Photoionization with excitation and double photoionization of the helium isoelectronic sequence

Anatoli S. Kheifets*
Institute of Advanced Studies, Research School of Physical Sciences, The Australian National University, Canberra Australian Capital Territory 0200, Australia

Igor Bray†
Electronic Structure of Materials Centre, The Flinders University of South Australia, G.P.O. Box 2100, Adelaide 5001, Australia
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We perform a systematic study of photoionization with excitation and double photoionization of H^-, He, and Li^+ using the convergent close-coupling formalism. The present calculations cover the photon energy range from the double-ionization threshold to 10 keV where the results go over continuously to the nonrelativistic limit of infinite photon energy. By consideration of scaling properties, tested by application to O^{6+}, accurate nonrelativistic results for photoionization with excitation to arbitrarily high n and double photoionization may be obtained for all heliumlike targets. [S1050-2947(98)01112-3]

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I. INTRODUCTION

Atomic photoionization with excitation and double photoionization are important many-electron processes that have attracted considerable attention from theoretical and experimental atomic collision physics. Much of this attention has been focused on the helium atom, which is the simplest two-electron target suitable for studying the Coulomb three-body breakup. This fundamental process can be quantified in terms of the ratio of the double to single photoionization cross sections $R=\sigma^{2+}/\sigma^{+}$ as a function of the photon energy ω. Recently, considerable progress has been made in determining this ratio, both experimentally [1–5], and theoretically [6–12].

Double photoionization of the other members of the helium isoelectronic sequence, H^-, Li^+, and the heavier ions, has been studied much less extensively. The negative ion of hydrogen H^- is a very important atomic system, both in terms of the strong two-electron correlation in a loosely bound ground state, and its practical significance for astrophysics [13]. However, due to experimental difficulties, only one measurement of double photoionization of H^- has been reported in the very narrow photon energy range close to the threshold [14]. On the theoretical side, a few calculations exist for H^- double photoionization [8,10,15,16]. These results differ among themselves much more considerably than for helium. Only the two most recent calculations [8,10] employ a state-of-the-art theory and can be considered reliable. The R-matrix theory of Meyer, Greene, and Esry [8] is likely to yield reliable results a little above threshold. The nonstationary perturbation theory of Nicolaides *et al.* [10] is expected to be accurate particularly close to the threshold.

The double-photoionization results on other two-electron ions are even more scarce. Wehlitz *et al.* [17] have recently measured the triple photoionization of lithium and compared their triple-to-single cross-section ratio with the calculated double-to-single ratio for double photoionization of Li^+ by Kornberg and Miraglia [16]. Qualitative agreement was found away from threshold. This has led Wehlitz *et al.* to conclude that the primary mechanism of triple photoionization is the double photoionization of the two core electrons followed by the shakeoff of the remaining valence electron into the continuum. Although the calculation of Kornberg and Miraglia [16] is well suited for such a qualitative comparison it yields a large difference between the double-to-single photoionization cross-section ratios calculated in the length and velocity forms of the electromagnetic operator.

There are also calculations of double photoionization of heliumlike ions Li^+, Be^{2+}, C^{4+}, and O^{6+} [18], using the R-matrix theory similar to the work on He and H^- [8]. Convergence of the three gauges of the electromagnetic interaction, length, velocity, and acceleration, is good in this calculation. Unfortunately, the double-to-single cross-section ratio displays some unphysical oscillations. This problem becomes more severe with increase of the nucleus charge.

Because of the fundamental importance of the double photoionization problem it is desirable to develop a general theory equally applicable to two-electron targets across a widest possible range of photon energies. In our previous work we have demonstrated that the convergent close-coupling (CCC) formalism coupled with an accurate description of the ground-state correlation is capable of producing a very accurate description of the helium double photoionization [12], including angular distributions [19]. In this work we extend this formalism to other members of the helium isoelectronic sequence. We demonstrate the accuracy of the CCC method near the double-photoionization threshold (Wannier regime), at intermediate photon energies and in the asymptotic region of very large (but still nonrelativistic) photon energies. We employ a 20-term Hylleraas expansion of Hart and Herzberg [20] to describe the ground-state correlation of the helium atom and the two-electron ions of hydrogen and lithium. This conceptually identical description of various two-electron targets allows us to study a systematic trend in double photoionization with an increase of the nuclear charge as the system becomes more bound by the Coulomb center and less governed by the two-electron correlation.

*Electronic address: ask107@rsphysse.anu.edu.au
†Electronic address: I.Bray@flinders.edu.au

TABLE I. Ground-state properties of various two-electron systems. The ratio are evaluated at infinite energies using the velocity gauge within the nonrelativistic framework. Note the unusually high σ_2/σ_1 ratio for H^-.

Target	Ground state	Energy		Partial cross-section ratio σ_n/σ_1(%)					
		Total (a.u.)	Correlation (%)	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	σ^{2+}/σ^{+}(%)
H^-	11-term [a]	0.527 559		68.895	0.2345	0.1564	0.0873	0.0519	1.5059
	20-term [b]	0.527 644		65.731	0.5193	0.1884	0.0915	0.0515	1.5082
	Near exact [c]	0.527 751							1.602
He	14-term [d]	2.903 700	99.94	4.7817	0.6054	0.1995	0.0918	0.0502	1.6924
	20-term [b]	2.903 717	99.98	4.7859	0.5956	0.1972	0.0909	0.0498	1.6713
	Near exact [c]	2.903 724	100						1.644
Li^+	10-term [d]	7.279 762	99.64	1.6648	0.2470	0.0857	0.0403	0.0223	0.9285
	20-term [b]	7.279 905	99.98	1.6102	0.2424	0.0837	0.0392	0.0217	0.8677
	Near exact [c]	7.279 913	100						0.856

[a]Henrich [23].
[b]Hart and Herzberg [20].
[c]Frankowski and Pekeris [25].
[d]Chandrasekhar and Herzberg [24].

The paper is organized as follows. In Sec. II we outline the CCC formalism and its implementation with a Hylleraas-type ground state. Section III presents calculations of the cross sections of double photoionization and ionization with simultaneous excitation of H^- (III A), He (III B), and Li^+ (III C), respectively. In Sec. III D we examine the Z^4 and n^3 scaling laws. Conclusions and future directions are formulated in Sec. IV.

II. THEORY

We follow our usual computational scheme outlined in Ref. [12]. We treat double photoionization or photoionization with excitation as a two-step process. The first is the full absorption of the photon energy by one electron. The second is the interaction of this electron with the nucleus and the remaining electron which results in the promotion of the remaining electron into an excited state (ionization with excitation) or into the continuum (double photoionization).

A. Two-electron ground state

To describe the first step of single photoionization of a two-electron system bound by a Coulomb center we employ a 20-term Hylleraas ground-state wave function due to Hart and Herzberg [20]

$$\begin{aligned}\Psi^{(20)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_{12}) = Ne^{-zs}[&1+a_1u+a_2t^2+a_3s+a_4s^2\\&+a_5u^2+a_6su+a_7t^2u+a_8u^3+a_9t^2u^2\\&+a_{10}st^2+a_{11}s^3+a_{12}t^2u^4+a_{13}u^4\\&+a_{14}u^5+a_{15}t^2u^3+a_{16}s^2t^2+a_{17}s^4\\&+a_{18}st^2u+a_{19}t^4],\end{aligned} \tag{1}$$

where $s=r_1+r_2$, $t=r_1-r_2$, and $u=r_{12}=|\boldsymbol{r}_1-\boldsymbol{r}_2|$. Properties of the ground state of various two-electron systems calculated with the wave function (1) are given in Table I. Presented are the ground-state energy, the asymptotic ratios for photoionization with excitation $R_n=\sigma_n/\sigma_1$, and double photoionization $R=\sigma^{2+}/\sigma^{+}$ in the limit $\omega\to\infty$ calculated according to the nonrelativistic expressions of Dalgarno and Stewart [21]

$$\sigma_n \propto \langle \phi_n|\psi\rangle, \quad \sigma_t \propto \langle \psi|\psi\rangle, \quad \sigma^{2+}=\sigma_t-\sum_{n=1}^{\infty}\sigma_n, \tag{2}$$

where $\psi(\boldsymbol{r}_1)=\Psi^{(20)}(\boldsymbol{r}_1,\boldsymbol{r}_2=0,\boldsymbol{r}_{12}=\boldsymbol{r}_1)$ and $\phi_n(\boldsymbol{r}_1)$ is the $l=0$ eigenstate with principal quantum number n. These ratios were calculated previously for the ground-state wave function (1) by Dalgarno and Sadeghpour [22] who obtained very similar results to those presented in the table.

To investigate the stability of our calculations with respect to the choice of the ground state we also used a somewhat inferior Hylleraas-type ground-state wave function due to Henrich [23] and Chandrasekhar and Herzog [24] truncated at 11 and 14 terms, respectively. The ratio $(E-E_{\rm HF})/(E_{\rm asym}-E_{\rm HF})\times 100\%$ is also given as a measure of the correlation energy recovered by the given Hylleraas expansion. Here $E_{\rm HF}$ is the nonrelativistic Hartree-Fock energy and $E_{\rm asym}$ is the ''asymptotically exact'' nonrelativistic energy due to Frankowsky and Pekeris [25]. As the negative hydrogen ion is not bound in the Hartree-Fock approximation the fraction of correlation energy is not given for H^-.

The terms involving powers of u require some effort to evaluate. We expand such terms over the Legendre polynomials [26]

$$u^n=\sum_L u_L^n P_L(\theta_{12}), \tag{3}$$

and separate the angular coordinates of the two electrons by making use of the Legendre polynomial expansion over the spherical harmonics

$$P_L(\theta_{12})=\frac{4\pi}{2L+1}\sum_{M=-L}^{L} Y_{LM}^*(\hat{\boldsymbol{n}}_1)Y_{LM}(\hat{\boldsymbol{n}}_2). \tag{4}$$

The radial coordinates can be separated by expanding the terms u_L^n in Eq. (1) over the Slater functions $F_L(r_1,r_2) = r_<^L/r_>^{L+1}$ where $r_<$ and $r_>$ are the lesser and the greater of r_1 and r_2, respectively. The following expansions have been used:

$$u_0^1=(r_1^2+r_2^2)F_0-\frac{2}{3}r_1r_2F_1, \tag{5}$$

$$u_L^1=r_1r_2\left[\frac{F_{L+1}}{2L+3}-\frac{F_{L-1}}{2L-1}\right],\quad L>0, \tag{6}$$

$$u_0^3=(r_1^2+r_2^2)^2F_0-\frac{4}{5}(r_1r_2)^2F_2, \tag{7}$$

$$u_1^3=-3r_1r_2(r_1^2+r_2^2)F_0+3(r_1r_2)^2\left\{\frac{3}{5}F_1+\frac{1}{35}F_3\right\}, \tag{8}$$

$$u_L^3=3(r_1r_2)^2\left[\frac{F_{L+2}}{(2L+3)(2L+5)}-\frac{2F_L}{(2L+3)(2L-1)}+\frac{F_{L-2}}{(2L-1)(2L-3)}\right],\quad L>1, \tag{9}$$

$$u_0^5=(r_1^2+r_2^2)(r_1^4+4r_1^2r_2^2+r_2^4)F_0-2(r_1r_2)^3\left\{F_1+\frac{3}{7}F_3\right\} \tag{10}$$

$$u_1^5=-5r_1r_2(r_1^2+r_2^2)^2F_0+\frac{3}{5}(r_1r_2)^2(r_1^2+r_2^2)\left\{3F_1+\frac{1}{7}F_3\right\}-\frac{4}{5}(r_1r_2)^3\left\{F_0-\frac{16}{7}F_2+\frac{1}{21}F_4\right\}, \tag{11}$$

$$u_2^5=(r_1r_2)^2(r_1^2+r_2^2)\left\{5F_0-\frac{2}{7}F_2+\frac{1}{21}F_4\right\}-\frac{2}{7}(r_1r_2)^3\left\{9F_1+\frac{1}{11}F_5\right\}, \tag{12}$$

$$u_L^5=15(r_1r_2)^3\left[\frac{-F_{L-3}}{(2L-5)(2L-3)(2L-1)}+\frac{3F_{L-1}}{(2L-3)(2L-1)(2L+3)}-\frac{3F_{L+1}}{(2L-1)(2L+3)(2L+5)}+\frac{F_{L+3}}{(2L+3)(2L+5)(2L+7)}\right],\quad L>2. \tag{13}$$

Expansion of u^2 and u^4 is relatively simple involving P_L with only $L\leqslant 2$.

B. CCC formalism

We use the multichannel expansion for the final-state wave function of the two-electron system:

$$\langle\Psi_j^{(-)}(\boldsymbol{k}_b)|=\langle\boldsymbol{k}_b^{(-)}j|+\sum_i\sum\!\!\!\!\!\!\int d^3k\frac{\langle\boldsymbol{k}_b^{(-)}j|T|i\boldsymbol{k}^{(+)}\rangle\langle\boldsymbol{k}^{(+)}i|}{E-\varepsilon_{\boldsymbol{k}}-\epsilon_i+i0}, \tag{14}$$

with boundary conditions corresponding to an outgoing wave in a given channel $\langle\boldsymbol{k}_b^{(-)}j\rangle$ and incoming waves in all other channels $|i\boldsymbol{k}^{(+)}\rangle$. Here $E=k_b^2/2+\epsilon_j$ is the final state energy. The channel wave function $\langle\boldsymbol{k}_b^{(-)}j|$ is the product of a one-electron orbital $\overline{\phi_j}$ with energy ϵ_j, obtained by diagonalizing the target Hamiltonian in a Laguerre basis, and a (distorted) Coulomb outgoing wave $\chi^{(-)}(\boldsymbol{k}_b)$ with energy $\varepsilon_{\boldsymbol{k}}$. The asymptotic charge seen by the Coulomb wave is $Z-1$ where Z is the charge of the nucleus. The half off-shell T matrix in Eq. (14) is the solution of the corresponding Lippmann-Schwinger integral equation [27]

$$\langle\boldsymbol{k}^{(+)}i|T|j\boldsymbol{k}_b^{(-)}\rangle=\langle\boldsymbol{k}^{(+)}i|V|j\boldsymbol{k}_b^{(-)}\rangle+\sum_{i'}\sum\!\!\!\!\!\!\int d^3k'\times\frac{\langle\boldsymbol{k}^{(+)}i|V|i'\boldsymbol{k}'^{(-)}\rangle\langle\boldsymbol{k}'^{(-)}i'|T|j\boldsymbol{k}_b^{(-)}\rangle}{E-\varepsilon_{\boldsymbol{k}'}-\epsilon_{i'}+i0}. \tag{15}$$

The photoionization cross section, as a function of the photon energy ω, corresponding to a particular bound electron state j is given by [28]

$$\sigma_j(\omega)=\frac{4\pi^2}{\omega c}\sum_{m_j}\int d^3k_b|\langle\Psi_j^{(-)}(\boldsymbol{k}_b)|\mathcal{D}|\Psi_0\rangle|^2\delta(\omega-E+E_0), \tag{16}$$

where $c\simeq 137$ is the speed of light in atomic units.

The dipole electromagnetic operator $\mathcal{D}$ can be written in one of the following forms commonly known as length, velocity, and acceleration [28]

$$\mathcal{D}^r=\omega(z_1+z_2),\qquad \mathcal{D}^\nabla=\nabla_{z_1}+\nabla_{z_2},\qquad \mathcal{D}^{\dot\nabla}=\frac{Z}{\omega}\left(\frac{z_1}{r_1^3}+\frac{z_2}{r_2^3}\right), \tag{17}$$

with the z axis chosen along the polarization vector of the photon.

The dipole matrix element with the CCC final-state wave function of Eq. (14) can be calculated as

$$\langle\Psi_j^{(-)}(\boldsymbol{k}_b)|\mathcal{D}|\Psi_0\rangle=\langle\boldsymbol{k}_b^{(-)}j|\mathcal{D}|\Psi_0\rangle+\sum_i\sum\!\!\!\!\!\!\int d^3k\frac{\langle\boldsymbol{k}_b^{(-)}j|T|i\boldsymbol{k}^{(+)}\rangle\langle\boldsymbol{k}^{(+)}i|\mathcal{D}|\Psi_0\rangle}{E-\varepsilon_{\boldsymbol{k}}-\epsilon_i+i0}. \tag{18}$$

After some angular momentum algebra the first-order dipole matrix element $\langle\boldsymbol{k}^{(+)}i\,|\mathcal{D}|\,\Psi_0\rangle$ breaks down into one-electron radial integrals and simple angular coefficients.

We separate the contribution from the final channels $\langle\boldsymbol{k}_b^{(-)}j|$ into single and double ionization according to the

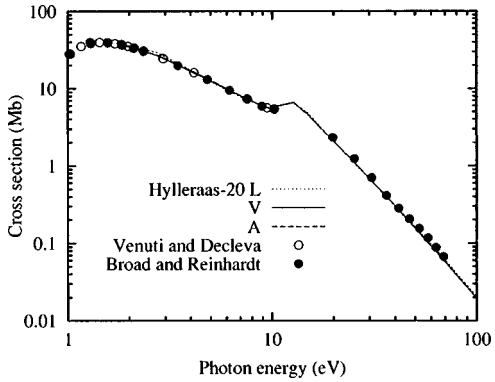

FIG. 1. H^- photodetachment cross section. The various gauges of the electromagnetic interaction (L, length; V, velocity; and A, acceleration) produce essentially identical results. The filled and empty circles are the reported values of Broad and Reinhardt [15] and Venuti and Decleva [32], respectively.

energy of the ϵ_j, which is positive for the double ionized channels and negative for the singly ionized channels. We also ensure that for the negative-energy state cross sections, contributions to the ionization plus excitation cross sections are multiplied by the projection of the state onto the true target discrete subspace as is done for electron-impact ionization [29].

In the present calculations the target space was generally described by $17-l, l=0,1,2$ pseudostates making a total of 48 s, p, and d pseudostates. At the higher energies, above 1 keV, up to $20-l$ were used to get a better discretization of the target continuum. The projectile continuum was treated using around 70 k-grid points with orbital momentum $l=0,\ldots,4$ There were also up to 9 projectile bound states included for every l. The calculations have been performed at approximately 50 energy points suitably distributed over the presented photon energy range. Note that no averaging of the CCC results is undertaken, we simply rely on taking sufficiently large bases sizes to ensure that pseudoresonances are of sufficiently small magnitude [30]. In addition, the Laguerre basis exponential falloff parameters are varied at each energy to ensure that the total (excess) energy E was exactly between two of the pseudothresholds, thereby ensuring that the integration rule associated with the discretization of the continuum always had E as an end point [31].

III. RESULTS

A. H^- ion

As the first test of our model we calculate the absolute cross section for photodetachment of H^- (equivalent to single photoionization for a neutral atom). Because of the strong correlation in the ground state of H^- even the single-photoionization cross section is sensitive to the choice of the ground-state wave function. We present the CCC calculated cross sections in the three gauges for the 20-parameter Hylleraas ground state in Fig. 1. Also presented are the results of Broad and Reinhardt [15] who used a multichannel J-matrix expansion in their calculation, and those of Venuti and Decleva [32] who employed a convergent multichannel expansion on a B-spline basis. Good agreement is found among

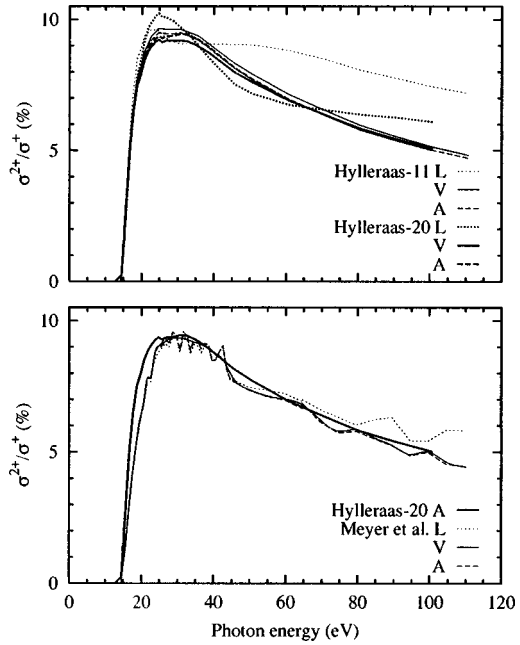

FIG. 2. The ratio of double-to-single photoionization cross sections in H^-. Calculations in the three gauges of the electromagnetic interaction are presented with the 11- and 20-parameter Hylleraas ground-state wave functions. Comparison is made with the coordinate space R-matrix calculation of Meyer *et al.* [8,18].

all calculations. The small maximum around 14-eV photon energy corresponds to the opening up of photoionization with excitation channels.

Having tested our model for photodetachment we proceed to photoionization with excitation and double photoionization. In Fig. 2 the double-to-single photoionization ratio for H^- are presented. To investigate the sensitivity of the double photoionization cross section with the choice of the ground-state wave function we present calculations performed with the 11- and 20-term Hylleraas expansions (obtained from Refs. [23] and [20], respectively). For comparison we also present the R-matrix calculations of Meyer *et al.* [8,18] in the three gauges of the electromagnetic interaction.

Comparison of the 11- and 20-term ground states shows good convergence in the V and A gauges, but there is still significant variation in the L gauge. The 20-term L gauge result is substantially closer to the other gauges than the corresponding 11-term result, as would be expected. Clearly even larger expansions are necessary to obtain convergence in the L gauge for this system at intermediate and high energies. The problem is due to a very strong two-electron correlation in the loosely bound H^- ion. This correlation cannot be properly accounted for at large distances by the 20-parameter Hylleraas ground state. These large distances are enhanced by the electromagnetic operator in the length form. The velocity and acceleration forms are more sensitive to small and intermediate distances that contribute significantly to the total energy of the two-electron system and where the ground-state wave function should be most accurate. Given the good agreement of the other two gauges, together with our previous experience [12], the V- and A-gauge results are likely to be quite accurate.

The CCC V and A results are very close to those of Meyer *et al.* [8,18], which show a little unphysical oscillation. In

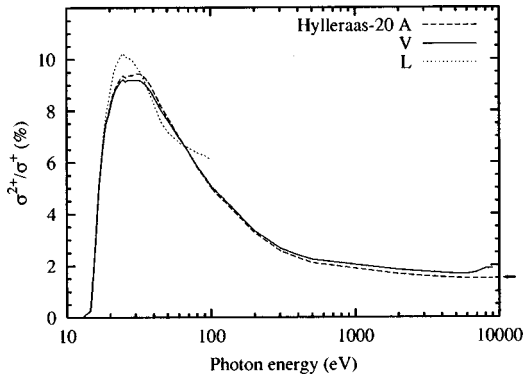

FIG. 3. The double-to-single photoionization cross-section ratio in H^-. The arrow indicates the nonrelativistic limit of infinite energy given in the table.

addition the CCC cross sections are systematically higher in the near-threshold region. This is likely to be due to the restriction on the size of the *R*-matrix box yielding a limitation on the accuracy of the *R*-matrix method near threshold, as was the case for electron-impact ionization [33]. The generally good agreement between the two theories is not only for the presented ratio, but also for absolute values of single and double photoionization.

The range of large photon energies is of special interest since an asymptotic expression of the double-to-single photoionization cross section can be obtained solely from the ground-state wave function [21]. In Fig. 3 we show our double-to-single photoionization ratio on an extended energy scale to 10 keV. We see from the figure that the ratio calculated in the velocity and acceleration forms of the electromagnetic operator becomes constant around 5 keV in agreement with the limit of infinite photon energy $\sigma^{2+}/\sigma^{+}|_{\omega\to\infty} = 1.51\%$ (see table).

In Fig. 4 we compare the CCC absolute values of the double-photoionization cross sections of H^- with the values of Broad and Reinhardt [15] and Kornberg and Miraglia [16]. Both older calculations are found substantially below the present results. Note the good agreement between the three gauges of the CCC results. Looking at this figure and Fig. 1 one would not expect to see the *L*-gauge ratio of Fig. 2 to be substantially different from the other gauges. Clearly the ratio of double to single photoionization is a more sensitive test of the theoretical accuracy.

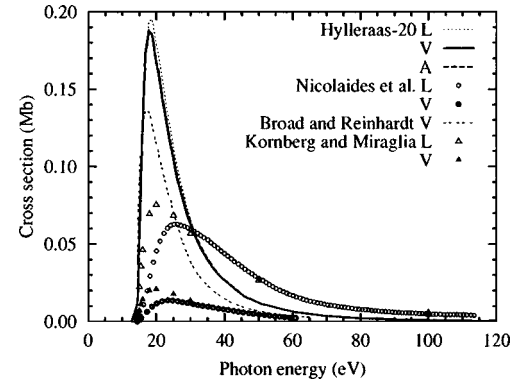

FIG. 4. Absolute double-photoionization cross section of H^-. The present CCC 20-parameter Hylleraas ground-state calculations are presented in the three gauges of the electromagnetic interaction. The literature values are due to Broad and Reinhardt [15] and Kornberg and Miraglia [16].

At low energies the prediction of the Wannier theory may be used. Wannier [34] predicts the near-threshold energy dependence to be

$$\sigma^{2+}(E,Z)\approx\sigma_0(Z)E^m, \tag{19}$$

where E is the excess energy above the threshold and

$$m=\frac{1}{4}\sqrt{\frac{100Z-9}{4Z-1}}-\frac{1}{4}. \tag{20}$$

The exponent m approaches unity with increasing Z and takes the values of 1.127, 1.056, and 1.036 for H^-, He, and Li^+, respectively.

Double photoionization of H^- near threshold was measured by Donahue *et al.* [14]. Their results seemed to be compatible with the Wannier power law $\sigma(E)=\sigma_0E^{1.127}$. The experimental cross section was not normalized. So the normalization-exponential factor σ_0 remained undetermined. McCann and Crothers [35], using a semiclassically derived final-state wave function, obtained in the velocity form $\sigma_0 = 31.4$ kb. Recently Nicolaides *et al.* [10] tried to fit their calculated cross section in the near-threshold region with the Wannier power law and found the exponents to be 1.20 or 1.37 depending on the energy range of the fit.

At high energies the single-photoionization cross section is known to fall off as $\omega^{-7/2}$ [28]. The fact that the double-to-single photoionization ratio is a nonzero constant at infinite energy implies that the double photoionization cross section also falls off as $\omega^{-7/2}\approx E^{-7/2}$. This provides for a good test of the calculations at high energies.

In Fig. 5 we present calculated double photoionization cross sections of H^- in the near-threshold and high-energy regions. The best fit with the Wannier exponent $m=1.127$ gives us the normalization factor $\sigma_0=95$ kb (for dimensionless E in eV), which is nearly three times larger than that of McCann and Crothers [35]. A similar difference in magnitude of the double-photoionization cross section was also found when compared with other early calculations as indicated in Fig. 4. At high energies we see a good match by the relation $\sigma^{2+}(E)\approx\sigma_\infty E^{-7/2}$, where $\sigma_\infty=6.5\times10^3$ Mb (for dimensionless E in eV).

As a by-product of our double-photoionization calculation we also obtain the cross sections for the photodetachment of H^- with simultaneous promotion of the remaining electron to one of the excited states of H. These cross-section ratios are presented in Fig. 6. The calculations in all three gauges of the electromagnetic interaction agree well with each other at the lower energies, with the $n=3$ ratio showing greatest sensitivity to the L gauge. At the intermediate and higher energies the L form becomes inaccurate, but the other two are quite close to each other and, we expect, the true result. It is remarkable that the ratio for $n=2$, in contrast to the other n, is close to unity and is nearly constant across a wide energy range. The A and V ratios stabilize around the 1-keV region and converge to the limit of infinite energy, given in the table.

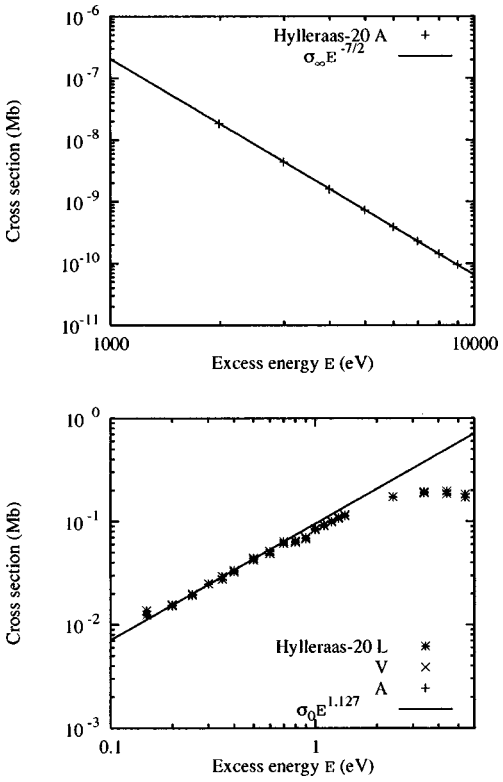

FIG. 5. Absolute double-photoionization cross section of H^- near threshold and at high energies. The solid line is the indicated fit with $\sigma_0 = 0.095$ Mb and $\sigma_\infty = 6.5 \times 10^3$ Mb for dimensionless E in eV.

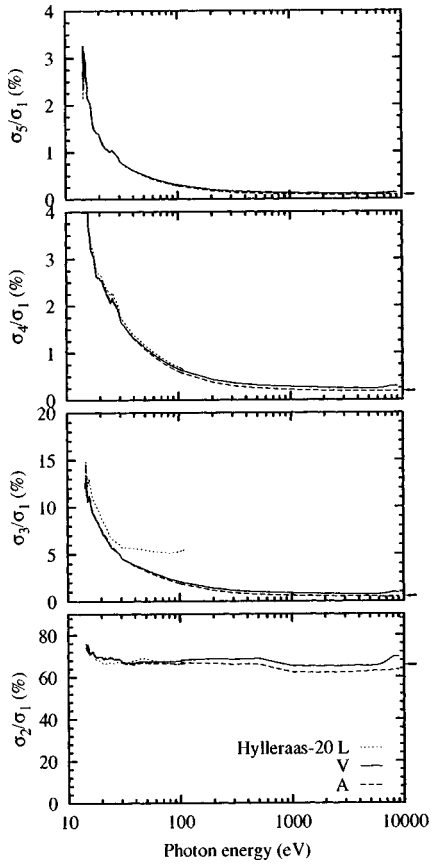

FIG. 6. The cross-section ratios σ_n/σ_1 for the photodetachment of H^- ion with simultaneous excitation. Theory as for Fig. 3.

B. Helium atom

The double-to-single photoionization ratio in helium has been studied very thoroughly both experimentally [1,2,4,5], and theoretically [7–10,12]. Only in the last few years have experiment and theory showed some stability in the results, which are now in good agreement with each other; see Fig. 7. In our previous work [12] we calculated the double-to-single photoionization ratio in helium using a 14-term Hylleraas expansion [24]. As we presently increase the number of terms to 20 the convergence between the calculations in the three gauges (L, V, and A) improves further with variation of no more than 2% below 1 keV. Our calculations are very close to the barely distinguishable A- and V-form calculations of Meyer *et al.* [8], except for the region close to the double-photoionization threshold. Agreement with the R-matrix theory is not only for the presented ratio, but for the absolute values of each cross section. The single-photoionization cross section, convergent to better than 1% in the three gauges, is in very good agreement with the measurements of Samson *et al.* [36].

In Fig. 8 we also plot the double-to-single helium photoionization ratio, but over a much extended energy scale to 10 keV. We see that the ratio stabilizes around 10 keV, where the limit of infinite photon energy $\sigma^{2+}/\sigma^{+}\big|_{\omega\to\infty} = 1.67\%$ is obtained.

Presented in Fig. 9 are the absolute double-photoionization cross sections near the threshold and the high energy regions. The Wannier power law $\sigma(E) = \sigma_0 E^m$ was confirmed experimentally by Kossman, Schmidt, and Andersen [37] with $m = 1.05 \pm 0.02$ and $\sigma_0 = 1.02$ kb. Pont and Shakeshaft [38] also confirmed the Wannier power law with a theoretical value $\sigma_0 = 0.97$ kb, which they obtained by extrapolating the velocity form calculation to the threshold. Nicolaides *et al.* [10] give the exponential $m = 1.032$ and $m = 1.060$ depending on the energy range used to fit their calculated data with the Wannier law. Our best fit with $m = 1.056$ gives $\sigma_0 = 1.1$ kb, which is in good agreement with the earlier predictions.

At high energies the $\sigma^{2+}(E) \approx \sigma_\infty E^{-7/2}$ power law is well satisfied with $\sigma_\infty = 2.8 \times 10^5$ Mb (for dimensionless E in eV). Beyond 3 keV this agrees well with the calculations of Forrey *et al.* [9] who used a highly correlated 112-term Hylleraas ground state and obtained good agreement between the three gauges. The discrepancy below 3 keV is due to neglect, in their calculations, of coupling in the final channel. Though not presented, the agreement between the present calculations and those of Hino *et al.* [39] using the many-body perturbation theory is excellent over the given energy range.

The cross-section ratios σ_n/σ_1 for single photoionization of He with excitation to $n = 2, \ldots, 6$ states are presented in Fig. 10. Compared to our previous calculation with a 14-term Hylleraas ground-state wave function reported in Ref. [12], convergence has been improved between the three gauges of electromagnetic interaction. The data are compared with the experimental results of Wehlitz *et al.* [5]. The calculations generally agree very well with experiment. Our results are also consistent with the R-matrix calculations of Meyer *et al.* [40] and the hyperspherical coordinate calculation by Tang

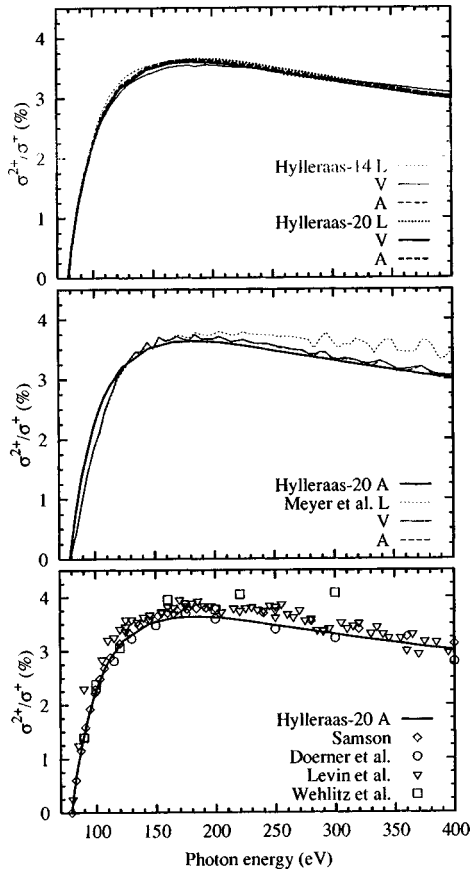

FIG. 7. The ratio of double-to-single photoionization cross sections in He. The CCC calculations are presented in the three gauges of the electromagnetic interaction for the present 20-parameter Hylleraas ground state and the 14-parameter Hylleraas ground state [12]. *R*-matrix calculation is due to Meyer *et al.* [8,18]. Experimental data are from Dörner *et al.* [1], Levin *et al.* [2,3], Samson *et al.* [4], and Wehlitz *et al.* [5].

and Burgdörfer [41]; see Ref. [12]. At energies above 1 keV the ratio stabilizes and is in good agreement with the infinite energy limit given in the table. The only exception is the $n=6$ case where the convergence is a little higher than the limit. This is due to the fact that the $n=6$ state used in the calculations is not a perfect true eigenstate.

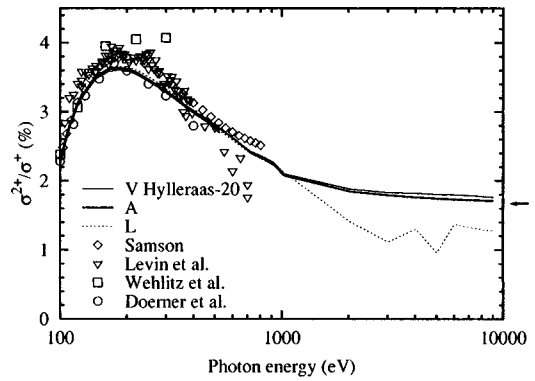

FIG. 8. Same as for bottom part of Fig. 7 plotted on an extended photon energy scale. The asymptotic value from the table is denoted by the arrow.

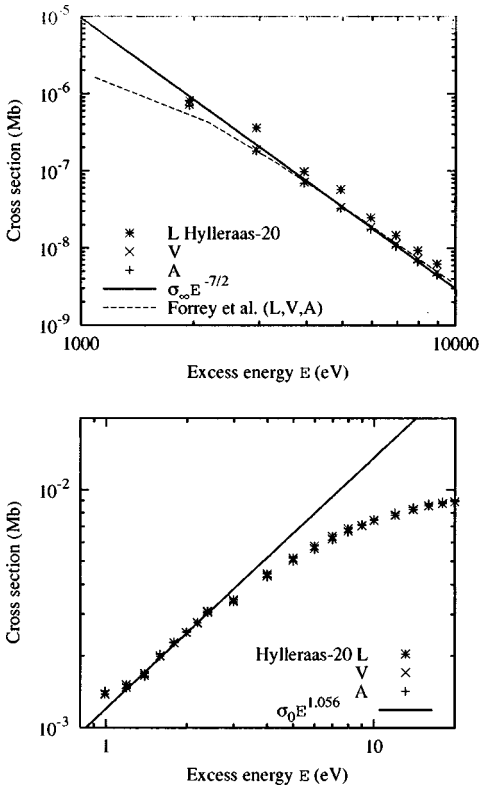

FIG. 9. The absolute double-photoionization cross section of He near threshold and at high energies. The solid line is the indicated fit with $\sigma_0=1.1$ kb and $\sigma_\infty=3.0\times10^5$ Mb for dimensionless E in eV. The calculations of Forrey *et al.* [9] employ a 112-term Hylleraas ground state.

C. Li^+ ion

Double photoionization of the Li^+ ion was studied theoretically by Kornberg and Miraglia [16] and more recently by Meyer [18]. Wehlitz *et al.* [5] measured triple photoionization of lithium and related their experimental triple-to-single photoionization cross sections ratio to the theoretical double-to-single ratio of the Li^+ ion reported by Kornberg and Miraglia [16]. This was done assuming the following two-stage mechanism of triple photoionization. In the first stage double photoionization of the valence $1s^2$ shell of the Li atom takes place. This is subsequently followed by the shakeoff of the remaining $2s$ electron into the continuum. It is reasonable to assume that the double photoionization of the $1s^2$ shell in the Li atom and the Li^+ ion is quite similar and therefore the resulting triple-to-single photoionization cross-section ratio for the Li atom can be calculated as the double-to-single ratio of the Li^+ ion multiplied by the probability of the shakeoff (0.00174 according to Wehlitz *et al.* [17]).

Our calculations of the double-to-single photoionization cross-sections ratio for the Li^+ ion are presented in Fig. 11. The two different ground-state wave functions were used to test the accuracy of the calculation: a 10-term Hylleraas expansion due to Chandrasekhar and Herzberg [24] and a 20-term expansion by Hart and Herzberg [20]. The difference between the three gauges of the electromagnetic operator is less than 1% for the best 20-term Hylleraas ground state, and so only a single curve is presented in this case. Comparison is made with the experimental triple-to-single photoioniza-

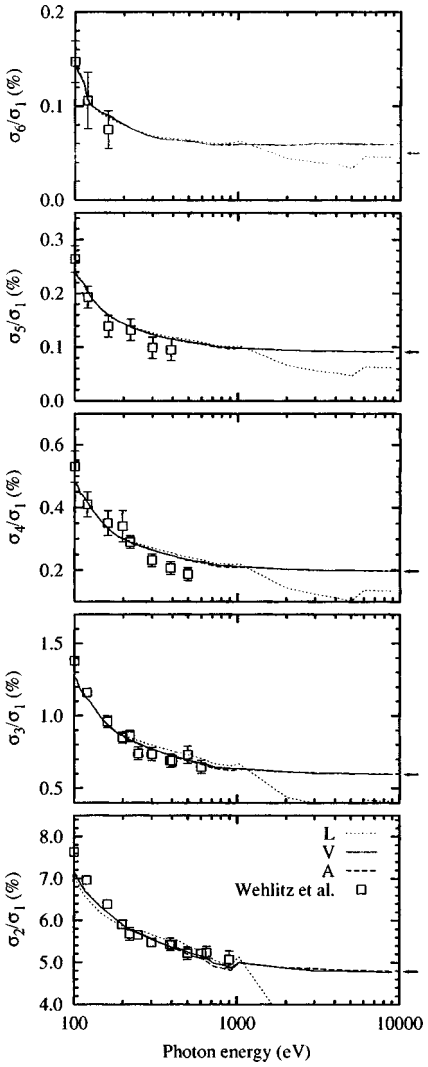

FIG. 10. The ratio σ_n/σ_1 for photoionization of He with simultaneous excitation. Theory and experiment are as for Fig. 7.

tion ratio of Wehlitz *et al.* [17]. For the best visual fit the experimental data were multiplied by the factor of 250. This is about one-half of the factor $0.001\,74^{-1}\approx 574$, which follows from the the shakeoff model. Agreement with the *R*-matrix calculations of Meyer [18] is excellent, except at high photon energies where the *R*-matrix calculation becomes unstable.

To show the asymptotic limit we present the ratio plotted on an extended energy scale to 10 keV in Fig. 12. Good agreement with the infinite photon energy limit $\sigma^{2+}/\sigma^{+}|_{\omega\to\infty}=0.87\%$ given in the table, should be obtained a little past 10 keV.

In Fig. 13 we present the absolute double-photoionization cross section of Li^+ ion and compare our results with the theoretical values of Kornberg and Miraglia [16]. The present calculations fall in between their length and velocity forms, which differ in magnitude by more than two times. As in the case of H^- and He agreement with the *R*-matrix results for the absolute cross sections is as good as it is for the ratio, and so is not presented.

The near-threshold and high-energy behavior of the double photoionization of Li^+ is illustrated in Fig. 14. Wannier power law (19) is fitted to the calculated absolute

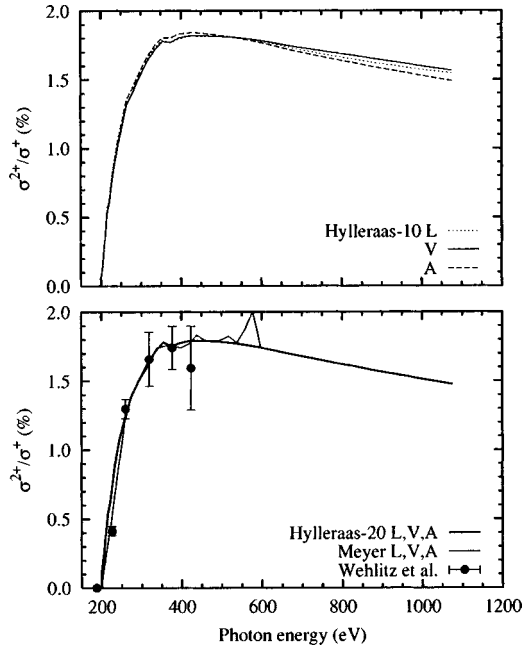

FIG. 11. The ratio of double-to-single photoionization cross sections in Li^+. Calculations are presented in the three gauges of the electromagnetic interaction. The *R*-matrix calculation is due to Meyer [18]. The experimental triple-to-single photoionization ratio of Wehlitz *et al.* [17] is rescaled to the present calculation, see text.

double-photoionization cross section with the exponent $m=1.036$ and resultant $\sigma_0=0.1$ kb. At high energies the $\sigma_\infty E^{-7/2}$ power also works very well, yielding $\sigma_\infty=1.2\times10^6$ Mb for dimensionless E in eV.

In Fig. 15 we present the calculated ratios $\sigma_n/\sigma_1\times100$ with $n=2,\ldots,5$ for photoionization of the Li^+ ion with simultaneous excitation. The *L* gauge is stable to nearly 4 keV, with the *V* and *A* gauges being nearly identical over the entire energy range. The asymptotic limit given in the table is obtained around 3 keV. We compare our results with the *R*-matrix calculation of Meyer [18], which is essentially identical in all three gauges. Generally, the presently calculated ratios are consistent with those of Meyer [18]. There are some unphysical oscillations indicating the numerical difficulties.

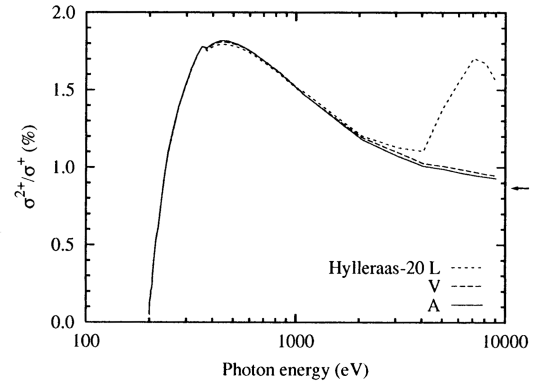

FIG. 12. The ratio of double-to-single photoionization cross section for Li^+. The asymptotic value, given in the table, is denoted by the arrow.

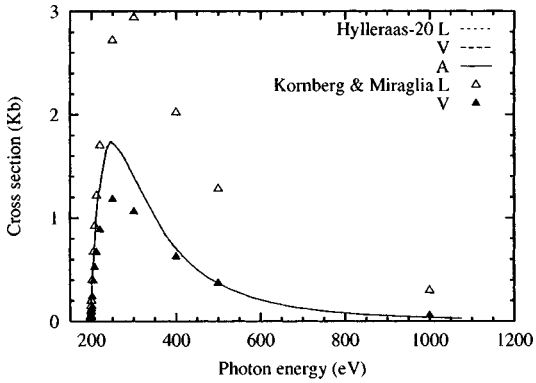

FIG. 13. Absolute double-photoionization cross section of Li^+. Calculations are presented in the three gauges of the electromagnetic interaction. The length- and velocity-gauge results of Kornberg and Miraglia [16] are also given.

D. Scaling laws

It has been suggested by Kornberg and Miraglia [16], for example, that the double-photoionization cross section of a two-electron atomic system can be scaled to a universal function

$$\overline{\sigma}^{2+}(E/Z^2,Z)=Z^4\sigma^{2+}(E,Z), \tag{21}$$

which varies only marginally with Z at E/Z^2. Here E is the excess energy carried away by the electron pair. Equation (21) is derived by neglecting the charge dependence of the reduced electron-electron repulsion $1/(Zr_{12})$, which is only justified in the limit of $Z\to\infty$. Nevertheless, Kornberg and Miraglia [16] showed that the scaling law (21) is more or less satisfied even for low Z targets starting from He and onwards. Similarly, the same conclusion arose from the study of electron-impact ionization of the H-like ion sequence in a model problem [31]. It is therefore interesting to plot our double-photoionization cross sections for H^-, He, and Li^+ in the reduced coordinates $\sigma^{2+}Z^4$ against E/Z^2 to investigate the universal scaling property. This is done in Fig. 16 where the double-photoionization cross sections of various two-electron targets are presented in the acceleration form calculated with the 20-parameter Hylleraas ground state, and indeed rapid scaling is found. Note that, except for the H^- length form, in the given energy range all three gauges give the double-photoionization cross section within an error of less than 2%. To test how well the scaling works also given are some calculations of double photoionization of O^{6+}. These confirm the scaling property.

From our calculations we extracted the following values of the normalization factors, which are essentially identical in all three gauges $\sigma_0(H^-)=95$, $\sigma_0(He)=1.1$, and $\sigma_0(Li^+)=0.1$ kb, for dimensionless energy in eV. Scaling of the Wannier law (19) according to Eq. (21) leads to

$$\overline{\sigma}^{2+}(E,Z)\approx Z^4\sigma_0(Z)(EZ^2)^m$$
$$\approx Z^6\sigma_0(Z)E. \tag{22}$$

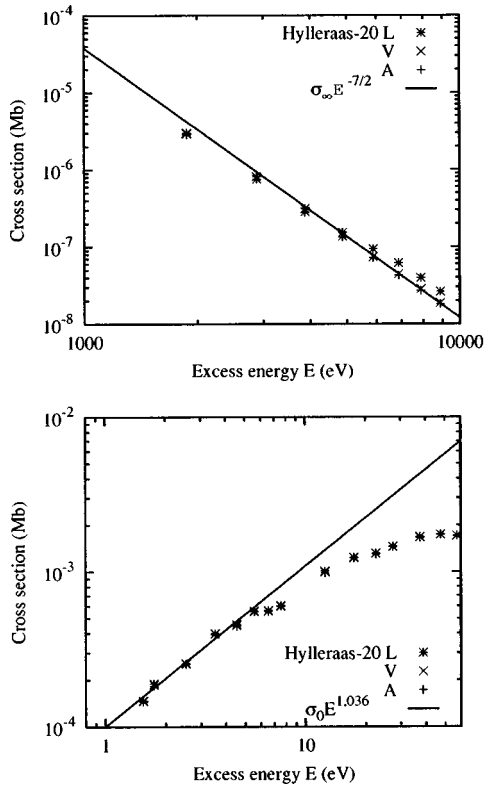

FIG. 14. The absolute double-photoionization cross section of Li^+ near threshold and at high energies. The solid line is the indicated fit with $\sigma_0=0.1$ kb and $\sigma_\infty=1.2\times10^6$ Mb for dimensionless E in eV.

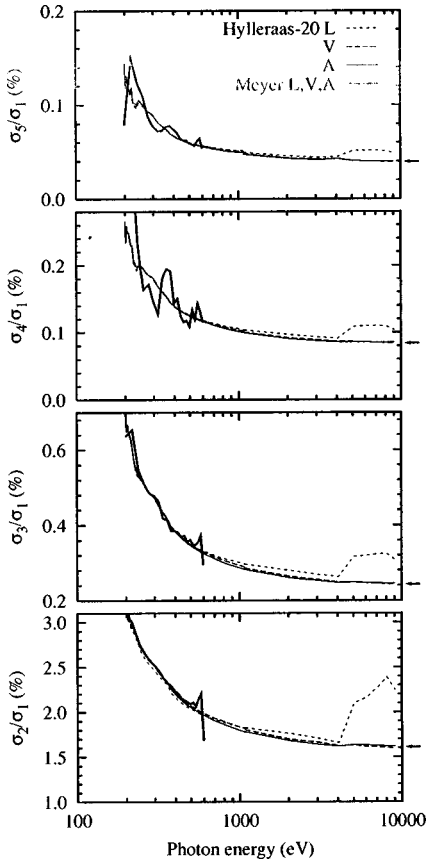

FIG. 15. The cross-section ratio σ_n/σ_1 for photoionization of Li^+ with simultaneous excitation. Calculations in the three gauges of the electromagnetic interaction are presented. The asymptotic value presented in the table is indicated by the arrows. *R*-matrix calculations are due to Meyer [18].

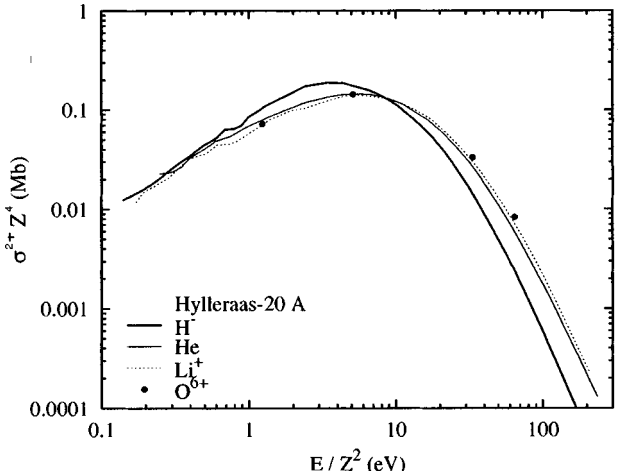

FIG. 16. Scaled, as indicated, double-photoionization cross sections for H^-, He, Li^+, and O^{6+} plotted against excess energy E/Z^2, where Z is the nuclear charge.

The three values of $Z^6\sigma_0(Z)$ are 95, 76.8, and 72.9. We suppose that for larger Z the value of $Z^6\sigma_0(Z)$ should be approximately 70 kb.

For sufficiently high energies to a good approximation

$$\sigma^{2+}(E,Z)\approx\sigma_\infty(Z)E^{-7/2}, \tag{23}$$

with $\sigma_\infty(H^-)=6.5\times10^3$, $\sigma_\infty(He)=3.0\times10^5$, and $\sigma_\infty(Li^+)=1.2\times10^6$ Mb for dimensionless energy in eV. Application of the scaling according to Eq. (21) we may write

$$\overline{\sigma}^{2+}(E,Z)\approx Z^4\sigma_\infty(Z)(EZ^2)^{-7/2}=Z^{-3}\sigma_\infty(Z)E^{-7/2}. \tag{24}$$

The three values of $Z^{-3}\sigma_\infty(Z)$ are 6.5×10^3, 3.8×10^4, and 4.4×10^4. We suppose that for higher Z the value of $Z^{-3}\sigma_\infty(Z)$ is approximately 4.6×10^4 Mb for dimensionless E in eV.

We now turn to the consideration of scaling of the photoionization with excitation cross sections. These are given in Fig. 17. In addition to the Z^4 scaling we also multiply by n^3 in order to observe for what values of n this scaling is sufficiently accurate. We see that the photoionization with no excitation ($n=1$) cross sections scale particularly poorly. For this reason the σ_n/σ_1 ratios presented in Figs. 3, 10, and 15 do not scale with Z at all. However, the scaling with Z improves rapidly with increasing n. Note how the H^- cross sections behave with respect to the others as n increases. The relatively large values of the $\sigma_2(H^-)$ particularly stand out. Turning to consideration of scaling with n we see that this becomes quite accurate for $n=5$, thereby allowing for estimation of σ_n with $n>5$.

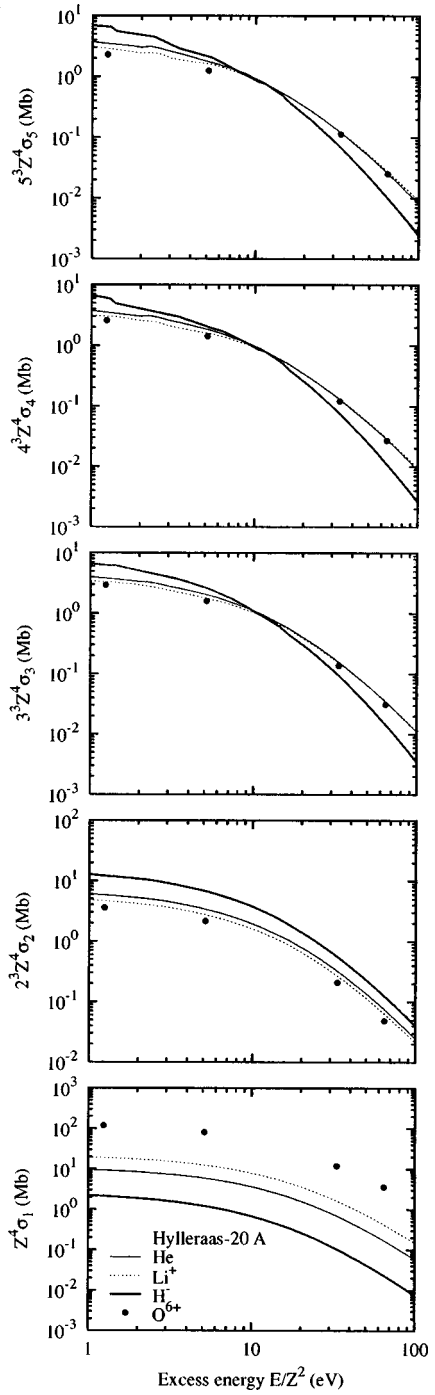

FIG. 17. Scaled, as indicated, photoionization with excitation, to the specified n levels, cross sections for H^-, He, Li^+, and O^{6+} plotted against excess energy E/Z^2, where Z is the nuclear charge.

IV. CONCLUSIONS

We have demonstrated that the convergent close-coupling formalism, in conjunction with a Hylleraas-type expansion for the ground state of a two-electron system, provides an accurate description of the nonrelativistic photoionization with excitation and double photoionization of the H^-, He, and Li^+ targets. This conclusion is based on good convergence between calculations performed in the three gauges of the electromagnetic interaction (length, velocity, and acceleration) at the low and intermediate energies. At the higher energies the length form diverges from the other two at 0.1, 1, and 4 keV for the H^-, He, and Li^+ targets, respectively. Thus, the convergence between the three gauges improves with increasing Z. This is due to the decrease of the relative strength of the two-electron correlation that is largest in the ground state of the negative hydrogen ion. Presently employed 20-term Hylleraas ground-state expansion recovers more than 99.98 % of the correlation energy. However, for sufficiently high energies it is still unable to reproduce the

transition probability to the double-ionized continuum due to insufficient accuracy at large distances, which is enhanced by the dipole operator in the length form. Nevertheless, the good agreement of the other two forms, coupled with the study of the nature of the convergence with increasing quality of the ground state and the usage of asymptotic and scaling behavior, suggests that accurate results for double photoionization and photoionization with excitation to any n level may be obtained at all energies above the double-photoionization threshold and for any two-electron target of arbitrary Z. Interestingly, the photoionization with no excitation cross section, and hence the total single-photoionization cross section, does not scale well with Z.

The present calculations generally agree well with experiment and the R-matrix theory of Meyer *et al.* [8]. Though we have concentrated here solely on integrated cross sections much more detailed information arises from the CCC calculations. This includes excitation of the individual nl levels, the asymmetry parameter $\beta(n)$, etc. We invite interested readers to obtain numerical data electronically.

We shall next concentrate on providing angle-differential $(\gamma,2e)$ cross sections, where initial indications are very promising [19,42]. In addition, the CCC approach will be applied to photoionization of the Be, Mg, and Ca atoms utilizing the successful implementation of the CCC method for their singly positive (hydrogenlike) ions [27].

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[1] R. Dörner *et al.*, Phys. Rev. Lett. **76**, 2654 (1996).
[2] J. C. Levin, G. B. Armen, and I. A. Sellin, Phys. Rev. Lett. **76**, 1220 (1996).
[3] J. C. Levin, unnormalized data plotted, published data believed to be incorrectly normalized (private communication).
[4] J. A. R. Samson *et al.*, Phys. Rev. A **57**, 1906 (1998).
[5] R. Wehlitz *et al.*, J. Phys. B **30**, L51 (1997).
[6] J. H. McGuire *et al.*, J. Phys. B **28**, 913 (1995).
[7] J. Z. Tang and I. Shimamura, Phys. Rev. A **52**, R3413 (1995).
[8] K. W. Meyer, C. H. Greene, and B. D. Esry, Phys. Rev. Lett. **78**, 4902 (1997).
[9] R. C. Forrey, Z.-C. Yan, H. R. Sadeghpour, and A. Dalgarno, Phys. Rev. Lett. **78**, 3662 (1997).
[10] C. A. Nicolaides, C. Haritos, and T. Mercouris, Phys. Rev. A **55**, 2830 (1997).
[11] Y. Qiu, J. Z. Tang, J. Burgdörfer, and J. Wang, Phys. Rev. A **57**, R1489 (1998).
[12] A. Kheifets and I. Bray, Phys. Rev. A **57**, 2590 (1998).
[13] A. R. P. Rau, J. Astrophys. Astron. **17**, 113 (1996).
[14] J. B. Donahue *et al.*, Phys. Rev. Lett. **48**, 1538 (1982).
[15] J. T. Broad and W. P. Reinhardt, Phys. Rev. A **14**, 2159 (1976).
[16] M. A. Kornberg and J. E. Miraglia, Phys. Rev. A **49**, 5120 (1994).
[17] R. Wehlitz *et al.*, Phys. Rev. Lett. **81**, 1813 (1998).
[18] K. Meyer, Ph.D. thesis, University of Colorado, 1997 (unpublished).
[19] A. Kheifets and I. Bray, J. Phys. B **31**, L447 (1998).
[20] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).
[21] A. Dalgarno and A. L. Stewart, Proc. R. Soc. London **76**, 49 (1960).
[22] A. Dalgarno and H. R. Sadeghpour, Phys. Rev. A **46**, R3591 (1992).
[23] L. R. Henrich, Astrophys. J. **99**, 59 (1944).
[24] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).
[25] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).
[26] L. C. Green, M. M. Mulder, and P. C. Milner, Phys. Rev. **91**, 35 (1953).
[27] I. Bray, Phys. Rev. A **49**, 1066 (1994).
[28] M. Y. Amusia, in *Atomic Photoeffect*, edited by K. T. Taylor (Plenum Press, New York, 1990).
[29] I. Bray and A. T. Stelbovics, Phys. Rev. Lett. **70**, 746 (1993).
[30] I. Bray and A. T. Stelbovics, Phys. Rev. Lett. **69**, 53 (1992).
[31] I. Bray and B. Clare, Phys. Rev. A **56**, R1694 (1997).
[32] M. Venuti and P. Decleva, J. Phys. B **30**, 4839 (1997).
[33] K. W. Meyer, C. H. Greene, and I. Bray, Phys. Rev. A **52**, 1334 (1995).
[34] G. H. Wannier, Phys. Rev. **90**, 817 (1953).
[35] J. F. McCann and D. S. F. Crothers, J. Phys. B **19**, L399 (1986).
[36] J. A. R. Samson, Z. X. He, L. Yin, and G. N. Haddad, J. Phys. B **27**, 887 (1994).
[37] H. Kossmann, V. Schmidt, and T. Andersen, Phys. Rev. Lett. **60**, 1266 (1988).
[38] M. Pont and R. Shakeshaft, J. Phys. B **28**, L571 (1995).
[39] K. Hinor *et al.*, Phys. Rev. A **48**, 1271 (1993).
[40] K. W. Meyer, J. L. Bohn, C. H. Greene, and B. D. Esry, J. Phys. B **30**, L641 (1997).
[41] J. Z. Tang and J. Burgdörfer, J. Phys. B **30**, L523 (1997).
[42] H. Bräuning *et al.*, J. Phys. B **31**, 5149 (1998).