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Direct ionization in the quasimolecule H-He

G. N. Ogurtsov, A. G. Kroupyshev, M. G. Sargsyan, and Yu. S. Gordeev
A. F. Ioffe Physical Technical Institute, 194021 St. Petersburg, Russia

S. Yu. Ovchinnikov*
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1501
and Oak Ridge National Laboratory, Post Office Box 2008, Oak Ridge, Tennessee 37831

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Doubly differential cross sections for electron ejection in H-He collisions have been measured in the incident atom energy range 2.3–10 keV. Analysis of the experimental data on the basis of the adiabatic theory of direct ionization has been made and parameters of the quasimolecule, namely, the energy of the initial $2p\sigma$ state coupled with the continuum, the effective charge, and the real and imaginary parts of the internuclear distance at which the "superpromoted" diabatic term crosses boundary of continuum, have been determined. The values of the initial-state energy and the effective charge agree well with the corresponding parameters of the Li united atom, whereas the dynamical characteristics Re$R(E)$ and Im$R(E)$ reveal considerable influence of electron correlations. The possibility for the development of an alternative method of quantitative spectroscopy of quasimolecules based on the analysis of experimental data on differential cross sections for direct ionization is discussed.

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I. INTRODUCTION

In recent years, considerable progress has been made in the study of direct ionization, i.e., the process of electron ejection caused by direct coupling of a discrete quasimolecular level with the continuum. This study has largely been stimulated by the experimental work of Woerlee *et al.* [1] in which a surprisingly simple empirical relation was obtained between doubly differential cross sections for ejection of electrons with energy E and parameters of an ion-atomic system that undergoes direct ionization (unless otherwise stated, atomic units are used throughout):

$$\frac{d^2\sigma}{dE\,d\Omega}=\frac{R_0^2}{4E}\exp\left(-\frac{\alpha_0(E-E_0)}{v}\right), \tag{1}$$

where the values R_0 and E_0 correspond to the internuclear distance at which direct ionization is most probable and to the energy of an ionized quasimolecular state. In Eq. (1) v is the projectile velocity and α_0 is a constant. The quantity in the exponent $\alpha_0(E-E_0)$ resembles the Massey parameter.

Two features of Eq. (1) are of particular interest. First, the pre-exponential factor does not depend upon the projectile velocity; rather, this dependence is contained only in the exponent. Second, the exponential dependence of the cross section on the quasimolecular level energy E_0 suggests that isolated energy ranges exist in the ejected electron energy spectra that correspond to contributions of only one quasimolecular orbital to direct ionization. These features facilitate considerably the analysis of experimental data and show a promising perspective to develop a new method for quantitative spectroscopy of quasimolecules.

Theoretical consideration of direct ionization has been given by Solov'ev and Ovchinnikov [2–4] in the adiabatic approximation using analytical features of potential-energy curves of the diatomic systems. In this approximation, the differential cross section for electron ejection via direct ionization can be written as

$$\frac{d\sigma}{dE}=A(E)\exp\left(-\frac{\alpha(E)}{v}\right), \tag{2}$$

$$A(E)=\frac{4\pi|R(E)|^2\,\mathrm{Im}R(E)}{\alpha(E)}, \tag{3}$$

$$\alpha(E)=2\int_{E_0}^{E}\mathrm{Im}R(\varepsilon)\,d\varepsilon, \tag{4}$$

where $R(E)$ is the generally complex reciprocal function of $E(R)$. Solov'ev and Ovchinnikov [3] have discovered several series of branch points in different ranges of internuclear distances where the structure of potential surfaces changes crucially. The present paper will deal only with the S series of branch points situated in the region where quasimolecular wave functions transform to those of the united atom.

The simplicity of Eqs. (2) and (4) reveals the possibility to determine several parameters of quasimolecules (i.e., energy of the level coupled with the continuum, effective charge of the core, and characteristic internuclear distances) directly from analysis of the electron energy spectra. Indeed, such proposals have been put forth in [5–7]. It is important that the determination of most parameters can be made using only relative (not absolute) values of differential cross sections, which can be measured very accurately. Some data on parameters of relatively simple diatomic and triatomic quasimolecules have been reported in two short communications [8,9]. It has been found that the values of parameters of

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*Permanent Address: Ioffe Physical Technical Institute, St. Petersburg, Russia.

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diatomic quasimolecules extracted from experimental data are close to those of united atoms. In the case of triatomic quasimolecules the situation is different, but this is a special problem, which is planned to be considered in our future work.

The remarkable similarity in the exponential behavior of cross sections and reasonable values of extracted parameters indicates that the range of applicability of the theoretical approach extends far beyond the system Z_1eZ_2. This has encouraged us to undertake experimental and theoretical studies to examine the adiabatic description of an electron ejection in non-Coulomb fields. We have chosen the system H-He characterized by the existence of the ''promoted'' diabatic $2p\sigma$ orbital that correlates with the $1s$ level of H in the limit of separated atoms and contains only one electron. Thus the process of direct ionization can be treated as ''promotion'' into a continuum state of a single electron in the field of a core formed by two nuclei and two electrons occupying $1s\sigma$ orbitals correlated with the $1s$ levels of He at $R\rightarrow\infty$. Therefore, one can expect that the one-electron approximation used in the theoretical calculations will work well in the case under study. On the other hand, the field of the core is not purely Coulombic, and this can lead to observable differences between theory and experiment.

II. EXPERIMENTAL TECHNIQUE

The main elements of our experimental apparatus for studying electron energy spectra were described earlier [10]. Since then, the spectrometer was modified considerably to increase its accuracy and reliability. A short description of these modifications is given below.

An ion beam from a duoplasmatron source entered a gas cell placed inside the cylindrical electrostatic mirror with entrance angle $\theta_{\mathrm{lab}}=54.5°$ and energy resolution $\Delta E/E=0.63\%$. The primary beam current was measured by a Faraday cup separated from the gas cell by a grounded ring and a guard electrode biased negatively to avoid penetration of secondary electrons from the Faraday cup into the analyzer volume. Energy-analyzed electrons passed through the exit slit of the analyzer and entered a detector consisting of a channeltron mounted behind a small conical analyzer with retarding voltage equal to two-thirds of that applied to the outer (mesh) electrode of the main analyzer. The background attained corresponded to (2–5)% of the signal at the target gas pressure $p = (2–4)\times10^{-4}$ Torr in the ejected electron energy range $E = 3–100$ eV. The electron counting rate was normalized to the primary beam current. The residual magnetic field in the collision region was reduced to $H<10$ mG by μ-metal shielding and compensation of the field using three pairs of Helmholtz coils. Our electron spectrometer was characterized by a very small contact potential difference $\Delta V<0.1$ eV, which allowed us to obtain reasonable results at ejected electron energies as low as $E\geqslant1$ eV.

Absolute values of the doubly differential cross sections are determined using the relation

$$\frac{d^2\sigma}{dE_e d\Omega}=\frac{1}{n\Delta E_e\eta\int\Omega dL}\left(\frac{N_e}{N_0}\right), \tag{5}$$

where n is the target gas density, ΔE_e is the absolute energy resolution, $\eta=0.74$ is the detection efficiency, $\int\Omega dL=3.7\times10^{-3}$ sr cm is the geometrical parameter characterizing the ejected electron solid angle and collection length, and N_e and N_0 are the fluxes of electrons and primary beam particles, respectively. The constants necessary for calculation of cross sections were determined both from special control experiments and from normalization to data available in the literature (in particular, the data of Ref. [11]). These experiments were performed using both a small electron gun placed inside the inner electrode of an analyzer and the elastically scattered electron beam as sources of electrons with fixed energy. The function $\Omega(l)$ was found from the variation of detected electron signal with the displacement of the electron source along the analyzer axis. The analyzer transmission was determined using two Faraday cups that measured currents of electrons entering the analyzer volume and deflected to the detector site by the analyzing voltage. The detection efficiency was determined from readings with the detector operating as a Faraday cup in a single-electron counting mode. The energy resolution was found by measuring profiles of lines from the electron gun, from electron elastic scattering, and from Auger transitions. Spectroscopic data on positions of Auger lines were used to determine the analyzer constant. The coefficients relating doubly differential cross sections with electron energy, gas pressure, and the ratio of fluxes determined from control experiments and from normalization were found to agree within 5%. When measuring energy spectra of electrons ejected by neutral atom impact, a differentially pumped neutralization chamber with deflecting electrodes was placed before the analyzer chamber. In that case, the primary atomic beam was measured using the method of secondary emission from a separated bottom of the Faraday cup, the secondary emission coefficients for protons and hydrogen atoms being assumed equal. (Special experiments [12] show that this assumption holds well at the atomic-beam incident energy $E_H\geqslant1$ keV.)

The accuracy of absolute values of measured cross sections was estimated as $\pm30\%$. Errors of relative measurements were $\pm$ (2–8)%, depending upon ejected electron energy.

Figure 1 shows electron energy distributions measured in the energy range $E_H = 2.3–10$ keV. The structure associated with autoionization transitions of helium is subtracted from the distributions. The exponential form of the distributions is clearly seen. Now we proceed to the theoretical relations, which form a basis for analysis of the experimental data.

III. THEORETICAL BACKGROUND

The semiclassical theory of nonadiabatic transitions in slow atomic collisions has been presented in many papers (e.g., see [13] and references therein). The main idea of the theory is to replace laborious summation of iteration terms of the same order of magnitude in solving a system of Born-Fock equations by considering the complex plane of t (or R) to find special points that give the main contribution to the nonadiabatic transition amplitude. It has been shown that such points are the branch points R_C of an analytical function $E(R)$ in the vicinity of which one can set $E(R)\propto\sqrt{R-R_C}$. The probability of nonadiabatic transition between the states

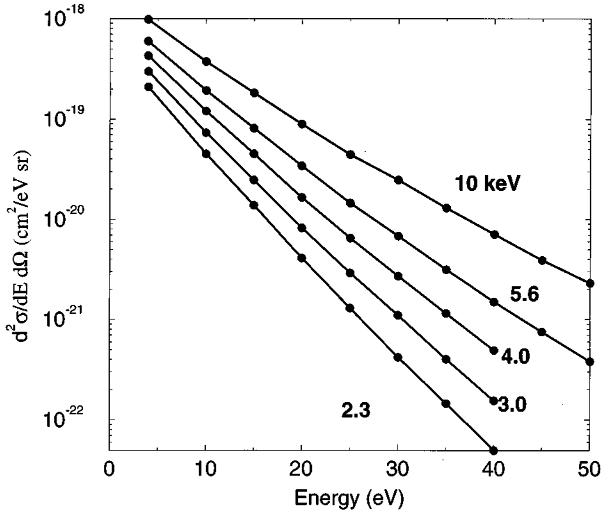

FIG. 1. Energy distributions of electrons ejected in H-He collisions. Figures near the curves indicate incident atom energy in keV.

whose levels are connected by a branch point is calculated by evaluating the relevant phase integral along a path that begins and ends on the real R axis and goes around the branch point R_C [14,15]. In our case the situation becomes complicated due to the fact that the points R_C are situated far enough from the real axis so that their existence has little effect on the behavior of energy levels at real internuclear distances ("hidden" crossings [16]). A special program is necessary for the calculation of energy levels at complex internuclear distances. Such a program to discern the R_C values in the vicinity of which $dE/dR \propto (R-R_C)^{-1/2} \rightarrow \infty$ as $R \rightarrow R_C$ has been developed in [2] and has been used successfully for the calculation of total and differential cross sections of direct ionization in the systems H^+-H, H^+-He^+, and H^+-He and of inner-shell ionization in more complex systems Ar^+-Ar and Ar^+-Kr [5].

In this section, we will not discuss the general theoretical assumptions. Our aim is only to review the theoretical relations needed for the determination of quasimolecule parameters.

The probability for a transition between a discrete state E_0 and a continuum state E in the adiabatic approximation can be written as [4]

$$P(E)=\frac{1}{2\pi}\left|\frac{1}{v}\frac{d\tau(E)}{dE}C(E)^2\right|\exp\left\{-\frac{2}{v}\mathrm{Im}\int_{E_0}^{E}\tau(\varepsilon)d\varepsilon\right\}, \tag{6}$$

where $\tau = vt$ and $C(E)$ is the normalization factor.

Now we will try to answer the following question: at which internuclear distance R_0 should the lower limit of integration $E_0 = E(R_0)$ be taken? The notation $E_0 = E_0^\infty = \lim_{R\rightarrow\infty} E_0(R)$ has been used in Ref. [17]. Since $E(R)$ is real along the real axis R, there is no change in the imaginary part of the integral in Eq. (6). The answer can be obtained from the Taylor expansion of $E(R)$ near R_0:

$$E(R) \approx E_0 + E'(R_0)(R-R_0) + \frac{1}{2}E''(R_0)(R-R_0)^2, \tag{7}$$

where $E_0 = E(R_0)$. Recognizing that $R_0, E_0, E(R)$ are real but R is a complex value and $E(R) > E_0$, we have

$$E'(R_0) \equiv \left|\frac{d}{dR}E(R)\right|_{R=R_0} = 0,$$

$$E''(R_0) \equiv \left|\frac{d^2}{dR^2}E(R)\right|_{R=R_0} < 0. \tag{8}$$

Usually the conditions (8) are fulfilled only at $R_0 = 0$.

To determine differential cross sections for electron ejection, it is necessary to integrate (6) over the impact parameter b:

$$\frac{d\sigma}{dE} = 2\pi \int_0^\infty P(E,b)\, b\, db. \tag{9}$$

The straight-line trajectory $R^2 = b^2 + \tau^2$ approximation is often used in Eq. (9). In our case this approximation is justified because corrections connected with departures from straight-line trajectories do not exceed 1%, even at incident atom energies 2.3 keV. Using the results from Refs. [17] and [18] that $\tau(E)$ and $C(E)$ may quite accurately be approximated by

$$\mathrm{Im}\tau(E) = \mathrm{Im}R(E)\left(1+\frac{b^2}{2|R(E)|^2}\right),$$

$$C^2(E) = 4\pi \mathrm{Im}R(E)\left|\frac{dR(E)}{dE}\right|^{-1} \tag{10}$$

and integrating over the impact parameter in Eq. (9), we obtain Eqs. (2) and (4) for differential cross sections.

Previous calculations have shown that the fast electrons ejected in low-energy ion-atom collisions are S-promotion electrons. The S-promotion electrons are associated with classical, periodic, and unstable trajectories, which represent electron motion along the axis joining the charges [19]. [Im$R(E)$ characterizes the instability of this motion. Smaller Im$R(E)$ corresponds to more stable motion.] The kinetic energy of electrons on these trajectories increases when the charges approach each other. The increase of kinetic energy leads to ionization even when the relative velocity is insufficient to ionize electrons in a single binary collision. A simple analog of this mechanism is the acceleration of elastic balls bouncing between two walls slowly approaching each other.

In the case of Ne-Ne, calculations are in satisfactory agreement with the data obtained from analysis of experimental cross sections at high ejected electron energies [1]; however, with decreasing electron energy, the discrepancy between theory and experiment exceeds the experimental error bars.

Finally, we should decide what is meant by effective charge in the case when the field of a core is not purely a Coulombic one and some screening takes place. This can be done starting from the existence of the "delay effect" associated with the fact that the motion of an ejected electron is governed by the form of Hamiltonian at the moment of ionization, but not at the moment of observation [20]. Since the theory treats the ionization process as being associated with formation of quasistationary states calculated in the same Hamiltonian as the bound states and $E_0 = E_0(0)$, it is reasonable to assume that the effective charge extracted from experimental data coincides with or is very close to that of a core for the ionized orbital in the limit of the united atom.

The above analysis permits us to use the following initial assumptions in the derivation of formulas necessary for the practical determination of quasimolecular parameters.

(i) The energy $|E_0|$ is equal to the binding energy of the ionized orbital in the united atom limit.

(ii) The effective charge Z_{eff} is equal to the charge of the ionized orbital in the united atom limit.

IV. DETERMINATION OF PARAMETERS OF QUASIMOLECULES

Using relation (2) the function $\alpha(E)$ can be determined as follows [5–7]:

$$\alpha(E) = \left(\frac{1}{v_2} - \frac{1}{v_1}\right)^{-1} \ln \frac{\sigma'(v_1, E)}{\sigma'(v_2, E)}, \tag{11}$$

where $\sigma' = d\sigma/dE$ and $v_1 > v_2$. To determine $\alpha(E)$, it is necessary to take a ratio of differential cross sections measured at the same electron energy but at different projectile velocities. By increasing the number of pairs v_1, v_2, one can determine $\alpha(E)$ to high accuracy; however, it is necessary to notice the spread of the values $\alpha(E)$ for different pairs v_1, v_2. If this spread is of a systematic nature (e.g., values at higher velocities always exceed those at lower energies), then it may indicate that more than one orbital contributes to direct ionization in the given electron energy range. Such behavior of $\alpha(E)$ was observed in the case of H^+-He [7]. Using the theorem of the mean, Eq. (4) can be written in the form

$$\alpha(E) = \alpha_0(E)(E - E_0), \tag{12}$$

where $\alpha_0(E)$ is a smooth function of electron energy and $\alpha_0(0) = 2\,\mathrm{Im}R(0)$. The use of Eqs. (11) and (12) makes it possible to determine the parameters $E_0, \alpha_0, \mathrm{Im}R(0)$.

All the expressions given above describe direct ionization in the center-of-mass coordinate system. To use them, it is important to transform our doubly differential cross sections measured in the laboratory coordinate system into singly differential cross sections in the center-of-mass system, so it is necessary to know the angular distribution of ejected electrons.

A reasonable approximation for the angular distribution in the molecular coordinate system employs the square of the spherical angular wave function Y_{lm} for the corresponding united atom state [17]. More consistent use of the united atom approximation, in our opinion, requires taking into account not only angular components of wave functions but also the angular component of the perturbation $\Delta H = \Sigma_i [Z_i/r - (Z_i|\mathbf{r} - \mathbf{R}_i|)]$, which at $r > R_i$ is expanded in terms of even-order Legendre polynomials $P_L(\cos\theta_{\mathrm{mol}})$ beginning with $L = 2$ [21]. (r is the electron coordinate.) In this case the angular part of transition probability can be written as

$$f(\theta_{\mathrm{mol}}) = (-1)^{l_0} B_{lL}^2 \sum_{\lambda} (2\lambda+1) \begin{pmatrix} \lambda & L & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & l & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \lambda & l & l \\ l_0 & L & L \end{Bmatrix} P_\lambda(\cos\theta_{\mathrm{mol}}), \tag{13}$$

where

$$B_{lL} = (2L+1)(2l+1) \begin{pmatrix} l & L & l_0 \\ 0 & 0 & 0 \end{pmatrix},$$

l_0 and l are the angular momenta of initial and final state, respectively, θ_{mol} is the electron ejection angle with respect to the internuclear axis, and $\left(\begin{smallmatrix} a & b & c \\ 0 & 0 & 0 \end{smallmatrix}\right)$ and $\left\{\begin{smallmatrix} a & b & c \\ e & d & f \end{smallmatrix}\right\}$ are $3j$ and $6j$ symbols. In our case $(2p\sigma)$ we find

$$f(\theta_{\mathrm{mol}}) = 1 + P_2(\cos\theta_{\mathrm{mol}}). \tag{14}$$

Further, performing a transformation to the space-fixed center-of-mass coordinate system

$$\cos^2\theta_{\mathrm{mol}} = \cos^2\theta_{\mathrm{c.m.}} + (1 - 3\cos^2\theta_{\mathrm{c.m.}}) \frac{b^2}{2|R(E)|^2} \tag{15}$$

and a Galilean transformation gives

$$\cos^2\theta_{\mathrm{c.m.}} = \frac{(\cos^2\theta_{\mathrm{mol}} - \delta)^2}{1 - 2\delta\cos\theta_{\mathrm{mol}} + \delta^2}, \tag{16}$$

$$E_{\mathrm{c.m.}} = E_{\mathrm{lab}}(1 - 2\delta\cos\theta_{\mathrm{mol}} + \delta^2), \tag{17}$$

where $\delta = (v_{\mathrm{c.m.}}/v_{\mathrm{elab}}) \ll 1$, $v_{\mathrm{c.m.}} = M_{\mathrm{H}} v_{\mathrm{H}}/(M_{\mathrm{H}} + M_{\mathrm{He}})$, and $v_{\mathrm{elab}} = \sqrt{2E_{\mathrm{lab}}}$. Integrating the distribution over the impact parameter gives expressions relating doubly differential cross sections in the laboratory system with singly differential cross sections in the center-of-mass system:

$$\sigma''_{\mathrm{lab}} = (1 - 2\delta\cos\theta_{\mathrm{mol}} + \delta^2)^{-1/2} \sigma''_{\mathrm{c.m.}}, \tag{18}$$

$$\sigma''_{\mathrm{c.m.}} = \frac{1}{8\pi} \sigma'_{\mathrm{c.m.}} \left[1 + 3\cos^2\theta_{\mathrm{c.m.}} + 3(1 - 3\cos^2\theta_{\mathrm{c.m.}}) \frac{v}{\alpha(E_{\mathrm{c.m.}})} \right], \tag{19}$$

$$\sigma'_{\mathrm{c.m.}} = \frac{4\pi |R(E_{\mathrm{c.m.}})|^2 \mathrm{Im}R(E_{\mathrm{c.m.}})}{\alpha(E_{\mathrm{c.m.}})} \times \exp\left[-\frac{\alpha(E_{\mathrm{c.m.}})}{v} \right] \left\{ 1 - \exp\left[-\frac{\alpha(E_{\mathrm{c.m.}})}{v} \right] \right\}. \tag{20}$$

The ‘‘survival factor’’ in curly brackets on the right-hand side of Eq. (20) accounts for a loss of flux on the returning

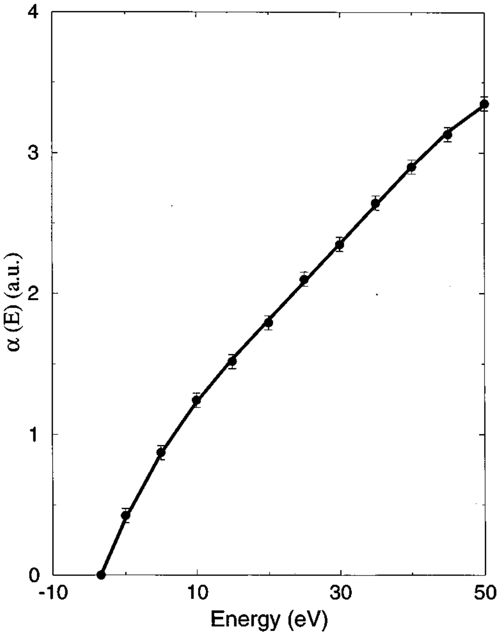

FIG. 2. Massey parameter as a function of ejected electron energy.

part of the trajectory; its contribution can be appreciable at low electron energies. It is worth mentioning some features of Eqs. (16)–(20) essential for our calculation. At high enough, but nearly equal, electron energies E_1 and E_2 , one can use the relation

$$\frac{\alpha(E_1)}{\alpha(E_2)}=\frac{E_1}{E_2},$$

so that

$$\frac{\alpha(E_1)}{v}=\frac{\alpha(E_2)}{v}+O(\delta).$$

Exponents corresponding to different electron energies in Eq. (20) differ by a constant factor, which cancels when using Eq. (11). Further, since our observation angle is very close to the "magic" angle $\theta_m=\arccos(1/\sqrt{3})$, $P_2(\theta_m=0)$ and the second term in the square brackets of Eq. (19) is proportional to the product of two small parameters δ and v/α; its contribution is compensated effectively by that of the survival factor in Eq. (20). As a result, the values $\alpha(E)$ determined from cross sections in the center-of-mass system and in the laboratory system practically coincide over the whole electron energy range under study. The data on $\alpha(E)$ are shown in Fig. 2.

In our previous communications [7,22], the values entered in Eq. (12) were determined from the logarithm of the ratio of differential cross sections measured at the same velocity and different, but nearly equal, electron energies. In this work a more accurate method of fitting Eq. (12) to the regression line obtained from statistical analysis of the data on $\alpha(E)$ has been used. For this reason, a large set of values determined using Eq. (11) has been collected and is characterized by the weighted mean dispersion $s^2=9\times10^{-4}$.

From regression and correlation analysis of α values on the "tail" of the measured energy distribution (see the Appendix), we find confidence limits of the regression line fit of which Eq. (12) yields $E_0=-(3.4\pm0.6)$ eV. This result can be used further for the determination of the parameters $Z_{\rm eff}=n\sqrt{2E_0}$, $\mathrm{Im}R(0)$, and $\mathrm{Re}R(0)=\mathrm{Im}R(0)^2/2Z_{\rm eff}$ (see Ref. [22]), where n is the principal quantum number of the united atom.

To find $\mathrm{Im}R(0)$, we pass to the low-energy part of the distribution, use the Taylor expansion of $\mathrm{Im}R(E)$ near $E=0$, and obtain

$$\alpha(E)\approx 2\ \mathrm{Im}R(0)(E-E_0)+g(E^2-E_0^2)+h(E^3-E_0^3),$$

$$g=\left|\frac{d}{dE}\mathrm{Im}R(E)\right|_{E=0},\quad h=\frac{1}{3}\left|\frac{d^2}{dE^2}\mathrm{Im}R(E)\right|_{E=0}. \tag{21}$$

Taking three values $\alpha(E_1)$, $\alpha(E_2)$, and $\alpha(E_3)$ in the low-energy part of the spectra and using Eq. (21), we obtain a system of three equations with three variables the solution of which yields [22]

$$\mathrm{Im}\,R(0)=\frac{1}{2}\frac{\begin{vmatrix}\alpha(E_1) & (E_1^2-E_0^2) & (E_1^3-E_0^3)\\ \alpha(E_2) & (E_2^2-E_0^2) & (E_2^3-E_0^3)\\ \alpha(E_3) & (E_3^2-E_0^2) & (E_3^3-E_0^3)\end{vmatrix}}{\begin{vmatrix}(E_1-E_0) & (E_1^2-E_0^2) & (E_1^3-E_0^3)\\ (E_2-E_0) & (E_2^2-E_0^2) & (E_2^3-E_0^3)\\ (E_3-E_0) & (E_3^2-E_0^2) & (E_3^3-E_0^3)\end{vmatrix}}. \tag{22}$$

Substituting the values and the limits of E_0 into Eq. (22), we find

$$\mathrm{Im}R(0)=1.7\pm0.2\ \text{a.u.},$$

$$\mathrm{Re}R(0)=1.5\pm0.2\ \text{a.u.},$$

$$Z_{\rm eff}=1.1\pm0.1.$$

Finally, we should determine the functions $\mathrm{Im}R(E)$ and $\mathrm{Re}R(E)$. The former can be determined very accurately from differentiation of the function $\alpha(E)$:

$$\mathrm{Im}R(E)=\frac{1}{2}\frac{d}{dE}\alpha(E). \tag{23}$$

The latter is determined with much larger errors since the absolute values of differential cross sections should be used for this purpose:

$$\mathrm{Re}R(E)=\sqrt{\frac{A(E)\alpha(E)}{4\pi\mathrm{Im}R(E)}-\mathrm{Im}^2R(E)}. \tag{24}$$

A comparison of the determined functions $\mathrm{Im}R(E)$ and $\mathrm{Re}R(E)$ with calculations is given in Figs. 3 and 4.

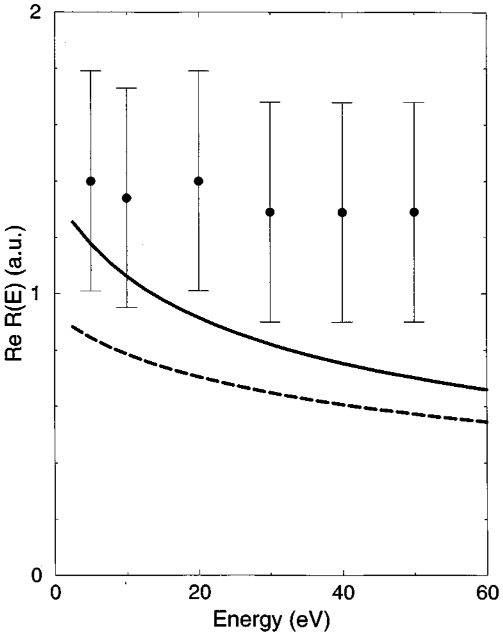

FIG. 3. Real part of the characteristic internuclear distance as a function of ejected electron energy. Circles with error bars are the values extracted from experimental data, the solid line is the calculation for $Z_1 = Z_2 = 0.55$, and the dashed line is the calculation for $Z_1 = 1$ and $Z_2 = 0.1$.

V. DISCUSSION

Figure 5 shows an approximate correlation diagram for the system H-He obtained by compilation of available calculation results (see [23] and references therein). The value E_0 determined in this work, as well as an approximate diabatic term in the complex plane, is shown in Fig. 5. The values determined $|E_0|$ and Z_{eff} agree well with the analogous data for the level $2p$ of the united atom Li (3.54 eV and 1.02, respectively).

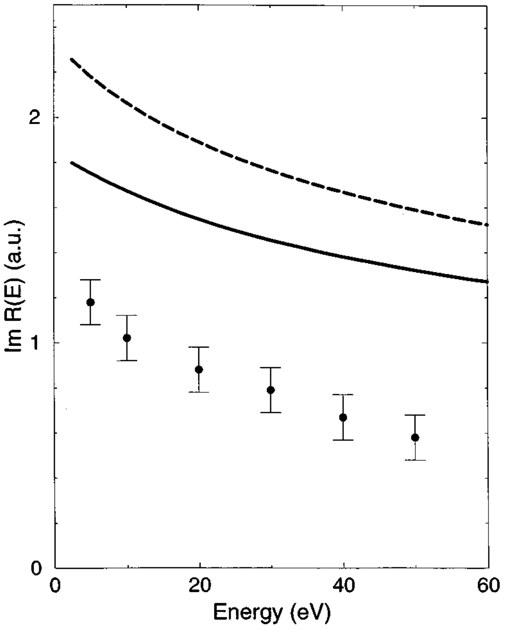

FIG. 4. Imaginary part of the characteristic internuclear distance as a function of ejected electron energy. Notations are the same as in Fig. 3.

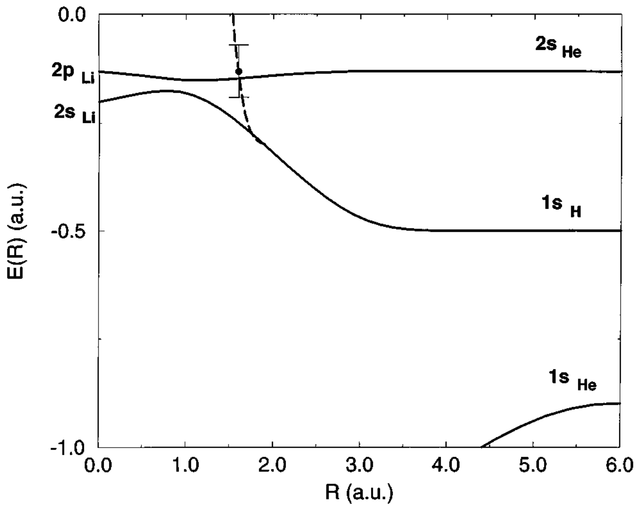

FIG. 5. Approximate correlation diagram for the system H-He. The circle with the error bar is the value of E_0 determined in this work. The dash-dotted curve shows the behavior of diabatic terms in the complex plane.

In the case of Re$R(E)$ and Im$R(E)$ (Figs. 3 and 4) the situation is more ambiguous. Experimental data and calculations agree satisfactorily at low electron energies $E \rightarrow 0$; however, this agreement becomes increasingly poorer with increasing electron energy. In this connection, it should be mentioned that the determination of experimental data on Re$R(E)$ and Im$R(E)$ is based on the relations (3) and (4) in which no particular type of interaction is incorporated. On the other hand, the corresponding theoretical values have been computed using the program of Ovchinnikov and Solov'ev [4] developed for the system Z_1eZ_2 and some assumptions about the charges Z_1 and Z_2 have been necessary. Assuming the experimental value of the total charge $Z_{\mathrm{eff}} = 1.1$, two limiting cases of charge distribution have been considered: $Z_1 = Z_2 = 0.55$ (symmetrical case) and $Z_1 = 1.0$, $Z_2 = 0.1$ (strongly asymmetrical case). As seen from Figs. 3 and 4, in the latter case (which seems to be more realistic), the agreement between experimental data and calculations is even poorer than in the former one. One can also see that with increasing electron energy, the calculated values Im$R(E)$ systematically exceed the experimental ones, whereas just the opposite situation occurs for the values Re$R(E)$.

The observed disagreement clearly shows that the approximation $Z_{\mathrm{eff}}(R) = Z_{\mathrm{eff}}(0) = \mathrm{const}$ can be used only at low electron energies. At high enough electron energies, the non-Coulombic nature of the system under study should be taken into account in the theoretical calculations. As follows from comparison of the data presented in Figs. 3 and 4, the diabatic $p\sigma$ term responsible for direct ionization in the H-He system is promoted to the continuum more sharply than in the Z_1eZ_2 system and crosses the boundary of the continuum at larger values of Re$R(E)$ than in Z_1eZ_2. Accordingly, by increasing the derivative dE/dR, the values of Im$R(E)$ decrease as follows from Eq. (10).

Apart from this screening effect, one more correlation effect should be taken into consideration, that is, the dynamical correlation between the major transition $2p\sigma$-$\varepsilon p\sigma$ and the transition $1s\sigma$-$\varepsilon s\sigma$, which involves the "passive" core electrons and is characterized by a higher effective charge. As follows from calculations for the system H^+-He [8], the contribution of the $1s\sigma$-$\varepsilon s\sigma$ transition is negligible at low electron energies, but increases considerably with increasing electron energy. Thus the role of the dynamical correlation is expected to be essential at higher electron energies and would lead to an additional decrease in Im$R(E)$. More detailed discussion of the dynamical parameters Re$R(E)$ and Im$R(E)$ and very difficult and elaborate theoretical calculations are needed.

Fortunately, the situation with parameters characterizing the ionized level of the united atom is not so involved. Good agreement of the data obtained in this work with spectroscopic data for the united atom reveals the possibility to use the method, based on analysis of energy spectra of electrons ejected, in direct ionization for quantitative spectroscopy of quasimolecules with many electrons. This method has evident advantages over methods [24,25] based upon analysis of electrons ejected in Auger ionization. First, it allows studying any level of a quasimolecule, even those to which Auger ionization is not allowed. Second, the accuracy of the method is defined mainly due to an uncertainty in the measurement statistics and is not affected by an uncertainty in the energy of final states in contrast to the measurements of Refs. [24,25].

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APPENDIX

We have made a regression analysis using six values on the "tail" of the measured energy distribution (E = 25–50 eV, energy separation $\Delta E = 5$ eV). When entering the designations $x_i = (E-25)/5-1$ (E in eV) and $y = \alpha(x_i)$, we construct the regression line using an expansion in terms of Chebyshev polynomials $P_j(x)$ [26]:

$$y(x) = \sum_j \beta_j P_j(x), \tag{A1}$$

$$\beta_j = \frac{\Sigma_i y_i P_j(x_i)}{\Sigma_i P_j^2(x_i)}, \tag{A2}$$

$$P_0(x) = 1, \quad P_1(x) = x-(k+1)/2,$$

$$P_2 = x^2-(k+1)x+(k+1)(k+2)/6; \tag{A3}$$

$$\sum_i P_0^2(x_i) = k, \quad \sum_i P_1^2(x_i) = k(k^2-1)/12,$$

$$\sum_i P_2^2(x_i) = k(k^2-1)(k^2-4)/180. \tag{A4}$$

k is the number of x values ($k=6$ in our case). Substituting experimental values $\alpha(E)$ (Fig. 2) into Eqs. (A1) and (A2), we find the equation for the regression line in the range E = 25–50 eV:

$$y = \alpha(E) = 0.280 + 2.23E - 0.296E^2 \quad (E \text{ in a.u.}). \tag{A5}$$

Calculation of zeroth-, first-, and second-order dispersions

$$S_0 = \sum_i y_i^2 - \frac{(\Sigma_i y_i)^2}{k} = 1.187, \tag{A6}$$

$$S_1 = S_0 - \beta_1^2 \sum_i P_1^2(x_i) = 0.0037, \tag{A7}$$

$$S_2 = S_1 - \beta_2^2 \sum_i P_2^2(x_i) = 0 \tag{A8}$$

shows that the ratio $D_1/D_2 = 3S_1/4S_2 \geqslant 9.1$ (the Fischer criterion is satisfied) and the dispersion $D_1 = 9.1\times 10^{-4}$ is just the same as the weighted mean dispersion s^2. This means that to a high degree of accuracy (the confidence probability 0.95), we can restrict ourselves to the quadratic term in Eq. (A5) when fitting Eq. (A5) to Eq. (12) and neglecting the second derivative $\alpha''(E)$. [Since we have no terms of the order E^3 on the right-hand side of Eq. (A5) we find $E_0 = -3.4$ eV.] To establish the confidence interval of E_0, we have made a correlation analysis using a linear regression approximation. In this case the allowed values of the angular coefficient β_1 can be determined using the Bartlett formula

$$\Delta\beta = \pm \frac{S_y}{S_x}\sqrt{\frac{1-r}{k-2}}\, t_{1-p/2}, \tag{A9}$$

where

$$S_y = \sqrt{\frac{k\Sigma_i y_i^2 - (\Sigma_i y_i)^2}{k(k-1)}}, \tag{A10}$$

$$S_x = \sqrt{\frac{k\Sigma_i x_i^2 - (\Sigma_i x_i)^2}{k(k-1)}}, \tag{A11}$$

$r = \beta_1 S_x/S_y$ is the correlation coefficient and $t_{1-p/2}$ is Student's quantile for a given confidence probability p. Taking the value $\bar{x}$ at the center of energy interval and substituting the values $y(\bar{x})+s$, $\beta_1 - \Delta\beta_1$ and $y(\bar{x})-s$, $\beta_1 + \Delta\beta_1$ into Eq. (A5), we find the lower and upper limits of E_0, respectively: $E_0 = -(3.4 \pm 0.6)$ eV.

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