterizing the incident trajectory. In chaotic scattering the scattering function is singular on a Cantor set of values of the input variable” [23].

The theory of chaotic scattering has been developed using

simple models as examples. As regards implementation to systems with quantal counterparts, noteworthy are recent results on one-dimensional atoms with model interactions, such as the work of Hillermeier, Blümel, and Smilansky [24] on ionization of H Rydberg atoms, of Gu and Yuan [25] on electron scattering from He^+ , and of Handke [26] on autoionization of doubly excited He-like atoms.

Given the above, it appeared appropriate and timely to us to attempt an understanding of a possible connection of the current theory of chaotic scattering to the dynamics of MPD. Indeed, the object of this work was to study the MPD of BeH^{2+} into $\text{Be}^+ + \text{H}^+$ by the methods of chaotic scattering, having as a reference quantum-mechanical results that were obtained recently [27]. The BeH^{2+} potential supports only a few vibrational levels, and it was found to dissociate for intensities which are smaller by orders of magnitude than those needed for molecules such as HF (treated as a Morse oscillator).

In the following sections we will show how chaotic scattering applies to this problem, and we will present results demonstrating that MPD can be separated into regular and chaotic, and that the regular properties of the classical dissociation rate (CDR) emerge as a function of the laser frequency ω . (We note that in most publications on CDR, interest has focused on the dependence on the laser intensity.) For example, the quantum-mechanical result [27] that the rate of MPD is optimized for a value of ω which is about 0.9 times the frequency for the $v=0 \rightarrow 1$ transition is verified here, and this agreement is used as input for a deeper analysis. (In Ref. [27] there were also interesting findings associated with tunneling. These do not concern us in the present work.)

In Sec. II we compute the CDR as a function of ω , where the molecule is in the ground vibrational level as well as in the first two excited ones. We conclude that the results offer

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Prediction of Nonclassical Hydrogen Complexes of Nontransition Metals

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In the past few years, theoretical and computational work, including the effects of electron correlation, allowed the prediction of nonclassical hydrogen complexes of nontransition metals. In this Comment, these results are connected to others, starting with H_3^+ , and a review of the "nonclassical" binding features of molecular H_2 to metals and nonmetals is given. As an example, the prediction of the structure of a new such complex, the $Li_4H_2^{2+}$, is made.

I. INTRODUCTION

Recent reviews¹⁻⁶ have presented and discussed the remarkable progress that has occurred during the past decade in the field of nonclassical hydrogen complexes (NCHC's) of *transition metal* compounds. The field took off after a report by Kubas *et al.*⁷ on the experimental finding that the hydrogen molecule may bind on a transition metal

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Time dependence and properties of nonstationary states in the continuous spectrum of atoms

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Abstract. The recently measured $\text{Li}^- 1s^2 2s 2p^3 P^0$ shape resonance, the Ca KLM $3d 5p^3 F^0$ doubly excited autoionizing state and the long-lived $\text{He}^- 1s 2s 2p^4 P^0_{3/2}$ metastable level were treated as nonstationary states satisfying the time-dependent Schrödinger equation (TDSE). The lifetimes of the first two are short, of the order of 10^{-14} s, and the solution of the TDSE well into times where nonexponential decay (NED) is established, is achievable via the state-specific expansion approach (SSEA), according to which the time-dependent solution has the form $\Psi(t) = c(t)\Psi_0 + X(t)$. Ψ_0 is the square-integrable wavefunction of the localized state at $t = 0$ and $X(t)$ is composed mainly of energy normalized scattering functions with time-dependent coefficients. The coefficient $c(t)$ is related to the survival amplitude, $\alpha(t)$, by $c(t) = \alpha(t) - \langle \Psi_0 | X(t) \rangle$, where the overlap matrix element appears when the function spaces are not completely orthonormal. For the diffuse $\text{Li}^- 1s^2 2s 2p^3 P^0$ resonance, its analysis as a decaying state has as a prerequisite the calculation of a reliable Ψ_0 , with correlation between the two valence electrons. This has been achieved by a special procedure and a related discussion is given. The proximity of the energy E to threshold (~ 50 meV), the closeness of the ratio E/Γ to unity (Γ is the resonance width) and the energy dependence of the bound-free matrix element, produced the result that NED should appear after only two lifetimes, when the probability of finding the system in the initial state is still non-negligible. From the exponential part of the decay curve, the width was found to be $\Gamma = 53$ meV, in agreement with the recent width of 64 ± 25 meV derived from measured cross sections in recent collision experiments (Lee *et al* 1996). The shortness of the time for which exponential decay (ED) holds and the fact that the survival probability, $P(t)$, is still significant at the beginning of the NED, does not allow the rigorous justification of the definition of the lifetime from $\tau = \frac{1}{\Gamma}$, or the equivalence of this Γ with the observed energy width. Thus, we propose that a mean life, $\bar{\tau}$, should be obtained from

$$\bar{\tau} = \langle t \rangle = \frac{\int_0^\infty t P(t) dt}{\int_0^\infty P(t) dt}.$$

Calculation produces $\tau = 1.2 \times 10^{-14}$ s and $\bar{\tau} = 1.7 \times 10^{-14}$ s. For the Ca $3F^0$ state, whose bound-free interaction is smooth and nearly constant from zero to about 5.5 eV, NED appears after 17 lifetimes. The lifetime of Ca $3F^0$ is deduced from the exponential decay (ED) part of $P(t)$ to be 3.5×10^{-14} s. From our examination of the case of the $\text{He}^- 4P^0_{3/2}$ level by a number of methods based on the use of state-specific wavefunctions, we conclude that for metastable states whose lifetimes are in the range 10^{-4} – 10^{-8} s, the *ab initio* calculation of $P(t)$ is, at present, prohibited by the huge requirements for computer time. Finally, having computed the amplitude $\alpha(t)$, we obtain numerically the energy distribution function, $g(E) \equiv |\langle E | \Psi_0 \rangle|^2$, of the two autoionizing states. In the case of Ca it is a perfect Lorentzian.

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Theory and computation of electron correlation in the continuous spectrum: Double photoionization cross section of H^- and He near and far from threshold

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We present a theoretical approach to the *ab initio* calculation of single or multiphoton double electron ionization cross sections, $\sigma^{++}(E)$, of polyelectronic atoms, near (Wannier region) and far from threshold. The overall computational method is variational, uses functions of real as well as of complex coordinates, and follows the many-electron, many-photon theory proposed by Mercouris and Nicolaides [J. Phys. B **21**, L285 (1988); **23**, 2037 (1990)]. It incorporates the electronic structure and the pair correlations in the continuum via configuration-interaction techniques. $\sigma^{++}(E)$ is obtained as the imaginary part of a complex eigenvalue that is computed by diagonalizing a state-specific non-Hermitian matrix constructed from separately optimized function spaces Q and P representing the field-induced resonance state. Q contains correlated wave functions of bound or quasibound states expanded over numerical and analytic orbitals of real coordinates. P is composed, in principle, of subspaces P_1 and P_2 , representing the one- and the two-electron channels, respectively, which are optimized separately and then are allowed to mix via the construction of the total non-Hermitian matrix. Both are spanned by basis sets of real coordinates for the ionized core and of complex coordinates for the outgoing part of the one- and the two-electron resonance state. The two-electron square integrable "continuum" function space is made orthogonal to the available single electron channels in order for $\sigma^{++}(E)$ not to include portions of the single electron ionization cross section $\sigma^+(E)$. Application is made to the single photon $\sigma^{++}(E)$ of the prototypical systems H^- and He, but without the mixing of P_2 and P_1 , due to numerical instabilities. The two-electron ionization channels were composed of Slater-type orbitals, symmetry-coupled according to (*sp*), (*pd*), and (*df*). Higher symmetries would also be needed at higher energies, with corresponding increase of angular correlation terms in the initial-state wave function. The continuous energy ranged from $E=0$ to $E=250$ eV. In the threshold region $E=0-2$ eV, the length and velocity results are in good agreement with experiment for H^- and in reasonable agreement with experiment for He. Far from threshold, there is discrepancy between length and velocity forms in this as well as in previous works by other methods. Apart from whatever inadequacies of the basis functions, this is possibly due to the exclusion of mixing of the single electron open channels into the correlated wave function of the two free electrons. By comparing the results from the use of correlated wave functions with those obtained when the calculation of the transition matrix element is done with wave functions of real coordinates, where the initial state is correlated but the final one is only a product of Coulomb wave functions, the effect of correlation of the two free electrons is deduced for the case of He, without considering the mixing of one- and two-electron channels. Finally, a by-product of the present development was the calculation of the He $\sigma^+(E)$ to the $n=1$ single ionization threshold. Comparison with previous accurate experimental results reveals very good agreement. [S1050-2947(97)05904-0]

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I. INTRODUCTION

When atoms or molecules with N electrons ($N \geq 2$) are probed by energetic photons or electrons and other particles or by intense laser light (multiphoton absorption), there is finite probability of producing final states with two or more free electrons. Such processes give rise to significant and challenging theoretical problems as regards the *ab initio* calculation of the related transition rates, especially for the near threshold region.

In this paper, we present a theory and method of calculation of the cross section of double photoionization, $\sigma^{++}(E)$, of ground or excited N -electron states by one or more pho-

tons. The application demonstrating the approach is to the one-photon ionization of the H^- and He $1S$ ground states that constitute the prototypical cases (especially He) for the application of a number of theoretical approaches and for experimental measurement. The continuous energy spectrum that was studied ranges from threshold ($E=0$) (relevant to the so-called *Wannier problem*—see Sec. IV) to 250 eV. Although this application of the method has as object the $1S$ ground state of two-electron atoms, the structure of the theory is such that it allows the computation of $\sigma^{++}(E)$ for arbitrary atomic states. This is because both the zeroth-order functions as well as electron correlation in the discrete and the continuous spectrum are represented by expansions over symmetry-adapted configurations with optimized numerical or analytic orbitals. For example, such a theory is capable of dealing reliably with the excited states as well. If excited states are metastable, they can be used as initial states. Or,

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LETTER TO THE EDITOR

Theory and computation of the profile of the free–free transition probability between autoionizing (resonant) states

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Abstract. We have derived the general expression for the energy-dependent cross section of the transition between two resonant states in the continuous spectrum of atoms and molecules, under the physically meaningful conditions of broadband excitation. The profile is expressed in terms of a symmetric, an asymmetric and a background component, and is cast in a form containing as limiting cases the discrete–discrete Lorentzian profile and the discrete–resonance Beutler–Fano profile. The theory has been implemented numerically by *ab initio* methods on the transition $\text{He}^{**} \text{'2s2p' } ^1\text{P}^0 \rightarrow \text{'2p3p' } ^1\text{D}$, for tunable radiation $h\nu$ around 3.4 eV.

As is well known, discrete–discrete one-photon electronic transitions give rise to a Lorentzian profile and the calculation of their probability requires the use of the two bound N -electron wavefunctions. Measuring such transition probabilities or calculating them from first principles is still an active field of atomic and molecular physics. Another broad category of one-photon-induced electronic transitions is that connecting a discrete state to a resonance (autoionizing, predissociating) state in the free-particle continuous spectrum. For atoms, the theory of Fano [1] confirmed and explained the appearance of asymmetric photoabsorption profiles [2, 3] as a result of interference between a localized wavefunction and the adjacent continuum of the same symmetry. Quantitative calculations of such a profile (Beutler–Fano profile), were first published by Burke and McVicar [4] who treated the final state in the $\text{He } 1s^2 \text{ } ^1\text{S} \rightarrow (2s2p + 1s\epsilon p) \text{ } ^1\text{P}^0$ transition by a close-coupling scattering calculation.

In this letter, we present the theory as well as the first *ab initio* calculation of the profile of the cross section of another category of possible one-photon transitions, those between two autoionizing (resonant) states in the continuous spectrum. From the point of view of theory, this case is the most general one since it involves the mixing of bound and scattering components in both initial and final states and the effect of their interference on the energy-dependent transition probability. From the point of view of physical reality, such transitions certainly occur in emission between inner hole Auger states (e.g. $\text{Ar}^+ 1s2s^22p^63s^23p^6 \text{ } ^2\text{S} \rightarrow 1s^22s^22p^53s^23p^6 \text{ } ^2\text{P}^0$). In principle, they can also take place in absorption between multiply excited states. For example, provided the choice of the systems is appropriate, such transitions may be studied in detail by a combination

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On the Application of Conventional Quantum Chemistry Methods of Computation to States Perturbed by the Continuous Spectrum

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ABSTRACT: The suitability for calculating accurately electron affinities (positive or negative) of the QCISD(T), of the B3LYP density functional, and of similar methods is examined critically, using as examples the $B^{-3}P$, 1D , and $Be^{-2}P$ states discussed recently by Bauschlicher [Int. J. Quantum Chem. **66**, 285 (1998)]. It is pointed out that for negative ion states above the threshold the framework of their calculation must be based on theory which accounts correctly for the contribution of the open channels. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 71: 209–213, 1999

Introduction

In recent articles in this journal, Jursic [1] and Bauschlicher [2] employed the code Gaussian 94 and applied a number of computational algorithms to the calculation of electron affinities (EA) of many atomic states. These algorithms are based on density functional theory (DFT) and on *ab initio* perturbation and configuration-interaction (CI) schemes. Having evaluated their results on the various EAs, Jursic and Bauschlicher concluded

optimistically as to the suitability and capacity for the accuracy of methods such as the “quadratic CI including single and double substitutions with a triples contribution to the energy (QCISD(T))” and the “hybrid B3LYP DFT.” Only for the cases of B^{-} , Al^{-} , and Ga^{-} did Jursic express concern, since he found them to be unbound, contrary to reality. However, Bauschlicher repeated the calculations with the same methods and basis sets and found that Jursic made the wrong assignment in the above cases. Specifically, instead of the ground 3P state, Jursic actually computed the EA corresponding to the 1D state. This EA is negative, that is, the 1D state lies in the continuous spectrum above the threshold of the corresponding $^2P^0$ neutral state. In fact, Bauschlicher stressed that the correct calculation of

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Molecular Shape, Shape of the Geometrically Active Atomic States, and Hybridization

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ABSTRACT: In a recent publication [C. A. Nicolaides and Y. Komninos, *Int. J. Quant. Chem.* **67**, 321 (1998)], we proposed that in certain classes of molecules the fundamental reason for the formation of covalent polyatomic molecules in their normal shape is to be found in the existence of a *geometrically active atomic state* (GAAS) of the central atom, whose *shape*, together with its maximum spin-and-space coupling to the ligands, predetermines the normal molecular shape (NMS). The shape of any atomic state was defined as that which is deduced from the maxima of the probability distribution $\rho(\cos \theta_{12})$ of the angle formed by the position vectors of two electrons of an N -electron atom. Because the shape of the GAAS determines the NMS and because the NMS allows the construction of corresponding hybrid orbitals, we examined and discovered the connection between the GAAS shape and Pauling's function for the strength of two equivalent orthogonal orbitals at angle θ_{12} with one another. It is shown that the computed $\rho(\cos \theta_{12})$ of the GAAS can be cast in a form which allows the deduction of the composition of the hybrid orbitals of maximum spin states with configurations sp^3 , sp^3d^5 , $sp^3d^5f^7$, sl^n , s^2l^n and the demonstration of the central atom's tendency to form bonds in directions which coincide with the nodal cones of the hybrid bond orbitals. These results not only reinforce the validity of the theory as to the fundamental "mechanism" for the formation in the normal shape of coordination compounds and covalently bonded polyatomic molecules, but also provide the justification for the relevance and importance of the hybridization model. © 1999 John Wiley & Sons, Inc. *Int J Quant Chem* **71**: 25–34, 1999

Key words: molecular shape; hybridization; geometrically active atomic state; Pauling's bond strength function; maximum spin states

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Theoretical resolution of the H^- resonance spectrum up to the $n=4$ threshold. I. States of $^1P^o$, $^1D^o$, and $^1F^o$ symmetries

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We report on a theoretical approach to the calculation of wave functions, energies E , and widths Γ of high-lying resonances of H^- , with application to the identification of 76 states of $^1P^o$, $^1D^o$, and $^1F^o$ symmetries up to the $n=4$ threshold, with widths down to about $1 \times 10^{-8} - 1 \times 10^{-10}$ a.u., depending on symmetry and threshold. The overwhelming majority of these resonances have not been detected experimentally. Previous calculations by different methods allowed the identification of 35 of these states, with only very few cases having a level of accuracy comparable to the one of the present work. We suggest that the measurement of these resonances might become possible via two-step excitation mechanisms using ultrasensitive techniques capable of dealing with the problems of very small widths and preparation cross-sections. In this work, the 1D state at 10.872 eV above the $H^- 1s^2 ^1S$ ground state, already prepared and measured by electron scattering as well as by two-photon absorption, is considered as the stepping stone for the possible probing of resonances of $^1P^o$, $^1D^o$, and $^1F^o$ symmetries via absorption of tunable radiation of high resolution. By classifying the results according to the Gailitis-Damburg model of *dipole resonances* (a product of a $1/r^2$ -like potential) we find that there are unperturbed as well as perturbed series, in analogy with the Rydberg spectra of neutrals and positive ions (a product of a $1/r$ -like potential). For the former, the agreement with the Gailitis-Damburg predictions as to the relationship of the extent of the outer orbital and of the energies and widths of states is excellent. The perturbed series result from interchannel coupling and the remaining electron correlation. One of the effects is the existence of overlapping resonances. For example, for two $^1P^o$ states below the $n=3$ threshold there is degeneracy on the energy axis ($E_1 = -0.0555763612$ a.u. and $E_2 = -0.0555763099$ a.u.) but the widths differ ($\Gamma_1 = 1.14 \times 10^{-4}$ eV and $\Gamma_2 = 5.45 \times 10^{-6}$ eV). We also comment on whether consideration of the relativistic Lamb shift splitting of the hydrogen thresholds is sufficient for deciding the truncation of the resonance series. Our calculations were carried out by implementing previously published theories, whereby the resonance E 's and Γ 's are determined from properly selected complex eigenvalues of non-Hermitian Hamiltonian matrices constructed in terms of physically relevant square integrable real and complex function spaces representing the localized and asymptotic parts of the resonance eigenfunctions. For the H^- series of resonances, the physical relevance of the real functions implies the systematic construction of basis sets with average $\langle r \rangle$ extending to thousands of atomic units, in order to account for the extreme diffuseness of the outer orbital as each threshold is approached. The complex one-electron basis sets are Slater-type orbitals of a complex coordinate $re^{-i\theta}$. Their inclusion into the overall calculation and their optimization via the variation of nonlinear parameters (including θ) accounts for the contribution of the asymptotic part of the resonance, and for the energy width and shift beyond the real energy E_o of the localized part.

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I. INTRODUCTION

The objective of the research reported here and in the accompanying paper [1], as well as in a recent letter [2], was to compute and analyze highly accurate resonance wave functions of the hydrogen negative ion H^- , and to completely resolve the resonance spectrum of H^- in the energy range up to the $n=4$ threshold. (In Ref. [2], the calculation of states of $^1P^o$ symmetry went up to the $n=5$ threshold). By resolution, we mean the accurate identification of all the physically relevant complex poles of the resolvent $R(z) \equiv (z - H)^{-1}$, where z is a complex variable and H is the total Hamiltonian of the system. These poles are associated with nonstationary (resonance) states $|\kappa\rangle$, whose energy is com-

plex; $z_\kappa = E_\kappa - (i/2)\Gamma_\kappa$, where E_κ is the total energy and Γ_κ is the total width.

Nonstationary states in the continuum of atomic negative ions (ANI's) or of any other atomic or molecular system are represented by electronic structures signifying multiple excitation from, or electron attachment to, or creation of a hole in a subshell of a particular configuration. A research program since 1972 [3], whereby the computation and analysis of the wave functions and properties of these states is done by considering them in a unified manner as *decaying states* (see Refs. [3–12], and references therein) breaks down the overall calculation into two steps, regardless of the number of electrons, of electronic structure, and of level of excitation.

The first step emphasizes the state-specific analysis and application of advanced many-electron methods for the calculation of electronic structures representing the localized part of resonances, ψ_o^k . These structures may be characterized in zero order by one configuration or by a superposition

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Variation of harmonic generation from He interacting with short laser pulses of 5 eV as a function of pulse rise time and intensity

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We have applied the state-specific expansion approach (SSEA) to the solution of the time-dependent Schrödinger equation describing the interaction of He with laser pulses of $\hbar\omega=5$ eV, which have a shape with a sharp rise and peak intensities in the range 5×10^{14} – 3.46×10^{15} W/cm². The calculations include the effects of the state-specific self-consistent field, the electron correlation, and the $n=2$ intrashell doubly excited states. The results show that, provided the pulses have fast rise times, neutral He can generate harmonics of higher order than previously thought before the He⁺ contribution takes over. The computed spectra agree with the observations of Sarukura *et al.* [Phys. Rev. A **43**, 1669 (1991)]. In particular, the SSEA results reveal “anomalously” high peaks for the 13th and 21st harmonics, in agreement with experiment.

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I. INTRODUCTION

The interaction of short laser pulses of very high intensity with atoms leads to high-order harmonic generation (HOHG). A number of experiments [1–10] and calculations performed on noble gases [8,11–17] during the 1990s have produced useful results and addressed the problem of understanding at the atomic level (i.e., apart from collective effects and phase matching) the origin and features of the harmonic spectra appearing during the interaction of noble gases with laser pulses of intensities in the range 10^{14} – 10^{17} W/cm² and photon energies in the range 1–5 eV, and their dependence on peak intensity I_0 and laser frequency ω . A related aim has been the possibility of creating harmonic spectra of high order using short and intense driving pulses from which very short pulses of very short wavelength can be extracted. Obviously, the shorter the source wavelength the quicker very short wavelengths from harmonics are reached. For example, Preston *et al.* [8] reported the observation of the 37th harmonic of the KrF laser (248.6 nm) from its interaction with He corresponding to an emitted photon wavelength of 67 Å.

In the works of [1–8,11–16], the question of the degree of participation of singly or even doubly [6] ionized atoms in the production of the high-order harmonics was raised and discussed. The emphasis of the related analysis was on the significance of the saturation intensity or effective intensity *vis à vis* the peak intensity. It has generally been accepted that due to the ionization that takes place during the rise of the intensity of the laser pulse, the neutral atom contributes only to the low-order part of the harmonic spectrum (for laser sources in the range 2–5 eV), while the high-order part is due to the ion (e.g., [8,11,12,14]). A dissenting view by Moiseyev and Weinhold appeared recently [16]. In earlier works, Sarukura *et al.* [1] and Sanpera *et al.* [14] they con-

cluded that “the intensity of 3.5×10^{15} W/cm² can be regarded as the field intensity where the transition from neutral He to He⁺ occurs.” They then proceeded with calculations of He-field interactions with $\hbar\omega=5$ eV and intensity up to 3.46×10^{15} W/cm² using a Floquet-type formalism with the assumption of an ac-field rather than of a pulse. They employed only two Floquet blocks: those of ¹S and ¹P^o symmetries. Their results led them to the conclusion that it is the neutral atom rather than the ion that produces harmonics of high order, and that the reason is the effective role of electron correlation in He, which keeps the two electrons apart. However, we took issue with this approach to the problem [17] since not only is the pulse temporal shape not accounted for, but, as was demonstrated via systematic calculations with electron correlation included [17], for such intensities the function space must also include state symmetries higher than ¹P^o for the overall calculation of the time-dependent wave function $\Psi(t)$ and the concomitant properties to reach convergence.

In this paper, we reexamine the issue of the capacity of neutral noble gases to produce harmonics of high order by paying attention to the effect of the rise time of the pulse. We note that Watson *et al.* [15] have found evidence in their numerical simulation, using a model for representing He, that the harmonic response depends critically on the shape of the pulse. In addition, Balcou *et al.* [4] experimentally demonstrated that the shorter the driving laser pulse the higher the order of the observed harmonics.

By solving *ab initio* the time-dependent Schrödinger equation (TDSE) for He interacting with laser pulses of 5 eV and peak intensities in the range 5×10^{14} – 3.46×10^{15} W/cm², we found that the rise time, which in principle can be controlled experimentally to some extent, drastically influences the level of contribution of the neutral atom to the overall high-order harmonics spectrum.

II. THEORY

The solution of the TDSE and the calculation of the harmonic spectra of He were achieved by the state-specific ex-

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Multiphoton detachment rates of H^- for weak and strong fields

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The time-independent Schrödinger problem for the H^- plus ac field system has been solved from first principles via the nonperturbative many-electron, many-photon theory (MEMPT) for a wide range of values of frequency ω and of intensity I of linearly polarized light. The calculations obtained the multiphoton electron detachment rates (MPEDRs) as the imaginary part of a complex eigenvalue and were done for combinations of values of ω and of I defining regimes of “weak” and of “strong” fields. Most of the results cover the cases of two-, three-, ..., seven-photon electron detachment, studied as a function of frequency and of intensity. However, special cases, such as the one of $I=2\times 10^{11}$ W/cm² for the CO₂ frequency of 0.117 eV, represent detachment processes into various symmetries requiring the absorption of at least 25 photons. The MEMPT results were obtained without any empirical adjustment of energies or of basis sets. The dressed-atom resonance wave function consisted of optimized function spaces for the initial and final states, including the lowest ¹S, ¹P^o, and ¹D doubly excited states (DES). The initial state was represented by a ten-term numerical multiconfigurational Hartree-Fock wave function whose energy, -0.5275 a.u., is very close to the exact one, -0.5277 a.u., and which accounts self-consistently for electron correlation as well as for the proper magnitude of the $1s$ orbital at large values of r . The H^- DES wave functions were correlated, yielding accurate energies. However, their presence does not affect the results at all. The results converged well when 15 photon blocks were used. In spite of the large number of absorbed photons required in cases such as the CO₂ frequency, the calculations converged well, within the numerical accuracy of the algorithms, by using free-electron angular momenta with 1 up to 7. The systematic quantitative study of the dependence of the MPEDRs on ω and I has led to conclusions as to the behavior at thresholds and as to the limits of validity of the predictions of the lowest-order perturbation theory. An interesting result is the appearance of intensity-dependent structures in the two-, four-, and six-photon detachment rates, which is caused by the interference of the ¹S and ¹D channels. For a number of (I, ω) pairs, comparison is possible with published results obtained by earlier large-scale calculations which either started from first principles or used parametrized one-electron models. Overall, there is good agreement. We conclude that the current level of theoretical knowledge of the H^- MPEDR spectrum is very satisfactory for a large set of experimentally possible laser parameters.

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I. INTRODUCTION

In order to compute reliably properties related to the non-linear response of a polyelectronic atomic state, ground or excited, to a laser field, it is necessary to solve the corresponding many-electron, many-photon (MEMPT) problem. If the result of the atom-field interaction is an average over many field cycles, there are observables, such as multiphoton electron detachment rates (MPEDRs), which are computable within a time-independent framework. When the expressions of lowest-order perturbation theory (LOPT) produce accurate results for the MPEDRs, the field can be characterized as *weak*. When the LOPT breaks down, the field is said to be *strong*. In this case, either all the necessary higher-order perturbation theory terms have to be computed or the whole approach must be nonperturbative. In all cases, the many-electron part of the problem remains.

Publications from this institute have proposed large-order perturbative as well as nonperturbative approaches for the systematic tackling of the many-electron problem in the

presence of an external static or dynamic field. These approaches are based on rigorous formalism and are implemented via computational methods that are characterized by two basic features: The first aims at the use of state-specific wave-function expansions, a fact which allows, via the diagonalization of appropriately constructed matrices, the incorporation of the necessary electronic structure characteristics of ground or excited states. The second involves the extension into the complex energy plane, where the imaginary part of the calculated state-specific energy is the decay rate. The large-order perturbative approach was demonstrated on the calculation of LoSurdo-Stark shifts and widths not only of the ground state but also of excited states of hydrogen [1], where one of the difficulties that had to be resolved is how to handle rigorously and efficiently the zero-order degeneracy. The nonperturbative approach has been implemented for the calculation of energy shifts and widths in magnetic fields, with applications to hydrogen and to doubly excited states (DES) of H^- [2]. Its most extensive implementation has been for the calculation of properties induced by dc and ac electric fields, with applications to a number of small atoms in ground or excited states ([3,4] and references therein).

It is the nonperturbative MEMPT theory (MEMPT) ([3]

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He in dichromatic weak or strong ac fields of $\lambda_1=248$ nm and $\lambda_2=(1/m) 248$ nm ($m=2,3,4$)

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We have computed multiphoton ionization rates for He irradiated by a dichromatic ac field consisting of the fundamental wavelength $\lambda = 248$ nm and its second-, third-, and fourth-higher harmonics. The intensities are in the range $1.0 \times 10^{12} - 3.5 \times 10^{14}$ W/cm², with the intensity of the harmonics being 1–2 orders of magnitude smaller. The calculations incorporated systematically electronic structure and electron correlation effects in the discrete and in the continuous spectrum, for ¹S, ¹P, ¹D, ¹F, ¹G, and ¹H two-electron states of even and odd parity. They were done by implementing a time-independent, nonperturbative many-electron, many-photon theory which obtains cycle-averaged complex eigenvalues, whose real part gives the field-induced energy shift, $\Delta(\omega_1, F_1; \omega_2, F_2, \varphi_2)$, and the imaginary part is the multiphoton ionization rate, $\Gamma(\omega_1, F_1; \omega_2, F_2, \varphi_2)$, where ω is the frequency, F is the field strength, and φ_2 is the phase difference. Through analysis and computation we show that, provided the intensities are weak, the dependence of $\Gamma(\omega_1, F_1; \omega_2, F_2, \varphi_2)$ on φ_2 is simple. Specifically, for odd higher harmonics, Γ varies linearly with $\cos(\varphi_2)$ whilst for even higher harmonics it varies linearly with $\cos(2\varphi_2)$. These relations may turn out to be applicable to other atomic systems as well, and to provide a definition of the weak-field regime in the dichromatic case. When the combination of (ω_1, F_1) and (ω_2, F_2) is such that higher powers of $\cos(\varphi_2)$ and $\cos(2\varphi_2)$ become important, these rules break down and we reach the strong-field regime.

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I. INTRODUCTION

In a recent publication [1], we reported the results of many-electron, many-photon theory (MEMPT) computations of the cycle-averaged multiphoton ionization rates (MPIR) and linear and nonlinear polarizabilities of He interacting with a linearly polarized ac field for frequencies in the range $\omega = 4.9 - 26.4$ eV. In this paper we extend the implementation of the MEMPT to the dichromatic case ($\omega_1 = \omega = 5$ eV or $\lambda_1 = 248$ nm) with commensurate frequencies of higher harmonics, $\lambda_2 = (1/m)248$ nm, $m = 2, 3, 4$, and provide reliable MPIRs which can be tested experimentally. The intensities are in the range $1.0 \times 10^{12} - 3.5 \times 10^{14}$ W/cm², with the intensity of the harmonics being 1–2 orders of magnitude smaller. Obviously, the MPIRs depend on intensity. Furthermore, they depend on the phase difference φ_2 between the two fields, and the present study has produced unique results not only for the particular system but also for the phenomenology of the problem, which should be applicable to multiphoton processes in other systems as well.

The fact that the response of atoms or molecules to dichromatic laser fields leads to the dependence of observables on φ_2 has been the subject of many theoretical and experimental publications. For representative analyses and results the reader is referred to Refs. [2–21]. The basic source of this dependence is the quantum-mechanical interference between the various possible excitation paths. For example, the weak-field model analysis of Brumer and Shapiro [3,4] illustrated how the irradiation of a bound state with

a field of commensurate frequencies, ω_1 and $\omega_2 = 3\omega_1$, may be used for the coherent phase control of the rate of production of the final products in the continuous spectrum. Additional early results based on one-electron calculations within time-dependent [7,11] and time-independent Floquet frameworks [8,9] showed the effect of φ_2 on field-induced properties, even for strong fields. Experimental work has also revealed the effect of phase-dependent interference on atomic observables [e.g., 5, 6, 13, 14, 20, 21].

The work described below was carried out by combining heuristic arguments with MEMPT all-order calculations. The former was applied in order to explore whether it is possible for the MPIR to be connected in a simple way to the phase difference when the intensities of the two interfering waves are weak. The latter (MEMPT) was applied in order to produce accurate results for weak as well as for strong fields, which, not only should be useful as such, but they could provide quantitative information about the degree of validity of the heuristic arguments. Indeed, the results show that, at least for He, and probably for other systems where similar conditions are met, there is an underlying simple “law” connecting the MPIRs with the phase difference φ_2 .

II. HEURISTIC ARGUMENTS FOR THE FORM OF THE DEPENDENCE OF THE MPIR ON THE PHASE DIFFERENCE

Let us consider a dichromatic field $F(t)$ in the form

$$F(t) = F_1 \cos(\omega_1 t + \varphi_1) + F_2 \cos(\omega_2 t + \varphi_2), \quad (1)$$

where $\varphi_1 = 0$ (without loss of generality for the present argument), and $\omega_1 = \omega$, $\omega_2 = m\omega$, and m is an even or odd

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The continuous spectrum in the solution of the time-dependent Schrödinger equation for laser–atom interactions

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Abstract. We present results from the application of the state-specific expansion approach (SSEA) to the *ab initio* calculation of the ionization probability of the ‘delta function atom’ interacting with a superstrong high-frequency laser pulse ($\omega = 1$ au, $I_{\text{peak}} = 0.1\text{--}100$ au). These results pertain to the extensively discussed notion of ‘stabilization’. A fully converged SSEA calculation does not produce any ‘stabilization’. However, approximations to it, resulting from the incomplete inclusion of the contribution of the continuous spectrum, do.

1. Introduction

The results of recent calculations by different methods for the solution of the time-dependent Schrödinger equation (TDSE) describing a one-dimensional ‘delta function atom’ (DFA) interacting with a superstrong high-frequency laser pulse [1–5] have led to different conclusions as to the reality or realizability of the much discussed, during the past decade, intriguing concept of ‘stabilization’. By stabilization for this problem we will mean the decrease of the ionization probability at the end of the high-frequency laser pulse, denoted by $P(t = \infty)$, as intensity increases beyond a certain large value. According to [1–3, 5], the decrease of $P(t = \infty)$ reaches one or more local minima as a function of peak intensity.

Su *et al* [1], Geltman [2] and Dörr and Potvliege [5] have applied the grid method and obtain overall similar stabilization-type results, although Geltman has argued for a different interpretation [2]. Figueira de Morisson Faria *et al* [3] applied an analytic method of solution with reasonable approximations and concluded that there is no evidence of stabilization for the parameters they used. Finally, the calculations which were carried out following the state-specific expansion approach (SSEA) [4], using the same laser parameters as those employed in [1, 2], did not reveal any stabilization for peak intensities up to 8.75×10^{17} W cm⁻² and frequency 1.0 or 1.5 au.

In view of the difference in the substance of the results obtained on the one hand by the grid method [1, 2, 5] and on the other by the SSEA [4], we have studied the problem further. In this paper we report additional results from the SSEA showing that when the calculations are approximate in the treatment of the contribution of the continuous spectrum, numerical phenomena resembling stabilization appear.

Complex energies and the polyelectronic Stark problem

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Abstract. The problem of computing the energy shifts and widths of ground or excited N -electron atomic states perturbed by weak or strong static electric fields is dealt with by formulating a state-specific complex eigenvalue Schrödinger equation (CESE), where the complex energy contains the field-induced shift and width. The CESE is solved to all orders nonperturbatively, by using separately optimized N -electron function spaces, composed of real and complex one-electron functions, the latter being functions of a complex coordinate. The use of such spaces is a salient characteristic of the theory, leading to economy and manageability of calculation in terms of a two-step computational procedure. The first step involves only Hermitian matrices. The second adds complex functions and the overall computation becomes non-Hermitian. Aspects of the formalism and of computational strategy are compared with those of the complex absorption potential (CAP) method, which was recently applied for the calculation of field-induced complex energies in H and Li. Also compared are the numerical results of the two methods, and the questions of accuracy and convergence that were posed by Sahoo and Ho (Sahoo S and Ho Y K 2000 *J. Phys. B: At. Mol. Opt. Phys.* 33 2195) are explored further. We draw attention to the fact that, because in the region where the field strength is weak the tunnelling rate (imaginary part of the complex eigenvalue) diminishes exponentially, it is possible for even large-scale nonperturbative complex eigenvalue calculations either to fail completely or to produce seemingly stable results which, however, are wrong. It is in this context that the discrepancy in the width of Li $1s^2 2s^2 S$ between results obtained by the CAP method and those obtained by the CESE method is interpreted. We suggest that the very-weak-field regime must be computed by the golden rule, provided the continuum is represented accurately. In this respect, existing one-particle semiclassical formulae seem to be sufficient. In addition to the aforementioned comparisons and conclusions, we present a number of new results from the application of the state-specific CESE theory to the calculation of field-induced shifts and widths of the H $n = 3$ levels and of the prototypical Be $1s^2 2s^2 S$ state, for a range of field strengths. Using the H $n = 3$ manifold as the example, it is shown how errors may occur for small values of the field, unless the function spaces are optimized carefully for each level.

1. Introduction

When an atomic ground or excited discrete state, of energy E_0 , is placed in a static electric field of strength F , ($1 \text{ au} = 5.14 \times 10^9 \text{ V cm}^{-1}$), the interaction mixes the discrete with the continuous spectra and the state turns into a resonance with a complex eigenvalue, z_0 . In other words, the effect of the field is to shift the energy by an amount $\text{Re } z_0 - E_0 = \Delta$, and to broaden it by an amount Γ , this being the field-induced tunnelling rate (FITR). In order to understand the physics of this situation quantitatively, by obtaining reliable values for Γ and

Existence and characterization of $n = 3$ triply excited resonances of He^-

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Abstract

We predict, via large-scale calculations carried out in the framework of the state-specific theory of resonance states and accounting for all the localized electron correlations, the positions of 11 new triply excited resonances of He^- in the region between 68.7 and 70.3 eV. These states can, in principle, be reached in electron–He $1s^2\ ^1S$ and $1s2s\ ^3S$ scattering, and have the symmetries 2S , $^4P^o$, $^2P^o$, 2D , $^4F^o$, $^2F^o$ and 2G . A few of these are essentially overlapping. Their zero-order representations consist of strongly mixing $n = 3$ configurations. Of special significance to achieving good convergence of the calculation to local energy minima in the continuous spectrum, while accounting for a large portion of the bound open-channel interactions, is the inclusion of open-channel-like configurations, included self-consistently via the multi-configurational Hartree–Fock method. Our results allow the long overdue confirmation and interpretation of Roy’s measurements (Roy D 1977 *Phys. Rev. Lett.* **38** 1062).

1. Introduction

The excitation of atomic negative ions (ANIs) into quasi-localized states of the continuous spectrum gives rise to resonance structures over the normally smooth background of the rate of the transition process being examined. The discovery, interpretation and *ab initio* calculation of such states have constituted the object of much research in atomic physics since the early 1960s. (For a review of the progress made until 1993 see [1].) About 25 years ago, Roy [2] reported remarkable experimental data from the measurement of the differential excitation function of the He $1s2s\ ^3S$ bound state, in e–He collisions. Distinct structures were recorded which, according to him, revealed for the first time in the region around 69 eV the existence of $n = 3$ intra-shell triply excited states (TES) of He^- . Specifically, Roy calibrated his $n = 3$ measurements to the previously known He^- $n = 2$ intra-shell resonances $2s^22p\ ^2P^o$ and $2s2p^2\ ^2D$, whose positions he determined to be at 57.19 ± 0.03 and 58.29 ± 0.03 eV with an energy separation of 1.094 ± 0.012 eV. Three features were recorded, at 68.83 ± 0.04 , 69.00 ± 0.04 and 69.67 ± 0.04 eV, indexed by 1, 1' and 2. Roy suggested that the 1–1' feature