PHYSICAL REVIEW A VOLUME 27, NUMBER 1 JANUARY 1983

Electronic *ab initio* quantum-defect theory. Low-resolution H_2 photoionization spectrum

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(Received 9 June 1982)

This paper presents a global *ab initio* approach, called the electronic *ab initio* quantum-defect theory (EAQDT), to molecular photoionization spectrum calculations. This method first obtains the *ab initio* electronic parameters by the hereafter developed electronic iterative-variational eigenchannel approach (EIVEA). Then these electronic parameters are used in the calculation of the final state and the corresponding photoionization cross section by the multichannel quantum-defect theory (MQDT) [Jungen and Atabek, J. Chem. Phys. 66, 5584 (1977)]. In EIVEA, an elaborate N-electron correlated final-state wave function is introduced. This wave function allows us to take into account the ionic-core relaxation, many ionic cores and electronic autoionizing interactions. In calculating the transition probability we also use an electron-correlated initial state. Compared with the standard MQDT, the EAQDT is free from the use of semiempirical parameters and therefore has a wider applicability. This method is applied, as a test, to the low-resolution photoionization spectrum of H_2. In the energy range between threshold and 23 eV studied here, where electronic autoionization does not take place, we obtain a theoretical cross section which bears comparison with the experimental one above 17.5 eV.

I. INTRODUCTION

Due to difficulties in the calculation of the continuum molecular wave function associated with the final state, it is only recently that theoretical studies of the molecular photoionization spectra have reached a reasonable level of accuracy. Accurate calculations reproducing high-resolution molecular photoionization spectra over an extended energy range are still to be performed. Compared to the atomic photoionization, the additional difficulties in these calculations are connected with the nonspherical nature of the molecular potential and with the presence of nuclear degrees of freedom associated with the molecular vibration and rotation.

In developing theoretical methods, the following two directions have been pursued.

(i) *ab initio* methods have placed emphasis on accurate calculation of the electronic interaction and consequently on the molecular continuum electronic wave function. The rotational-vibrational function is generally reduced to the simple vibrational function summing on different rotational functions. As a result, one can calculate a low-resolution photoionization spectrum over an extended energy range. Some of the methods of this class calculate the final-state continuum electronic function by one-center molecular close-coupling[1-4] or L^2 (Refs. 5 and 6) approaches. Others divide the Cartesian space into two[7-8] or several regions[9] taking advantage of the difference in nature and strength of the electronic interaction in each region. Most of these methods perform calculations at the fixed-core static exchange (FCSE) level, i.e., only one ionic unrelaxed core is considered and static and exchange bound-continuum interaction is included. Williams and Langhoff,[10] for N_2, and O'Neil and Reinhardt,[6] for H_2, use a more elaborate wave function allowing for ionic-core relaxation and many-core interaction. No electronic autoionization is allowed in these last two calculations. For isolated electronic autoionizing resonances the golden-rule-type formulation was used for H_2 (Ref. 11) and CH.[12] In the case of H_2 photoionization, electronic autoionization width has also been calculated directly by Takagi and

Nakamura[13] from energy variation of the final-state quantum defect.

(ii) Semiempirical methods where the emphasis is placed on the accurate description of the vibrational[14] or vibrational-rotational interaction[15,16] (especially vibrational and rotational autoionization). These methods restrict the energy range to the near-photoionization-threshold regions and calculate the high-resolution photoionization spectrum. The electronic interaction is introduced using either a simple electronic function[14] or semiempirical parameters.[15,16] The vibrational-rotational function is taken as a sum of Born-Oppenheimer products in the most elaborate theory, multichannel quantum-defect theory (MQDT) initiated by Fano[15] and applied to rotational-vibrational interaction by Jungen and co-workers.[16] With semiempirical electronic parameters corresponding to one effective electronic configuration and taking full account of rotational-vibrational interaction, Jungen and co-workers[16] were able to reproduce the complicated rotational-vibrational near-threshold resonances in the H_2 photoionization spectrum of Dehmer and Chupka.[17]

The aim of the present study is to initiate a global approach combining the advantages of the existing methods. We start with an *ab initio* electronic molecular calculation using a new method which we have developed,[18] called the electronic iterative variational eigenchannel approach (EIVEA), an extension of the atomic eigenchannel approach of Fano and Lee.[19] Our approach uses a many-configuration N-electron molecular wave function while the approach of Fano and Lee uses a one-electron atomic self-consistent field (SCF). As a consequence, a new formulation will be introduced in this paper. We divide the coordinate space into two regions: the inner one (In) near the nuclei, which is a sphere of radius r_0; and the outer one (Out) including the remaining space. The radius r_0 is chosen so that all nonlocal (electron exchange) effects are included in the inner region, as should any noncentral potential generated by the core. This last requirement is necessary to reduce the asymptotic channels to only the physically significant ones. In the inner region, we deal with N indistinguishable electrons and we use standard bound configuration interaction (CI) restricted to a finite domain. We therefore are able to introduce electronic exchange and correlation, i.e., ionic-core relaxation, many-ionic, and electronic-autoionizing interactions. Correct calculations with a two-region method like our EIVEA imply a constrained inner-region calculation to fulfill the hermiticity and continuity of the logarithmic derivative between the two regions. Moreover, one of the eigenvalues of the discrete spectrum of the CI calculation must be constrained to coincide with the actual total energy of the molecule. In the outer region, $N-1$ indistinguishable electrons are completely decoupled from the Nth departing electron and, therefore, separate calculations are performed for the different ionic states in solving $(N-1)$-electron CI problem and for the free electron in solving Schrödinger equation in a Coulomb field. The results are expressed in terms of asymptotic electronic channels $\beta = |n^+\Lambda^+, l\lambda\rangle$ (Λ^+ is the projection of the electronic angular momentum of the ion on the internuclear axis, n^+ labels the same Λ^+ ionic state and l,λ are the departing-electron angular momentum and its projection on the same axis). These channels will be mixed by the full N-electron interactions of the inner region and the mixed channels are labeled α. The comparison between the electronic wave function of the inner region [Eq. (1) below] and the same function in the outer region [Eq. (8) below] enables us to introduce, following Greene, Fano, and Strinati,[15c] "strongly closed" channels. For these channels, the wave function decays so rapidly with increasing r as to be itself vanishingly small at $r \geq r_0$. Naturally, the inner-region wave function contains a summation over the strongly closed channels while the outer-region wave function is restricted to only open and weakly closed channels. The EIVEA is an expansion method and therefore special attention is paid to the choice of the basis set. As explained in Sec. II D below, we have used a hybrid basis set of Slater and standard Coulomb functions, and followed the prescriptions of Rudge[20] to attain the convergence of the calculations. Greene, Fano, and Strinati[15c] defined two other sets of Coulomb functions having the advantage of eliminating the bound state and the ionization-threshold discontinuities. In our approach, we can introduce any one of the three sets of Coulomb functions, therefore allowing the calculation of smooth electronic parameters in any spectral range.

Starting from the results of electronic calculation, we define new asymptotic electronic-vibrational-rotational MQDT channels $|i\rangle = |n^+\Lambda^+ l, v^+ N^+\rangle$ in the laboratory frame (v^+ is vibrational quantum number of the ion, N^+ represents the type of coupling between angular momenta defining the corresponding rotational functions, l is the excited-electron angular momentum). These $|i\rangle$ channels are appropriate for the description of the high-Rydberg and continuum electrons which we are considering in this paper. The separation in regions A and B, where the electron is more appropriately described in terms of the molecular and laboratory frames used by Jungen and Atabek,[16a] is conserved here. The core region, a subregion of their region A of radius r_c, is our inner region (In) of radius r_0.

The link between $|\beta\rangle$ or $|\alpha\rangle$ electronic channels in the molecular frame and $|i\rangle$ channels in laboratory frame is established through the standard MQDT procedure of reexpansion of $|\alpha\rangle$ channels in terms of $|i\rangle$ channels as given by Jungen and co-workers.[16]

In the example of H_2 photoionization, the EAQDT discussed above will allow the simultaneous fully *ab initio* calculation of the low-energy region of 15.4—18 eV, rich in rotational and vibrational autoionization, and the region near 27 eV where the electronic autoionization seems to take place. The spectrum of the first region was obtained by the Dehmer and Chupka[17] and calculated by a semiempirical electronic-parameters MQDT approach by Jungen and co-workers.[16] The 27-eV electronic autoionization was seen in the angular-distribution asymmetry parameter spectrum by Marr *et al.*[21] and in the anomalous kinetic-energy distribution of $H+H^+$ by Strathdee and Browring[22] and calculated by Kirby *et al.*[11a] and Takagi and Nakamura.[13]

The paper is organized as follows: Sections II and III present the EAQD theory; Sec. II introduces the electronic theory using EIVEA while Sec. III deals with the link between EIVEA and MQDT. Section IV specifies our treatment for the

$$H_2(X\,{}^1\Sigma_g^+)+h\nu+H_2{}^+(X\,{}^2\Sigma_g^+)+e\left\{\begin{smallmatrix}\sigma_u\\ \pi_u\end{smallmatrix}\right\}$$

photoionization, summing over different rotational levels and considering for the final-state four open electronic channels $p\sigma, f\sigma, p\pi, f\pi$ augmented by vibrational levels. Details of the calculation and results are given in Secs. IV B and IV C. Finally, Sec. V compares our EAQDT method to the other existing methods.

II. FINAL-STATE ELECTRONIC ITERATIVE-VARIATIONAL EIGENCHANNEL APPROACH

In this section the expansion method for the inner-(In) and outer-(Out) region electronic wave functions is introduced. Then the eigenchannel problem is solved through an iterative-variational procedure and the continuity of the total electronic wave function is enforced.

A. Wave function and Hamiltonian

The total electronic wave function, valid all over the coordinate space, is taken as an expansion in terms of N-electron wave functions:

$$\Psi_\alpha(1,2,\ldots,N;\Lambda,R)=\sum_I \Phi_{I\alpha}(1,2,\ldots,N;\Lambda,R)C_{I\alpha}\ ,\quad \forall\Lambda\ . \tag{1}$$

The functions $\Phi_{I\alpha}$ are linear combinations of Slater determinants called configuration-state functions (CSF) having the same total electronic angular momentum component Λ_r^π with respect to the internuclear axis where $\pi=\pm1$ ($\pm$ is not to be confused with the Λ^+ used in the following to denote ionic-core state) represents the symmetric and antisymmetric reflection with respect to a plane containing the internuclear axis and $r=g,u$ with respect to the symmetry center of the molecule. The electronic interaction is diagonal in Λ_r^π and parametric in R, the internuclear distance. Therefore, only one Λ_r^π and one value of the continuous R are explicitly considered in (1). To simplify the notation we shall use, whenever possible, "Λ,R" instead of "Λ_r^π,R" and even completely suppress Λ_r^π,R in Ψ_α. We shall have as many solutions labeled α as functions having the same total electronic energy. Two solutions may arise from interacting (same Λ,R) or noninteracting (different Λ,R) functions. The CSF $\Phi_{I\alpha}$ is explicitly a function of the solution α we are considering. To simplify the notation, whenever unambiguous, we shall henceforth use Φ_I instead of $\Phi_{I\alpha}$. Furthermore, in expanding the CSF in terms of one-electron functions we shall identify it, for brevity, with only one Slater determinant of the following form:

$$\Phi_{I\alpha}=\mathscr{A}[\phi_{j_1}(1)\phi_{j_2}(2)\cdots\phi_{j_N}(N)]\ , \tag{2}$$

here $\phi_{j_p}(p)$ is the one-electron molecular function of the pth electron, implicitly a function of α. It has an angular momentum λ_{j_p} omitted to simplify the present notation. $\mathscr{A}$ is the antisymmetrization operator.

Now, we introduce electronic asymptotic channels β (mentioned in the Introduction):

$$|\beta\rangle=|n^+\Lambda^+L\rangle\ , \tag{3}$$

where n^+ labels the electronic states of the ionic core having the same Λ^+, and $L=(l,\lambda)$ specifies the angular momentum of the departing electron and its projection on the internuclear axis. The total electronic angular momentum Λ satisfies the relation $\Lambda=\Lambda^++\lambda$. The different asymptotic channels have the same total electronic energy E^e. E^e is chosen so that the kinetic energy of the departing electron $\epsilon_{(n^+\Lambda^+L)}$ satisfies the total-energy (electronic, vibrational, and rotational) requirement, Eq. (35) below. E^e is then equal to

$$E^e=E_{(n^+\Lambda^+)}+\epsilon_{(n^+\Lambda^+L)}\ , \tag{4}$$

where $E_{(n^+\Lambda^+)}$ is the electronic energy of the ionic core which is implicitly dependent on R. Note that the number of channels $|\beta\rangle$ of (3) equals the number of solutions α of (1) having the same total electronic energy. The development in what follows will be conducted so that α of Eq. (1), corresponds to the eigenchannel solution [Eqs. (8) and (9) below] of the fixed-nuclei problem.

The N-electron Hamiltonian can be written as a sum of three terms referring, respectively, to the ionized core, the excited electron moving in a Coulomb field, and an interaction term. This latter term accounts for the departures from a pure Coulomb interaction of the excited electron at short range:

$$H(1,2,\ldots,N;R) = H^{+}(1,2,\ldots,N-1;R)+H(N) + H^{\mathrm{int}}(1,2,\ldots,N-1;N), \tag{5}$$

$$H^{+}(1,2,\ldots,N-1;R) = \sum_{p=1}^{N-1}\left[-\tfrac{1}{2}\nabla^2_{\vec{r}_p}-\frac{Z_A}{r_{pA}}-\frac{Z_B}{r_{pB}}\right]+\sum_{p'<p}^{N-1}\frac{1}{r_{pp'}}, \tag{6a}$$

$$H(N) = -\tfrac{1}{2}\nabla^2_{\vec{r}_N}-\frac{1}{r_N}, \tag{6b}$$

$$H^{\mathrm{int}}(1,2,\ldots,N-1;N) = -\frac{Z_A}{r_{NA}}-\frac{Z_B}{r_{NB}}+\frac{1}{r_N} + \sum_{p=1}^{N-1}\frac{1}{r_{pN}}, \tag{6c}$$

where H^{int} is the interaction term. In (6) atomic units have been used and the origin of the coordinate system is the center of mass. The excited electron is here labeled N. As stated in the Introduction we now divide the entire space in two distinct regions regarding the location of the excited electron with respect to the nuclei. The inner region is a sphere of radius r_0 and the outer region is the remaining coordinate space.

In the inner region the full N-electron interaction must be taken into account, since $H^{\mathrm{int}}\neq 0$. The N electrons are indistinguishable and the wave function has the form (1) and will be written as $\Psi_\alpha^{(\mathrm{In})}$. As explained below, in this region we perform a full N-electron calculation using EIVEA.

In the outer region, the $N-1$ electrons and the Nth electron are nearly decoupled and distinguishable since the residual interaction is small. In fact, we neglect it in setting $H^{\mathrm{int}}=0$. We perform separate calculations for the $(N-1)$-electron system and the Nth, outer electron. We write the ionic wave function in a form similar to (1):

$$\Psi_{(n^+\Lambda^+)}(1,2,\ldots,N-1) = \sum_{I^+}\Phi_{I^+}^{\Lambda^+}(1,2,\ldots,N-1)D_{I^+(n^+\Lambda^+)}, \quad \forall n^+,\Lambda^+ . \tag{7}$$

Here the notations and the simplifications are the same as in Eq. (1) but refer to $N-1$ electrons with the total electronic angular momentum projection of the ion Λ^+. Note that we change the notation of the CI coefficients from C to D to avoid confusion. In the present partitioning of the Hamiltonian, where $H(N)$ is the Coulomb operator, the exact solution of the Nth-electron wave equation is given in terms of regular and irregular analytic Coulomb functions $f_l(N,k_l)$ and $g_l(N,k_l)$, energy normalized at $r\rightarrow\infty$ as defined, e.g., by Dehmer and Fano[23]. From now on, whenever this identification is unambiguous, we put $\vec{N}\equiv\vec{r}$, $N\equiv r$, and $\hat{N}\equiv\hat{r}$ [(e.g., $f_l(N,k_l)\equiv f_l(r,k_l)$, $g_l(N,k_l)=g_l(r,k_l)$]. In the outer region, (1) is still valid and will be noted as $\Psi_\alpha^{(\mathrm{out})}$. We recast it in a form explicit in terms of asymptotic channels $|\beta\rangle$ defined in (3). In this new form we can neglect the antisymmetry between the $N-1$ electrons and the Nth electron as the two sets are separated and $H^{\mathrm{int}}=0$. Furthermore, as stated in the Introduction, we exclude from the summation in (8) the strongly closed channels and obtain the following:

$$\begin{aligned}\Psi_\alpha^{(\mathrm{Out})}(1,2,\ldots,N) &= \sum_{(n^+,\Lambda^+)}\Psi_{(n^+\Lambda^+)}(1,2,\ldots,N-1) \times\sum_L Y_L(\hat{r})\mathscr{F}_{(n^+\Lambda^+L),\alpha}(r,k_{(n^+\Lambda^+L)})\\ &=\sum_\beta \Psi_\beta(1,2,\ldots,N-1;\hat{r})\mathscr{F}_{\beta\alpha}(r,k_\beta)\ ,\end{aligned} \tag{8}$$

where in (8) we have introduced the notation Ψ_β combining the ionic wave function $\Psi_{(n^+\Lambda^+)}$ with the spherical harmonics $Y_L(\hat{r})$ of the excited electron,

$$\Psi_\beta(1,2,\ldots,N-1;\hat{r}) = \Psi_{(n^+\Lambda^+)}(1,2,\ldots,N-1)Y_L(\hat{r}). \tag{9a}$$

The radial wave function of the departing electron $\mathscr{F}_{\beta\alpha}(r,k_\beta)$ is expressed as an eigenchannel function of the following form:

$$\mathscr{F}_{\beta\alpha}(r,k_\beta)=f_l(r,k_\beta)U_{\beta\alpha}\cos(\pi\mu_\alpha) - g_l(r,k_\beta)U_{\beta\alpha}\sin(\pi\mu_\alpha)\ , \tag{9b}$$

where in (9b) the matrix $\underline{U}$ and the vector $\underline{\mu}$ are mixing coefficients and quantum defects being constant in the outer region. They are the result of the inner-region $(N-1)$-electrons—Nth-electron interaction and couple the regular and irregular f_l and g_l functions of the departing electron. Note that in (9b) we have replaced k_l by k_β to satisfy the total-energy requirement (4).

B. Iterative-variational method

No explicit EIVEA calculations are performed in the outer region. Nevertheless, for separate $(N-1)$-electron and Nth-electron problems we solve the following equations:

$$H^{+}(1,2,\ldots,N-1)\Psi_{(n^{+}\Lambda^{+})}(1,2,\ldots,N-1) =\Psi_{(n^{+}\Lambda^{+})}(1,2,\ldots,N-1)E_{n^{+}\Lambda^{+}}\,, \tag{10a}$$

$$H(r)f_l(r,k_\beta)=f_l(r,k_\beta)\epsilon_\beta\,, \tag{10b}$$

and another solution of (10b) is the irregular function $g_l(r,k_\beta)$. The Eqs. (10) define all the functions appearing in (8) and (9b) except the coefficients $\underline{U}$ and $\underline{\mu}$. In the MQDT (Sec. III) we shall use the collision form (8) and therefore we must be able to obtain these coefficients. $\underline{U}$ and $\underline{\mu}$ are calculated, as detailed below, from the iterative-variational procedure of the inner region and the wave-function matching at r_0.

Using Eqs. (1) and (5) we write the inner-region Schrödinger equation as

$$H(1,2,\ldots,N)\,|\,\Psi_\alpha^{(\mathrm{In})}(1,2,\ldots,N)) =|\,\Psi_\alpha^{(\mathrm{In})}(1,2,\ldots,N))E_\alpha\,. \tag{11a}$$

By introducing (1) in (11a) we obtain the following form:

$$\sum_{II'}C_{I'}H_{II'}C_I=E_\alpha \tag{11b}$$

with

$$H_{I,I'}=(\Phi_I^{(\mathrm{In})}\,|\,H\,|\,\Phi_{I'}^{(\mathrm{In})})\,. \tag{11c}$$

The round brackets in Eqs. (11) refer to integration over the limited $[0,r_0]$ range. The above equations yield a discrete variational solution in the sphere. We solve Eqs. (11) with the following constraint:

$$E_\alpha=E^e\,. \tag{12}$$

Several solutions α of (11a) can satisfy (12) where E^e is the total electronic energy defined in (4).[24] In solving Eq. (11) with the constraint (12), the following problems, linked with the general quantum-mechanical and scattering-theory requirements arise:

(i) As we integrate in a finite range, H is *a priori* non-Hermitean.

(ii) Each CSF Φ_I is, in general, discontinuous through the sphere surface.

(iii) The variational procedure in a finite domain gives a discrete spectrum, whereas E^e is continuous. Therefore, normally $E_\alpha\neq E^e$. The problems (i) and (ii) are solved below by introducing a constrained and a $\underline{\mu}$-dependent one-electron molecular basis. Problem (iii) is solved by having the quantum defect μ_α in (9b), which is a function of total energy, varied iteratively until the condition (12) is fulfilled. This iterative procedure was already developed in the one-electron atomic case by Lee.[19]

To implement the iterative-variational procedure, we first require a continuous logarithmic derivative of each CSF across the surface of the sphere:

$$\left[\frac{\dfrac{\partial}{\partial r}\Phi_I^{(\mathrm{In})}}{\Phi_I^{(\mathrm{In})}}\right]_{r_0}=\left[\frac{\dfrac{\partial}{\partial r}\Phi_I^{(\mathrm{Out})}}{\Phi_I^{(\mathrm{Out})}}\right]_{r_0}\,. \tag{13}$$

It is to be remembered that in (13) the derivative is performed with respect to the coordinate of the Nth, excited electron. At r_0, $H^{\mathrm{int}}=0$ and the amplitude of the $(N-1)$-electron function is negligible. Therefore, the CSF (2) can be written as

$$\begin{aligned}\Phi_{I\alpha}^{(\mathrm{In})}&(1,2,\ldots,N)\\ &=|\,\phi_{j_1}(1)\phi_{j_2}(2)\cdots\phi_{j_{N-1}}(N-1)\,|\,\phi_{j_N\alpha}(N)\\ &=\Phi_{I^+}^{\Lambda^+}(1,2,\ldots,N-1)\phi_{j\alpha}^{(\mathrm{In})}(\vec{\mathrm{r}})\,,\end{aligned} \tag{14}$$

where $\Phi_{I^+}^{\Lambda^+}$ is the CSF of the ion introduced in (7) found by inspection and the notation $\phi_{j_N\alpha}^{(\mathrm{In})}(\vec{\mathrm{r}})\equiv\phi_{j\alpha}^{(\mathrm{In})}(\vec{\mathrm{r}})$ is used. To proceed further, we expand the inner-region two-center molecular orbital at the coordinate-system origin and write its value at r_0 as

$$\phi_{j\alpha}^{(\mathrm{In})}(\vec{\mathrm{r}}_0)=\sum_L Y_L(\hat{r})F_{(Lj)\alpha}^{(\mathrm{In})}(r_0)\,. \tag{15}$$

From now on, we shall suppress the subindex α in (15). The derivative of the N-electron determinant wave function is reduced at r_0, using (14), to the derivative of $\phi_j^{(\mathrm{In})}$:

$$\begin{aligned}\left[\frac{\partial\phi_j^{(\mathrm{In})}(\hat{r})}{\partial r}\right]_{r_0}&=\sum_L Y_L(\hat{r})\left[\frac{\partial F_{(Lj)}^{(\mathrm{In})}(r)}{\partial r}\right]_{r_0}\\ &=-\sum_L Y_L(\hat{r})b_{(Lj)}^{(\mathrm{In})}(r_0)F_{(Lj)}^{(\mathrm{In})}(r_0)\,,\end{aligned} \tag{16}$$

where in (16) we have introduced b, the logarithmic derivative of the one-electron radial wave function. For the outer-region Slater determinant, we can apply a procedure similar to the one used above [Eqs. (14)–(16)]. We find

$$\Phi_{I\alpha}^{(\text{Out})}(1,2,\ldots,N)=\Phi_{I+}^{\Lambda^+}(1,2,\ldots,N-1)Y_L(\hat{r})[f_l(r_0,k_\beta)\cos(\pi\mu_\alpha)-g_l(r_0,k_\beta)\sin(\pi\mu_\alpha)]\ . \tag{17}$$

Note that in Eqs. (14)—(16) the Nth-electron function depends on the inner-region molecular orbital j, whereas in (17) this function is written in terms of the asymptotic channel β and solution α. Now, rewriting (16) with the use of (17), we can define the outer-region logarithmic derivative $b_\beta^{(\text{Out})}$ as

$$b_\beta^{(\text{Out})}(r_0,k_\beta,\mu_\alpha)=\frac{\left[\dfrac{\partial f_l(r,k_\beta)}{\partial r}\right]_{r_0}\cos(\pi\mu_\alpha)-\left[\dfrac{\partial g_l(r,k_\beta)}{\partial r}\right]_{r_0}\sin(\pi\mu_\alpha)}{f_l(r_0,k_\beta)\cos(\pi\mu_\alpha)-g_l(r_0,k_\beta)\sin(\pi\mu_\alpha)}\ . \tag{18}$$

Now, requiring the continuity of the logarithmic derivative (13) separately for each L leads us in (16) to replace $b_{Lj(r_0)}^{(\text{In})}$ by $b_\beta^{(\text{Out})}(r_0,k_\beta,\mu_\alpha)$. Consequently, the Slater determinant $\Phi_{I\alpha}^{(\text{In})}$ of Eq. (14) will now become a function of the quantum defect μ_α and it will be piecewise continuous across r_0. As explained in Sec. II C it is only the total function Ψ_α and its derivative which will be continuous everywhere.

As stated above, the inner-region Hamiltonian matrix (11c) is non-Hermitian (nonsymmetric in the case of our real functions). Let us rewrite (11c) as

$$\begin{aligned}H_{II'}&=(\Phi_I^{(\text{In})}\,|\,H\,|\,\Phi_{I'}^{(\text{In})})\\&=\left(\Phi_I^{(\text{In})}\left|\sum_{p=1}^{N}-\tfrac{1}{2}\nabla^2_{\vec{r}_p}\right|\Phi_{I'}^{(\text{In})}\right)\\&\quad+\left(\Phi_I^{(\text{In})}\left|H+\sum_{p=1}^{N}\tfrac{1}{2}\nabla^2_{\vec{r}_p}\right|\Phi_{I'}^{(\text{In})}\right).\end{aligned}\tag{19}$$

The kinetic-energy operator is a differential operator and therefore the first term in (19) is nonsymmetric. Let us rewrite it for the orthogonal one-electron basis set as

$$\begin{aligned}&\left(\Phi_I^{(\text{In})}\left|\sum_{p=1}^{N}-\tfrac{1}{2}\nabla^2_{\vec{r}_p}\right|\Phi_{I'}^{(\text{In})}\right)\\&\qquad=-\tfrac{1}{2}\sum_{j,j'}\left(\phi_j^{(\text{In})}(\vec{r})\left|\nabla^2_{\vec{r}}\right|\phi_{j'}^{(\text{In})}(\vec{r})\right)\\&\qquad=-\tfrac{1}{2}\sum_{j,j'}T_{jj'}\ .\end{aligned}\tag{20}$$

In (20) $\phi_j(\vec{r})$ and $\phi_{j'}(\vec{r})$ are one-electron molecular orbitals appearing in the determinants $\Phi_I^{(\text{In})}$ and $\Phi_{I'}^{(\text{In})}$. The summation over j and j' is restricted by the Slater rules. Applying Green's theorem separately to each term of (20) (we replace the normal derivative $\partial/\partial n$ by $\partial/\partial r$ in our spherical case) we find

$$\begin{aligned}T_{jj'}&=\int_{r=0}^{r=r_0}\int_{\hat{r}}\phi_j^{(\text{In})}(\vec{r})\nabla^2_{\vec{r}}\phi_{j'}^{(\text{In})}(\vec{r})d^3r\\&\equiv V_{jj'}+G_{jj'}\end{aligned}\tag{21}$$

with

$$V_{jj'}=\int_{\hat{r}}\phi_j^{(\text{In})}(\vec{r}_0)\left[\frac{\partial}{\partial r}\phi_{j'}^{(\text{In})}(\vec{r})\right]_{r_0}d\hat{r}\ ,$$

$$G_{jj'}=-\int_{r=0}^{r=r_0}\int_{\hat{r}}\vec{\nabla}_{\vec{r}}\phi_j^{(\text{In})}(\vec{r})\cdot\vec{\nabla}_{\vec{r}}\phi_{j'}^{(\text{In})}(\vec{r})d^3r\ .$$

The matrix element $G_{jj'}$ is symmetric while $V_{jj'}$ is a nonsymmetric one-electron surface term. Using (16) we rewrite it as

$$\begin{aligned}V_{jj'}&=\int_{\hat{r}}\phi_j^{(\text{In})}(\vec{r}_0)\left[\frac{\partial}{\partial r}\phi_{j'}^{(\text{In})}(\vec{r})\right]_{r_0}d\hat{r}\\&=\sum_L F_{(Lj)}^{(\text{In})}(r_0)\left[\frac{\partial}{\partial r}F_{(Lj')}^{(\text{In})}(r)\right]_{r_0}\\&=-\sum_L b_{(Lj')}^{(\text{In})}(r_0)F_{(Lj)}^{(\text{In})}(r_0)F_{(Lj')}^{(\text{In})}(r_0)\ .\end{aligned}\tag{22}$$

As $\underline{T}$ is a one-electron property matrix, it is block diagonal in irreducible representation (IR) and following (22) it will be symmetric if we require the same $b_{(Lj)}^{(\text{In})}$ for each IR. The replacement in $\underline{V}$ of $b_{(Lj)}^{(\text{In})}(r_0)$ by $b_\beta^{(\text{Out})}(r_0,k_\beta,\mu_\alpha)$ will satisfy the above requirement of symmetry (Hermiticity) of $\underline{V}$, $\underline{T}$, and $\underline{H}$ matrices as well as the requirement of the continuity of the Slater-determinant logarithmic discussed earlier in this subsection.

In practice, we use the following procedure to obtain the molecular-orbital (MO) basis $\underline{\phi}^{(\text{In})}$ which is a function of μ_α and satisfies the requirement of continuity and Hermiticity. We start from a trial MO written for convenience as a line vector $\underline{\phi}^{\infty}$. We rewrite (22) as

$$B_{jj'}=\sum_L B_{jj'}^{(L)}=\sum_L\left[F_{(Lj)}^{(\text{In})}(r_0)\left[\frac{\partial}{\partial r}F_{(Lj')}^{(\text{In})}(r)\right]_{r_0}+b_\beta^{(\text{Out})}(r_0,k_\beta,\mu_\alpha)F_{(Lj)}^{(\text{In})}(r_0)F_{(Lj')}^{(\text{In})}(r_0)\right]=0\ ,\quad\forall j,j',L. \tag{23}$$

Now, we define a new matrix $\underline{\mathscr{B}}$ similar to $\underline{B}$ but with $\underline{\phi}^{(\mathrm{In})}$ replaced by $\underline{\phi}^{(\infty)}$ in the definition. This matrix is non-null and our task is to change $\underline{\phi}^{(\infty)}$ such as $\underline{\mathscr{B}}=\underline{B}=0$. We note that by a unitary transformation, we cannot change the rank of $\underline{\mathscr{B}}$ and therefore constrain the matrix to be null. But we can set $\underline{\mathscr{B}}$ to zero with the help of additional basis functions $\underline{\phi}(s)$ one per channel β. These functions are centered at the molecular center of mass and therefore can be written as

$$\begin{aligned}\phi_\beta^{(s)}(\vec{r}_0)&=Y_L(\hat{r}_0)F^{(s)}_{(n^+\Lambda^+L)}(r_0)\\&=Y_L(\hat{r}_0)F_\beta^{(s)}(r_0)\;.\end{aligned}\tag{24}$$

We have used β in place of L in (24) as this notation is unambiguous in the many-core case. Next, we write a new MO under the following form:

$$F^{(\mathrm{NIn})}_{(Lj)}(r_0)=F^{(\infty)}_{(Lj)}(r_0)+F_\beta^{(s)}(r_0)c^{(s)}_{\beta j}\;,\tag{25}$$

where in (25) the superindex (NIn) stands from nonorthogonal inner region and $c^{(s)}_{\beta j}$ is found on the condition that $\mathscr{B}^{(L)}_{jj'}$ be identically zero. Introducing (25) in (23) in place of $F^{(\mathrm{In})}$ we obtain

$$C^{(s)}_{\beta j}=-\frac{\left[\left[\dfrac{d}{dr}+b_\beta^{(\mathrm{Out})}(r_0,k_\beta,\mu_\alpha)\right]F^{(\infty)}_{(Lj)}(r)\right]_{r_0}}{\left[\left[\dfrac{d}{dr}+b_\beta^{(\mathrm{Out})}(r_0,k_\beta,\mu_\alpha)\right]F^{(s)}_{(Lj)}(r)\right]_{r_0}}\;.\tag{26}$$

By using (24)–(26), the MO of the inner region setting $\underline{\mathscr{B}}$ to zero is given by the following transformation from the $\underline{\phi}^{(\infty)}$:

$$\phi_j^{(\mathrm{NIn})}(\vec{r})=\phi_j^{(\infty)}(\vec{r})+\sum_\beta^{(\lambda)}\phi_\beta^{(s)}(\vec{r})c^{(s)}_{\beta j}\;.\tag{27}$$

Here $\underline{\phi}^{(\mathrm{NIn})}$ is a MO basis of the same size as $\underline{\phi}^{(\infty)}$, and we sum over all channels having the same projection λ of the angular momentum on the internuclear axis. Finally, we orthogonalize $\underline{\phi}^{(\mathrm{NIn})}$ to obtain the MO basis $\underline{\phi}^{(\mathrm{In})}$ we shall use to construct (11c). This last MO basis preserves the correct behavior of $\underline{\phi}^{(\mathrm{NIn})}$ as the orthogonalization could not change the rank of $\underline{\mathscr{B}}$.

In this subsection we have set up our iterative-variational procedure. We introduce a piecewise-continuous one-electron MO basis $\underline{\phi}^{(\mathrm{In})}$. This basis used in the construction of (11) solves the problems [(i)–(iii)] and meets the simultaneous requirements of (12) and (11).

C. Total-wave-function continuity. Normalization and mixing coefficients

As a last step of EIVEA, we must take the total function Ψ_α and its first derivative continuous across the sphere surface:

$$N_\alpha(\Psi_\alpha^{(\mathrm{In})})_{r_0}=(\Psi_\alpha^{(\mathrm{Out})})_{r_0}$$

$$\text{and}\tag{28}$$

$$N_\alpha\left[\frac{\partial\Psi_\alpha^{(\mathrm{In})}}{\partial r}\right]_{r_0}=\left[\frac{\partial\Psi_\alpha^{(\mathrm{Out})}}{\partial r}\right]_{r_0}\;.$$

In (28) we require the total wave function to be energy normalized in accordance with the normalization of the outer-region wave function $\Psi_\alpha^{(\mathrm{Out})}$. Now, the iterative-variational solution $\Psi_\alpha^{(\mathrm{In})}$ obtained in the preceding subsection is converted, using the continuity equation (28) to the collision wave-function form [Eq. (8)]. Consequently, we call this procedure In-Out continuity as opposed to the CSF logarithmic derivative continuity [Eq. (13)] where we start from the outer-region function. As in the preceding subsection, we enforce the continuity (28) separately for each element β of $\Psi_\alpha^{(\mathrm{In})}$ with $\Psi_\alpha^{(\mathrm{Out})}$. We rewrite the inner-region expansion (1) at r_0 using (14) and (15) as

$$\begin{aligned}[\Psi_\alpha^{(\mathrm{In})}(1,2,\ldots,N)]_{r_0}&=\sum_I C_{I\alpha}\sum_L\Phi_{I^+}^{\Lambda^+}(1,2,\ldots,N-1)Y_L(\hat{r}_0)F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)\\&=\sum_L Y_L(\hat{r}_0)\sum_I F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)\Phi_{I^+}^{\Lambda^+}(1,2,\ldots,N-1)C_{I\alpha}\;,\end{aligned}\tag{29}$$

where we can reverse the two summations as they are independent from each other. Multiplying Eq. (29) by (9a) and integrating over the $N-1$ electrons (element of integration $d\tau'$) and the angular part of the Nth electron and using Eq. (7), we obtain

$$\int\Psi_{(n^+\Lambda^+)}(1,2,\ldots,N-1)Y_{L'}(\hat{r}_0)(\Psi_\alpha^{(\mathrm{In})}(1,2,\ldots,N))_{r_0}d\tau' d\hat{r}_0=\sum_I^{(n^+,\Lambda^+)}D_{I^+(n^+\Lambda^+)}F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)C_{I\alpha}\;,\tag{30}$$

where in (30) orthogonality between the ionic cores and spherical harmonics has been used and that only the configurations having the same ionic core (n^+,Λ^+) have been retained in the summation. We proceed similarly for the outer-region function (8) which is multiplied by (9a) and then integrated in the same way as (30). Using the first expression (28) we find the following continuity requirement:

$$\mathcal{F}_{\beta\alpha}(r_0,k_\beta)=N_\alpha \sum_{I}^{(n^+,\Lambda^+)} D_{I^+(n^+\Lambda^+)}F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)C_{I\alpha} \; . \tag{31}$$

The expression (31) corresponds to the expression (3.36) of Lee[19] generalized for the CI mixing. Introducing (9b) in (31) we find the interchannel mixing coefficients $\underline{U}$:

$$U_{\beta\alpha}=\frac{N_\alpha \sum_{I}^{(n^+,\Lambda^+)} D_{I^+(n^+\Lambda^+)}F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)C_{I\alpha}}{f_l(r_0,k_\beta)\cos(\pi\mu_\alpha)-g_l(r_0,k_\beta)\sin(\pi\mu_\alpha)} \; . \tag{32}$$

Using the unitarity of $\underline{U}$ demonstrated by Lee,[19] we can find the normalization coefficient

$$N_\alpha^{-2}=\sum_{n^+\Lambda^+L}\left[\frac{\sum_{I}^{(n^+,\Lambda^+)} D_{I^+(n^+\Lambda^+)}F^{(\mathrm{In})}_{(Lj)\alpha}(r_0)C_{I\alpha}}{f_l(r_0,k_\beta)\cos(\pi\mu_\alpha)-g_l(r_0,k_\beta)\sin(\pi\mu_\alpha)}\right]^2 . \tag{33}$$

The preceding derivation only takes the first equation (28) into account. The continuity of the derivative of the wave function is automatically fulfilled as $\underline{U}$, $\underline{\mu}$, and $\underline{N}$ are independent of r. Note that in the above derivation, the preceding subsection continuity of the logarithmic derivative of each CSF was implicitly assumed.

D. Inner-region one-electron molecular basis

The choice of a one-electron molecular basis for the inner-region expansion method is a nontrivial problem as this choice determines the stability of the results obtained with the present EIVEA. Buttle,[25] Zvijac, Heller, and Light,[26(a)] and also Rudge[20] and Nesbet[26(b)] have pointed out that we must find a separable H_0 [in our case $(N-1)$ electron and Nth-electron separable] having known solutions and being as close as possible to the full Hamiltonian. These known zeroth-order solutions will then be used as a basis set in our actual calculations. The obvious zeroth-order choice here is the product of wave functions of the outer-region with the Hamiltonian $H_0=H^+(1,2,\ldots,N-1)+H(N)$ and $H^{\mathrm{int}}=0$. It satisfies separate equations (10) where (10a) is an approximate solution to the ionic problem. As this solution is independent of $\epsilon_{(n^+\Lambda^+L)}$ of (4) and identical for inner- and outer-region calculations, it will only indirectly influence the collision result. The equation (10b), being a second-order differential equation, has two exact solutions: the Coulomb regular (f_l) and irregular (g_l) functions. These exact solutions correspond to the case of infinite basis set. Nesbet[26(b)] has pointed out that for expansion methods the convergence, with the number of basis functions, is extremely rapid if we use in the inner-region regular and irregular continuum functions.

The bound-state $(N-1)$-electron wave function of the ionic core is given by (7) as a linear combination of Slater determinants built on one-electron MO functions. These molecular functions are taken here as linear combinations of (Slater) atomic orbitals (LCAO) centered on each atom. This ionic-core LCAO, together with the Coulomb regular and irregular functions [solution of (10b)], will therefore form the one-electron molecular basis in our problem called linear combination of Coulomb and Slater functions (LCCSF). The irregular Coulomb wave function of this basis is made regular by matching it at the turning point to a function having the correct r^{l+1} behavior at the origin. In practical calculations this basis is augmented by one-center diffuse functions to represent the influence of H^{int} on the solutions Ψ_α [Eq. (11a)].

The present EIVEA with the particular LCCSF choice of basis set allows, as demonstrated by Rudge[20] and Nesbet[26(b)] in the case of a model problem, the eigenphase to converge monotonically to the true value. The condition for this monotonic convergence is that the bound-state eigenvalues supported by the actual potential remain stable when the basis set is augmented.

III. TOTAL WAVE FUNCTION OF THE FINAL STATE AND DIPOLE-TRANSITION PROBABILITY. SUMMARY OF THE MQDT FORMULATION (REF. 16)

A. Final-state electronic vibrational and rotational wave function

In the preceding section we have discussed the electronic wave function of the final state. An expression of it, relevant for the present analysis, was given in Eq. (8) in terms of asymptotic electronic channels $|\beta\rangle = |n^+\Lambda^+L\rangle$ defined in (3). The total electronic vibrational and rotational wave function is given here, as mentioned in the Introduction, in terms of asymptotic laboratory-frame channels $|i\rangle$ used for the description of high-Rydberg and continuum electrons in the MQDT:

$$|i\rangle = |n^+\Lambda^+l,v^+N^+\rangle \ , \qquad (34)$$

where l is the departing electron angular momentum, v^+ the vibrational quantum number of the ion, and N^+ represents the type of coupling between angular momenta in the laboratory frame defining the corresponding rotational functions. For $|i\rangle$ channels, total angular momentum J and its projection M on the laboratory frame is conserved. Further, when compared with $|i\rangle$ channels, $|\beta\rangle$ will be augmented by $\vec{R}$ to give $|\beta\vec{R}\rangle$. Finally, we note that our $|i\rangle$ channels are the same as $|iv^+N^+\rangle$ and $|i\rangle$ channels introduced by Jungen and Atabek (JA) [Ref. 16(a)] and Jungen and Dill (JD) [Ref. 16(b)].

To proceed further, we express the conservation of the total energy of the N-electron system taking into account the vibrational-rotational energy:

$$E = E_{n^+\Lambda^+v^+N^+} + \epsilon_{n^+\Lambda^+l,v^+N^+} \ , \qquad (35)$$

where $\epsilon_{n^+\Lambda^+l,v^+N^+}$ is the kinetic energy of the excited electron. In (35) we have added vibrational and rotational energies to the electronic energy of (4) and therefore $E \neq E^e$ and, following the convention of Eq. (4), we set $\epsilon_{n^+\Lambda^+l,v^+N^+} = \epsilon_{n^+\Lambda^+L}$.

In the standard MQDT calculation (see, e.g., JD) all the channels are considered as open and only when solving the MQDT system is the condition that some channels are closed introduced. Here, we maintain this approach but we also introduce, following Greene *et al.*[15(c)], strongly closed channels, defined in the Introduction. In Eq. (8), these channels are already implicit and they only influence the numerical value of the quantum defect $\underline{\mu}$ and mixing coefficients $\underline{U}$ of the remaining open channels. The link between the electronic calculation performed using EIVEA and MQDT is established through the relation between $|\beta\vec{R}\rangle$ and $|i\rangle$ channels. We follow the procedure detailed by JA relating the molecular-frame Born-Oppenheimer products to $|i\rangle$ channels. For a solution ρ, the result of different transformations is expressed in a simple form in terms of channels $|i\rangle$ by Eq. (5) of JD:

$$\Psi_\rho^{JM} = \sum_i |i\rangle^{lJM} \sum_{i'} [f_l(r,k_i)\langle i|c|i'\rangle - g_l(r,k_i)\langle i|s|i'\rangle]\mathscr{B}_{i'\rho} \ , \qquad (36)$$

where the core ionic state $|i\rangle^{lJM}$ is written as

$$|i\rangle^{lJM} = |n^+\Lambda^+\rangle \sum_m \Theta^{JM}_{v^+N^+}(\vec{R})Y_{lm}(\hat{r}') \times (lm,N^+M-m|JM) \ .$$

Here $|n^+\Lambda^+\rangle$ is the electronic wave function of the ion, $\Theta^{JM}_{v^+N^+}(\vec{R})$ is its vibrational-rotational function, $\hat{r}'$ refers to the laboratory frame and $(lm,N^+M-m|JM)$ is a Clebsh-Gordan coefficient. The coefficients $\langle i|c|i'\rangle$, $\langle i|s|i'\rangle$, and $\mathscr{B}_{i'\rho}$ can be expressed as

$$\langle i|c|i'\rangle = \sum_\Lambda \langle N^+|\Lambda\rangle\langle N^+v^+|\bar{c}_{\beta\beta'}|v^{+\prime}N^{+\prime}\rangle \times \langle\Lambda|N^{+\prime}\rangle \ , \qquad (37\text{a})$$

where when all the electronic channels are open

$$\bar{c}_{\beta\beta'} = c_{\beta\alpha}\delta_{\beta'\alpha} = U_{\beta\alpha}(R)\cos[\pi\mu_\alpha(R)]\delta_{\beta'\alpha} \ ,$$

$$\mathscr{B}_{i'\rho} = \mathscr{B}_{\beta' v^{+\prime}N^{+\prime},\rho} = B_{v^{+\prime}N^{+\prime},\rho}\delta_{\beta'\alpha} \ , \qquad (37\text{b})$$

and when some electronic channels are closed

$$c_{\beta\beta'} = \sum_{\alpha'} U_{\beta\alpha'}(R)\cos[\pi\mu_{\alpha'}(R)]U^\dagger_{\beta'\alpha'}(R) \ ,$$

$$\mathscr{B}_{i'\rho} = \mathscr{B}_{\beta' v^{+\prime}N^{+\prime},\rho} = B_{v^{+\prime}N^{+\prime},\rho}\delta_{\beta'\alpha} \ . \qquad (37\text{c})$$

In (37b) and (37c) $B_{v^{+\prime}N^{+\prime},\rho}$ is identical to $B_{v^{+\prime}N^{+\prime}}$ defined by JA and the cases of electronically open and closed channels have been discussed in the atomic case by Lu.[15(b)]. Equations (37b) reduced to only one electronic channel ($U_{\beta\alpha} = 1$) have been explicitly treated by JA. Equations (37c) have been given in a slightly modified form by Dill.[16(d)]. Equations (37b) and (37c) have been obtained by introducing in the JA derivation the electronic wave functions of the following form:

$$\Psi^{(e)}_{\beta'} = \delta_{\beta'\alpha}\Psi^{(e)}_\alpha \ , \qquad (38\text{a})$$

$$\Psi^{(e)}_{\beta'} = \sum_{\alpha'} \Psi^{(e)}_{\alpha'} U_{\beta'\alpha'} \ , \qquad (38\text{b})$$

where the $\Psi^{(e)}_\alpha$ have been defined in (8) and we have replaced the superindex (Out) with (e) [(e) stands electronic]. Equation (38b) allows for a recombination of electronic solutions α' to give the needed flexibility to the MQDT system of equations to fulfill the condition that the coefficient of the rising exponential is zero in the case of closed electronic channels.

Equations (37) allow for the interaction between the electronic channels: l mixing and interionic core mixing. These equations can be viewed as a generalization of JA and JD equations following Lu[15(b)] and Dill[16(d)]. Now the MQDT system of equations can be solved for the standing-wave functions following the procedure of JD (Eqs. 7 and 15). Finally, following JD and regardless of the spectral region studied, a unique procedure can be used to impose the outgoing complex normalization to the real standing-wave function Ψ_ρ. The resulting function is the total function of the final state.

B. Dipole-transition probability

In the calculation of the photoionization cross section, the dynamical quantity to be found is the transition probability between the initial bound state $|\Lambda''J''M''\rangle$ and the final continuum one $\Psi_\rho^{J'M'}(1,2,\ldots,N;\vec{\mathrm{R}})$ (Eq. 36). Here, we have used the spectroscopic notation for the initial and final states, changing for this last state the J and M used until now to J' and M'. Assuming only one Born-Oppenheimer product in the initial state, which in this case is a fairly good approximation, we write the corresponding wave function, in spectroscopic notation $|\Lambda''J''M''\rangle$, as

$$|\Lambda''J''M''\rangle=\Psi^{(\mathrm{init})}(1,2,\ldots,N;\Lambda'',R)\Theta_{v''\Lambda''}^{J''M''}(\vec{\mathrm{R}}) , \tag{39}$$

where $\Psi^{(\mathrm{init})}(1,2,\ldots,N;\Lambda'',R)$ is the electronic wave function of the form (1):

$$\Psi^{(\mathrm{init})}(1,2,\ldots,N;\Lambda'',R) = \sum_I C_I^{(\mathrm{init})}\Phi_I^{(\mathrm{init})}(1,2,\ldots,N;\Lambda'',R) \tag{40}$$

and $\Phi_I^{(\mathrm{init})}$ is an initial-state CSF. $\Theta_{v''\Lambda''}^{J''M''}(\vec{\mathrm{R}})$ is the vibrational-rotational wave function of the initial state.

The transition probability from the initial $|\Lambda''J''M''\rangle$ (Eq. 39) to final $\Psi_\rho^{J'M'}$ (Eq. 36) states is given in dipole approximation as

$$\langle\Psi_\rho^{J'M''}|\vec{\mathrm{r}}|\Lambda''J''M''\rangle=\sum_{(\beta',v^{+\prime},N^{+\prime})}\mathscr{B}_{(\beta v^{+}N^{+})',\rho}\sum_{\Lambda}\int dR\,\langle N^{+\prime}|\Lambda\rangle\chi_{v^{+\prime}}^{N^{+\prime}}(R)\bar{d}_{\beta'}(R) \times\chi_{v''}^{\Lambda''J''}(R)\langle\Lambda|J''\rangle(J'M''|J''M'',10) . \tag{41}$$

In (41) we have used the transition-probability expression as developed by Dill.[27] The vibrational wave functions of the initial and final states are $\chi_{v''}^{\Lambda''J''}(R)$ and $\chi_{v'}^{\Lambda'J'}(R)$. $\langle N^{+\prime}|\Lambda\rangle$ and $\langle\Lambda|J''\rangle$ are the frame transformation coefficients defined in Eq. (20) of JA. The electronic transition probability $\bar{d}_{\beta'}$ is written in the transition density-matrix formulation of Lowdin[28] as

$$\bar{d}_{\beta'}(R)=\left[\frac{4\pi}{3}\right]^{1/2}\delta_{\beta'\alpha}N_\alpha\sum_{j,j'}t_{jj'}\Gamma_\alpha(j'|j) \tag{42a}$$

and

$$\bar{d}_{\beta'}(R)=\left[\frac{4\pi}{3}\right]^{1/2}\sum_{\alpha'}U_{\beta'\alpha'}N_{\alpha'}\sum_{j,j'}t_{jj'}\Gamma_{\alpha'}(j'|j) . \tag{42b}$$

The two expressions (42) correspond to having all the asymptotic electronic channels opened and some asymptotic electronic channels closed, respectively, as discussed in the preceding subsection. N_α is the energy-normalized constant defined in (33). The one-electron transition integral and the corresponding first-order transition density matrix are written as

$$t_{jj'}=\langle\phi_j(\vec{\mathrm{r}})|rY_{1m_\gamma}(\hat{r})|\phi_{j'}(\vec{\mathrm{r}})\rangle \tag{43a}$$

and

$$\Gamma_\alpha(j'|j)=\sum_{I}^{(j)}\sum_{I'}^{(j')}C_I^{(\mathrm{init})}C_{I'\alpha}^{(\mathrm{fin})*} . \tag{43b}$$

In (43a) $Y_{1m_\gamma}(\hat{r})$ is the spherical harmonic of the laboratory to molecular-frame transformation of the dipole operator and $\phi_j(\vec{\mathrm{r}})$ is the one-electron molecular orbital defined in Sec. II. In (43b) $C_I^{(\mathrm{init})}$ and $C_{I'\alpha}^{(\mathrm{fin})*}$ are the CI coefficients defined in (40) for the initial state [superscript (init)] and in (1) for the final state [superscript (fin)].

Equation (41) gives the transition probability for the final state ρ. This transition matrix element can be used in Eq. (18a) of JD and the photoionization oscillator strength calculated following Eq. (16) of JD. As in the case of the final-state wave-function equation, Eq. (36), the transition-probability formula (41) derived in this subsection allows us to generalize the MQDT expressions as given by JA and JD to the case of l mixing and interionic core mixing. The electronic transition probability $\bar{d}_{\beta'}(R)$ (Eq. 42) is written in the transition-matrix formulation of Lowdin[28] which allows the use of the CI wave function for the initial and final states and therefore the calculation of $\bar{d}_{\beta'}(R)$ taking into account the strongly closed channels defined in the Introduction.

IV. H_2 PHOTOIONIZATION CROSS SECTION

To illustrate the theory developed in the preceding sections, we have chosen to calculate the low-resolution H_2 photoionization spectrum:

$$H_2(X\,^1\Sigma_g^+)+h\nu \rightarrow H_2^+(X\,^2\Sigma_g^+)+e\ . \tag{44}$$

H_2 is a simple molecule but the molecular potential is nonspherical and one nuclear degree of freedom is present. As stated in the Introduction, these difficulties appear for any more complicated molecules and therefore H_2 is a good example to start with.

Let us first analyze the preceding work concerning the calculation of the final-state properties and photoionization spectrum of this molecule. The continuum electronic function entering in the final-state wave function has been taken as a plane wave,[29] one-center Coulomb wave,[11(a),30] two-center Coulomb wave,[31] one-center deformed Coulomb wave,[32] one-center fixed-core static exchange molecular close-coupling function,[1–4,33] and continuum multiple-scattering function.[9] All these different functions are obtained by explicit resolution of the continuum-electron Schrödinger equation. Another approach initiated by Langhoff[5] and applied to H_2 photoionization by O'Neil and Reinhardt[6] and to autoionization widths by Hazi[11(b)] represents the continuum function by the L^2 bound basis set using the Stieltjes-Chebyshev imaging technique.[5] The initial electronic state in H_2 photoionization has been calculated either at the SCF level or with the two-configuration (Weinbaum approximation[34]) wave function, except in the case of Ford *et al.*,[30] O'Neil and Reinhardt,[6] and Kirby *et al.*,[11(a)] where an elaborate electronic CI wave function has been used. From the preceding initial and final states, the electronic photoionization cross section in the dipole approximation, was calculated by standard procedure.[35,37] The total photoionization cross section was usually obtained in the Born-Oppenheimer (BO) framework with a further simplification, the Franck-Condon (FC) approximation. The results obtained are reasonably accurate as compared with the full BO approximation when the energy conservation of the entire electron-ion system is taken into account[6,37] [as in our Eqs. (4) and (35)].

The experimental photoionization and photodissociation spectra of the H_2 molecule are complex. The synchrotron radiation[38] and low-resolution electron-energy-loss[39] spectra exhibit a smooth photoionization cross section which is reasonably well reproduced by the elaborate calculations of O'Neil and Reinhardt.[6] The high-resolution absorption spectrum of Dehmer and Chupka[17] [see also Ref. (38)] just above the first ionization threshold (15-18 eV), exhibits very complicated structure due to rotational and vibrational autoionization and the calculations cited above can not take these features into account. As stated in the Introduction, quantitative agreement between theory and experiment has been reached in the region near the first ionization threshold. The calculation has been performed with the semiempirical MQDT[16] where electronic parameters were semiempirical or extrapolated from discrete region data. Above 18.07 eV (686 Å) and below the second electronic ionization threshold, two new physical phenomena appear: first, the dissociation channel $H_2^+(X\,^2\Sigma_g^+)\rightarrow H+H^+$ is open; second, several super excited bound states, only one being dipole-transition allowed ($^1\Sigma_u^+$: $2p\sigma_u 2s\sigma_g$) are coupled to the ionization and dissociation continua. A $^1\Sigma_u^+$ superexcited state seems responsible for the anomalous angular distribution behavior near 27 eV recently reported.[21] Moreover, the H^+ kinetic-energy spectrum[22] has a maximum at 3 eV which could be explained by the autoionization from the same $^1\Sigma_u^+$ repulsive state.[11(a)]

As this section must be viewed as a test of EIVEA mainly, we will introduce in the next subsection a simplified version of the theory developed in Sec. III.

A. Simplified MQDT formulation

In this subsection, we rewrite the Sec. III formulas by neglecting the vibrational and rotational interchannel coupling and by summing over all rotational levels. All the channels are open and degenerated and we restrict to only one ionic core $|n^+\Lambda^+\rangle = X\,^2\Sigma_g^+$. We further restrict l to p and f waves and m to 0 and 1. Each of these electronic channels is augumented by vibrational and rotational functions giving the following asymptotic MQDT channels:

$$|i\rangle=|lv^{+}N^{+}\rangle=\begin{cases}|1v^{+}N^{+}\rangle\,,\\|3v^{+}N^{+}\rangle\,.\end{cases}\tag{45}$$

We start from the relevant expressions of the final-state wave function Eq. (36), 37(a), and 37(b) and transition-probability Eqs. (41) and 42(a). As we neglect vibrational and rotational interchannel coupling, $\mathscr{B}_{i'\rho}=1$. We introduce the FC approximation[40] calculating the R-dependent $\underline{U}$ and $\underline{\mu}$ at some internuclear distance R_c. We rewrite 37(a) with 37(b) for the open-channel case as

$$\begin{aligned}\langle i\,|\,c\,|\,i'\rangle&=\sum_{\Lambda}\langle N^{+}\,|\,\Lambda\rangle U_{L,\alpha}(R_c)\\&\quad\times\cos[\pi\mu_\alpha(R_c)]\langle\Lambda\,|\,N^{+}\rangle\\&=W_{lv^{+}N^{+},\rho}\cos(\pi\tau_\rho)\end{aligned}\tag{46}$$

and a similar equation with the sine instead of cosine. As there is no vibrational-rotational coupling $\underline{W}$ and $\underline{i}$ can be directly obtained from (46) without solving the MQDT system of equations. The wave function (36) is rewritten in the present simplified case as

$$\Psi_\rho^{J'M'}=\sum_{l,v^{+},N^{+}}|lv^{+}N^{+}\rangle[f_l(r,k_{lv^{+}N^{+}})W_{lv^{+}N^{+},\rho}\cos(\pi\tau_\rho)-g_l(r,k_{lv^{+}N^{+}})W_{lv^{+}N^{+},\rho}\sin(\pi\tau_\rho)]\,.\tag{47}$$

With the final state defined above, we now calculate the photoionization cross section. The initial electronic state is the ground state $|{}^1\Sigma_g^{+}\rangle$ and we restrict the vibrational levels to $v''=0$. Using the FC approximation we rewrite dipole-transition probability (41) as

$$\langle\Psi_\rho^{J'M''}\,|\,\vec{\mathrm{r}}\,|\,\Lambda''J''M''\rangle=\sum_{\Lambda}\langle N^{+\prime}\,|\,\Lambda\rangle\bar{\bar{d}}_{\beta'}(R_c)\langle\chi_{v^{+\prime}}^{N^{+\prime}J'}\,|\,\chi_{v''}^{\Lambda''J''}\rangle\langle\Lambda\,|\,J''\rangle(J'M''\,|\,J''M'',10)\,,\tag{48}$$

where $\bar{\bar{d}}_{\beta'}(R_c)$ is the electronic transition moment as given by 42(a) but calculated in the FC approximation at R_c. The complex-outgoing-energy—normalized transition moment takes the following expression [see JD, Eq. 18(a)]:

$$D_{\bar{i}}^{J''M''}=\sum_{\rho}e^{i\pi\tau_\rho}W_{\bar{i}\rho}\langle\Psi_\rho^{J'M''}\,|\,\vec{\mathrm{r}}\,|\,\Lambda''J''M''\rangle\,.\tag{49}$$

The photoionization oscillator strength and the photoionization cross section are now written in atomic units as

$$\left[\frac{df}{dE}\right]_{\bar{i}}=2h\nu(2J''+1)^{-1}\sum_{M''}(D_{\bar{i}}^{J''M''})^2\tag{50}$$

and

$$\sigma_{v^{+}}(\epsilon_{\bar{i}})=\frac{\pi e^2h}{mc}\sum_{N^{+}}\left[\frac{df}{dE}\right]_{\bar{i}}\,.\tag{51}$$

The above, simplified formulas will be used in the following to calculate quantum defects, mixing coefficients, and photoionization cross section.

B. Framework of the calculation and final-state results

The quantum defects $\underline{\mu}$ and the mixing coefficients $\underline{U}$ have been calculated by the EIVEA described in Sec. II. The corresponding programs have been developed from the molecular integral program written by Schaefer[41] and the ALCHEMY system of programs.[42] The Schaefer molecular integral program calculates all the integrals numerically and therefore is appropriate for our LCCSF basis set. It has been partly recoded and it now allows for three atomic centers and finite-range calculation of integrals.[43] It has been further extended, by one of us (G.R.) to allow for iterative variation of $\underline{\mu}$ and calculation of the logarithmic derivative at the sphere surface required for the EIVEA. The ALCHEMY CI program has then been used for the finite-range CI calculations. The interface between the two programs has been written by one of us (G.R.). Finally, the dipole-transition probability and the photoionization cross section have been calculated using a program written by one of us (G.R.) following the formulas given in Sec. III B and IV A.

In practice, the one-electron LCCSF (See Sec. II D) molecular basis set used in the calculation of states appearing in (44) was constructed as follows. First, using the SCF ALCHEMY code,[42] the MOs of the $X\,{}^1\Sigma_g^{+}$ state have been calculated with a Liu[44] atomic basis truncated to the σ and π molecular subspaces; then a subset of $2\sigma_g$, $1\sigma_u$, $1\pi_u$, and $1\pi_g$ two-center orbitals has been retained in the further calculations. This two-center molecular basis set has then been augumented by $2\sigma_g$, $9\sigma_u$, $9\pi_u$, and $1\pi_g$ diffuse one-center (s,p,d,f) center-of-mass orbitals (see Table I). The main continuum character of σ_u and π_u orbitals has been taken into account since

TABLE I Additional[a] center-of-mass Slater functions for the inner-region LCCSF basis.

Symmetry	n	l	ζ[b]
σ_g	4	0	3.6364
	3	0	1.3043
σ_u or	6	1	8.5714
π_u	4	1	2.8571
	6	1	2.5
	2	1	0.5
	8	1	1.2308
	6	3	8.5714
	5	3	3.5714
	6	3	2.2222
	6	3	1.5
π_g	3	2	1.5

[a] The two-center σ and π basis is taken from Liu, Ref. (44). We have already added the Coulomb regular and irregular functions (p and f components) to this initial basis.

[b] The standard definition of the Slater orbital, which can be found in, e.g., ALCHEMY program reference (42) has been assumed.

two Coulomb (regular and irregular) one-center center-of-mass functions have been present for each p and f components. The above $4\sigma_g, 10\sigma_u, 10\pi_u, 2\pi_g$ basis set is $\underline{\phi}^{(\infty)}$, we introduced in Sec. II B. It is transformed into the orthogonal basis set $\underline{\phi}^{(\text{In})}$ having the correct boundary condition following the procedure developed in that subsection. Using a bound-state version of EIVEA [i.e., solving Eq. (11) in an infinite box] with the LCCSF basis described above, we have calculated the $H_2(X\,{}^1\Sigma_g^+)$ and $H_2{}^+(X\,{}^2\Sigma_g^+)$ bound states at $R=1.4$ a.u.; the energies and the ionization potentials are given in Table II. The energy of the $X\,{}^1\Sigma_g^+$ state has been obtained with a wave function of 121-configuration-state functions and is close to the Liu[44] and Kolos and Wolniewicz[45] values, the difference being attributable, as stated by O'Neil and Reinhardt,[6] to the truncation of the one-electron LCCSF basis set to the σ and π subspace. The energy of the $X\,{}^2\Sigma_g^+$ state of $H_2{}^+$ has been calculated with four CSF and it compares well with the value given by the very accurate wave function of Wind.[46] The CI ionization potential is close to the vertical ionization potential taken from the experimental compilation of Sharp.[47] We have also calculated the transition probability between the initial $(X\,{}^1\Sigma_g^+)$ and final state $(B\,{}^1\Sigma_u^+)$ with a result close to that of O'Neil and Reinhardt[6] and Kolos and Wolniewicz.[45] From the preceding comparisons (Table II) it seems that our one-electron LCCSF and the CI expansions are appropriate for the bound states studied here. The Coulomb functions, already present in the basis, give no contribution to the calculated total electronic energies, ionization potentials, and transition probabilities of these states.

The continuum electronic $\mathscr{C}\,{}^1\Sigma_u^+$ and $\mathscr{C}\,{}^1\Pi_u$ stated ($\mathscr{C}$ stands for the continuum) are calculated using a continuum-state version of EIVEA, i.e., solving (11) with the constraint (12). The sphere dimension r_0 was determined from calculation at fixed (0.4 a.u.) kinetic energy of the departing electron.

TABLE II. Total energies in different approximations of the $X\,{}^1\Sigma_g^+$ and $X\,{}^2\Sigma_g^+$ states of H_2 and $H_2{}^+$. Ionization potential between these states ($R=1.4$ a.u.).

	Energy (a.u.)			
	Present			
State	SCF	CI	Best	Reference
$X\,{}^1\Sigma_g^+$	−1.1336	−1.1709	−1.1737 −1.1744	Liu, Ref. (44), with σ, π, δ, ϕ basis Kolos and Wolniewicz, Ref. (45) with James Coolidge function
$X\,{}^2\Sigma_g^+$	−0.5390	−0.5696	−0.5699	Wind, Ref. (46)
	Vertical			
Transition	ionization potential (eV)			
$X\,{}^1\Sigma_g^+ \to X\,{}^2\Sigma_g^+ + e$	16.1810	16.3615	16.34	Sharp, Ref. (47)

Aside from the fact that the Slater basis set is augmented slightly as r_0 increases, the results are insensitive to the r_0 value ranging from 8 to 15 a.u. In the calculations detailed below, we use the value of $r_0=8.5$ a.u. This value minimizes the number of basis functions to be considered for a converged calculation. As a further test, we have performed a series of calculations at various kinetic energies using the FCSE approximation. The ionic $X\,{}^2\Sigma_g^+$ state has been represented by only one $1\sigma_g$ orbital and the continuum states $\mathscr{C}\,{}^1\Sigma_u^+$ and $\mathscr{C}\,{}^1\Pi_u$ by configurations $1\sigma_g n\sigma_u$ and $1\sigma_g n\pi_u$, where n spans the σ_u and Π_u subspaces. The two p and f quantum defects are very close to the values obtained when using the molecular close-coupling method[1] at the same FCSE and bound basis level of approximation.[48] Next, we have performed an extended static exchange (ESE) calculation. The $\mathscr{C}\,{}^1\Sigma_u^+$ and $\mathscr{C}\,{}^1\Pi_u$ states were described, respectively, by configurations of the following forms: $n\sigma_g m_1\sigma_u$ and $n\sigma_g m_2\pi_u$ where n, m_1, and m_2 span the respective full one-electron molecular spaces. Finally, we have performed calculations at the interchannel-coupling (ICC) level adding $n\pi_g m\pi_u$ and $n\pi_g m\sigma_u$ configurations to the preceding ones for ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states, respectively.

As seen from the Fig. 1 the different calculations at $R=1.4$ a.u. are close to each other giving a σ quantum-defect sum of ~ 0.05 and a π quantum-defect sum between -0.086 and -0.064. These values are to be compared with the quantum-defect analysis[16(c)] of the Kolos and Wolniewicz[45] potential curves. As the scale of the Fig. 1 is extremely extended, the agreement between EIVEA and semiempirical MQDT is very satisfactory in the case of the π channel. However, in the σ case the difference is 0.02. A similar discrepancy, between MQDT extrapolation procedure and direct calculation, was found for μ_0 at $R=2.0$ a.u. by Takagi and Nakamura.[13] As discussed by Raoult and Jungen[16(c)] μ_σ is more sensitive to the principal quantum number than μ_π. Therefore the extrapolated μ_σ can be less accurate in this case, thus explaining the discrepancy we have found.

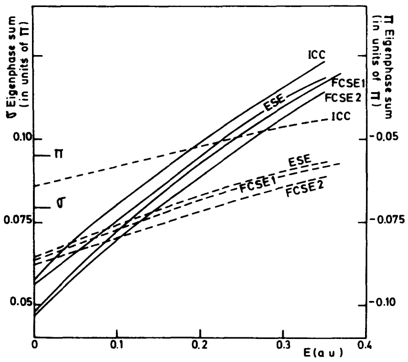

FIG. 1. β channels eigenphase sum for σ (full line, left ordinate) and π (dotted lines, right ordinate) symmetries of the departing electron and the $X\,{}^2\Sigma_g$ final ionic state ($R=1.4$ a.u.). FCSE1 results are taken from Ref. (4) and FCSE2 are our results in Fixed Core Static Exchange approximation. ESE and ICC are our Extended Static Exchange and Inter Channel Coupling approximations results as explained in the text. The two dashes for zero kinetic energies of the electron are results obtained by MQDT Rydberg-series extrapolation (Ref. 16c).

C. Photoionization cross section

We have calculated the electronic and total photoionization cross sections using the formulation given in Sec. IV A and with the same level of approximation as the calculation of the quantum defect of Sec. IV B. The electronic and total photoionization cross section results are shown in Figs. 2 and 3.

The FCSE electronic results (Fig. 2) have been compared to the calculations of Lucchese and McKoy[4] and to the molecular close-coupling calculations.[48] The Lucchese and McKoy result is slightly higher than ours and the difference at low energy is attributable to the less flexible bound atomic basis used in their calculation. The close-coupling FCSE

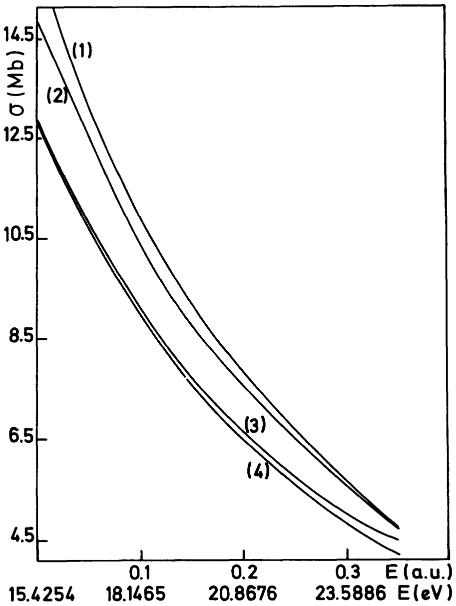

FIG. 2. Electronic photoionization cross section as function of the kinetic energy of the departing electron (or total photon energy) at $R=1.4$ a.u. (1) FCSE, calculation from Ref. 4; (2) FCSE, present calculation; (3) ESE, present calculation; (4) ICC, present calculation.

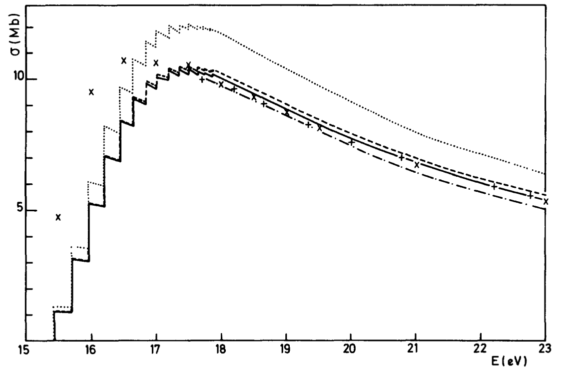

FIG. 3. Vibrationally unresolved photoionization cross section as function of photon energy. +, experimental from Ref. (49); *x*, experimental from Ref. (39); —.—.—, calculations from Ref. (6); ....., FCSE, present calculation; — — —, ESE, present calculation; ——, ICC, present calculation.

calculations[48] performed with the same bound atomic basis are indistinguishable from EIVEA-FCSE calculations at the scale of Fig. 2. The ESE and ICC calculations have lower electronic cross sections since the used initial- and final-state CI wave functions diminish the contribution of the main configurations to the cross section. Note the small difference between ESE and ICC calculations. When, as for H_2, there are no shape or other resonances present (see the different conclusion in the case of N_2 photoionization[10]), it can be concluded that the ESE level of approximation gives very satisfactory photoionization cross sections.

In Fig. 3 we have calculated the total photoionization cross section in the energy-conserving Eq. (35) FC approximation (Sec. IV A).[40] The FC factors, provided to us by Raoult and Jungen, have been used in Ref. 16(c) and correspond to the accurate potential curves of Kolos and Wolniewicz.[45] Above 17.5 eV, our results have the same shape as energy-loss (e,$2e$) (Ref. 39) and line-source experimental cross sections.[49] As has been previously pointed out,[33(c)] we find that our FCSE approximation overestimates the cross section. The other ESE and ICC approximations are very close to the experiment above 17.5 eV where the rotational-vibrational autoionization, neglected in the present calculation, is less important. We have also plotted in Fig. 3 the initial- and final-state electronic correlated results of O'Neil and Reinhardt.[6] This calculation is very good at moderate energies but is slightly lower than our calculation and experiment at higher energies. The discrepancy is most probably due to the less accurate representation of the electronic continuum at higher energies.

From the calculations presented in this section, we may conclude that the new EAQDT we have developed gives, in its simplified form, very encouraging results for the quantum defects and low-resolution photoionization cross section.

V. DISCUSSION

In this paper we have developed an EAQDT approach devised for the simultaneous calculation of direct and indirect processes in molecular photoionization. This is a global *ab initio* approach in the sense that it allows for the simultaneous treatment of electronic, vibrational, and rotational autoionization. In Sec. IV, as a test, we have applied the method to the study of the low-resolution photoionization spectrum with very encouraging results.

Let us compare EIVEA on its own with other methods calculating the electronic parameters *ab initio*. One of the existing methods, close to EIVEA and able, in principle, to introduce the electronic autoionization directly, is the R matrix.[7,8] To our knowledge, this method has not yet been applied to molecular photoionization. It is a discrete-spectrum finite-domain method, i.e., it solves Eq. (11) only once and then extracts from this result the collision information at each energy. Our EIVEA method, with one-electron molecular LCCSF basis set, is superior to the standard R-matrix method since our calculations are implicitly performed at a variationally corrected R-matrix level.[26(a)] To reach this better approximation, a calculation at each kinetic energy of the departing electron is required. Another approach described by Greene, Fano, and Strinati[15(c)] is based on explicit bound and continuum configuration mixing (i.e., introduce indirect processes) and solves formally in the atomic case the one-electron integral equation with full potential using Green's functions. Our inner-region method uses a standard bound CI method defined in a finite domain thus giving a discrete spectrum, and it is only the iterative-variational approach which introduces the electronic continuum in the calculations. Our method is better adapted to the study of molecular photoionization where the multicenter environment makes the calculation with the Green's function difficult. Our approach can easily use the particular continuum regular and irregular Coulomb functions defined by Greene, Fano, and Strinati,[15(c)] which allows for the definition of smooth electronic parameters in the electronic discrete region and through the ionization thresholds. These electronic parameters can therefore be calculated at a coarse energy mesh point unrelated with the actual spacing of electronic, vibrational, and rotational levels.

Other methods ranging from molecular close coupling[1–4] to L^2 (Refs. 5,6) are, in principle, able to introduce directly the electronic indirect processes but, to our knowledge, this level has not yet been reached. One exception is the method developed by Takagi and Nakamura[13] and applied to a *e*-H_2^+ collision. In the H_2 case, this method has been able to locate and calculate the two-electron resonances through the kinetic-energy variation of the quantum defect [τ_ρ in Eq. (46)]. Presently, this method is limited to only one spheroidal wave and does not calculate the photoionization cross section.

The molecular MQDT approach, as introduced by Fano[15(a)] and developed by Jungen and co-workers,[16] uses a semiempirical electronic parameter and includes calculations up to now with only one partial wave. This approach depends on the resolution of the existing experimental spectra. Our completely *ab initio* EAQDT method can be used in cases where the experimental information needed for the semiempirical MQDT is not available. Moreover, phenomena such as two partial-wave shape resonances and electronic autoionization cannot be treated with the semiempirical MQDT as the experimental information is not sufficient to extract the MQDT electronic parameters. They can easily be handled with EAQDT.

The next step in the test and development of the present approach is the recalculation, with the *ab initio* parameters obtained in this work, of the low-energy near-ionization-threshold region (<17.5 eV) of the photoelectron spectrum of H_2. Then the 27-eV electronic autoionization, seen in the angular distribution of the electrons,[21] is to be considered. As a further step, we shall apply our EAQDT method to the photoelectron spectrum of other molecules.

ACKNOWLEDGMENTS

We are very grateful to Christian Jungen and Dan Dill for suggesting the original idea of this work. We are indebted to P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine for making the ALCHEMY system of programs available. One of us (G.R.) is indebted to Christian Jungen, Maurice Raoult, and Annick Giusti for interesting discussions concerning the MQDT and to Christian Jungen and Hélène Lefebvre-Brion for constant encouragements during the course of this work. He acknowledges J. C. Lorquet and the Université de Liège for the permission of leave of absence and the CNRS and the FNRS for a joint fellowship during his stay at Laboratoire de Photophysique Moléculaire in Orsay.

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