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Finite-volume variational method: First application to direct molecular photoionization

H. Le Rouzo
Laboratoire de Photophysique Moléculaire du Centre National de la Recherche Scientifique, Université Paris—Sud, Bâtiment 213, F-91405 Orsay Cedex, France

G. Raşeev
Laboratoire de Photophysique Moléculaire du Centre National de la Recherche Scientifique, Université Paris—Sud, Bâtiment 213, F-91405 Orsay Cedex, France
and Département de Chimie Générale et de Chimie Physique, Université de Liège, Sart-Tilman, B-4000 Liège 1, Belgium

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A new finite-volume variational method (FVVM) devised for *ab initio* calculation of molecular continuum wave functions is presented. It is a generalization of Kohn's FVVM which appeared in the same paper [W. Kohn, Phys. Rev. 74, 1763 (1948)] as the well-known principle for phase shifts. In FVVM, the inner-region continuum wave functions are expanded onto a finite basis set. A symmetrization of the Hamiltonian matrix is realized by introducing a set of unknown logarithmic derivatives b at the surface boundary. This leads to a generalized system of eigenequations in terms of the unknowns, namely, the expansion coefficients and eigenvalues b. The proposed method combines the respective advantages of R-matrix and eigenchannel theories in the sense that the system of eigenequations is solved only once and that the eigenfunctions so obtained are uniformly convergent at the surface boundary, where collision information may be extracted by matching. As a model calculation, we use FVVM to calculate eigenphases and cross sections for the photoionization of $H_2{}^+(1\sigma_g \rightarrow E\sigma_u)$. Very encouraging results are obtained that demonstrate the numerical feasibility of the method.

I. INTRODUCTION

The observable quantities that describe interactions between particles in collision processes, like photoionization or electron scattering by atomic or molecular targets, can be accurately calculated provided one has a good representation of the continuum wave function over all space. Reliable values of such observables (total and partial cross sections, angular distribution, phase shifts, etc.) have been obtained for atomic targets via the direct *numerical* integration of sets of coupled differential (or integral) equations derived from the Schrödinger equation.[1] More recently, such methods[2,3] as well as methods based upon the Schwinger variational principle[4] have provided results for diatomic targets in the case of electron scattering and photoionization processes. However, the nonspherical symmetry of molecular targets highly increases the number of coupled equations to be propagated and so implies a large amount of computational effort. Hence, it can be thought that the use of *algebraic variational methods,* where continuum functions are expanded as finite linear combinations of multicentered basis orbitals, will become a more and more attractive alternative to the numerical route, as has been the case for the bound states.

At the present time, current algebraic variational methods are essentially of three types. First, methods relying on an entirely bound-type approach without explicit reference to the continuum function calculation, e.g., the Stieltjes imaging technique[5] or complex-coordinate method.[6] Second, methods making use of finite linear expansions of some basis orbitals *over the entire space* and whose coefficients are determined via the minimization of various functionals.[7,8] Thirdly, methods dealing with similar functionals but only over a *finite reaction volume,* thus taking advantage of the fact that the complicated many-particle dynamics is essentially confined in an internal region.

The most widely known finite-volume variational method (FVVM) is probably the R-matrix theory, first introduced in nuclear physics by Wigner and Eisenbud[9] in 1947, further developed in various forms by several authors,[10] and more recently applied to atomic and molecular scattering problems.[11] Among these R-matrix approaches, it should be noted that a variational version developed by Nesbet[12] involves bound-bound integrals over the full coordinate range.

The second (related) FVV method is the eigenchannel theory. Originally devised for nuclear reactions,[13(a)] this method has been introduced into atomic physics by Fano and Lee,[13(b)] and recently extended in this laboratory to molecular predissociation by Jungen[14] and to molecular photoionization by the present authors.[15] From the practical point of view, the respective merits of the two above FVV methods are now well established. For instance, it is known that R-matrix theory produces wave functions at all energies from a single diagonalization of a Hamiltonian matrix subjected to arbitrary boundary conditions. On the contrary, the eigenchannel method involves an iterative process, and hence, repeated diagonalizations of the Hamiltonian matrix for each energy and each eigenchannel. On the other hand, the eigenchannel approach has the important advantage of providing uniformly convergent expansions at the boundary surface, where most of the physical quantities are extracted from the wave functions.[13]

However, there exists an alternative FVV principle suggested by Kohn in his classic paper,[8] together with the much more familiar principle for phase shifts. Since its publication in 1948, only little attention has been devoted to this method. Some authors, particularly Lane and Robson[16(a)] and Zvijac, Heller, and Light[16(b)] have compared it to *R*-matrix and other variational methods. A very recent application of the method has been made by Greene.[17] In Ref. 16(b) it was pointed out that *R*-matrix expansions reduce to a single term and generate stable results if an eigenvalue of the (modified) Hamiltonian coincides with the desired energy.

It is then particularly attractive to develop a new FVV method, relying on Kohn's principle, which combines the respective advantages of the *R*-matrix and eigenchannel theories. Within the proposed framework, the representation of the Hamiltonian in an *arbitrary* finite basis set is computed only once. Then a generalized eigensystem is solved for each desired energy and *directly* provides all the (degenerate) solutions of the Schrödinger equation. This is in contrast with the *R*-matrix scheme which gives, at this stage, only eigenstates of a Hamiltonian satisfying arbitrary boundary conditions, i.e., with no direct physical meaning.

In Sec. II, we present the extension for an arbitrary reaction volume of Kohn's formalism. Then, we specialize this general FVV method to the case of direct molecular photoionization. In Sec. III A some computational details concerning our calculations are given. Sections III B and III C are then devoted to the report of results concerning the photoionization of the simplest atomic and molecular one-electron systems, H and H_2^+, respectively. The number of solutions of the generalized eigensystem is theoretically derived in the Appendix.

II. FORMULATION OF THE THEORY

A. The finite-volume variational method

In order to describe the photoionization or the electron-molecule collision processes, we will focus in this paper on the explicit calculation of the wave function of the excited electron in the average frozen potential of $N-1$ bound electrons. This is the usual frozen core static exchange approximation (FCSE) and the corresponding wave equation reads (in atomic units)

$$(\vec{\nabla}^2+k^2-2\mathscr{V})\psi(\vec{r})=0\ , \tag{1}$$

where $k^2=2(E-E_0)$ defines the energy of the continuum electron and E_0 is the energy of the $N-1$ electrons of the target. The potential $\mathscr{V}$ in Eq. (1) comprises nuclear attraction of the Nth excited electron and electron repulsion of static and exchange types between each of $N-1$ electrons and the Nth excited one. Equation (1) is *local*, i.e., valid at every point $\vec{r}$ of the one-electron space. In order to transform the differential problem into a matricial one, it is customary to deduce from Eq. (1) the *global* equation

$$\langle\psi\,|\,(\vec{\nabla}^2+k^2-2\mathscr{V})\psi\rangle_V=0\ , \tag{2}$$

where $\langle\ldots\rangle_V$ denotes integration over an arbitrary volume V. If, moreover, V is enclosed by a surface Σ admitting an outward normal $\vec{n}$ at every point, Green's theorem enables us to express Eq. (2) as

$$\langle\vec{\nabla}\psi\,|\,\vec{\nabla}\psi\rangle_V+\langle\psi\,|\,(2\mathscr{V}-k^2)\,|\,\psi\rangle_V-\left\langle\psi\left|\frac{\partial\psi}{\partial n}\right.\right\rangle_\Sigma=0\ . \tag{3}$$

Without any loss of generality, the surface integral appearing in Eq. (3) can be related to a simpler nondifferential term

$$-\left\langle\psi\left|\frac{\partial\psi}{\partial n}\right.\right\rangle_\Sigma=b\langle\psi\,|\,\psi\rangle_\Sigma\ . \tag{4}$$

Equation (4) constitutes the definition of the (unknown) parameter b, whose value only depends on the surface Σ and on the (also unknown) wave function ψ. It should be noted that the b parameter is, in fact, a straightforward generalization of the radial logarithmic derivative[8] which is only an approximation for nonspherical boundary Σ.

Hence, inserting Eq. (4) in Eq. (3) yields

$$\langle\vec{\nabla}\psi\,|\,\vec{\nabla}\psi\rangle_V+\langle\psi\,|\,2\mathscr{V}-k^2\,|\,\psi\rangle_V+b\langle\psi\,|\,\psi\rangle_\Sigma=0\ . \tag{5}$$

With this appropriate form of the Schrödinger equation it is convenient to solve Eq. (5) for a continuum wave function ψ^{in} represented, within V, by a finite linear combination of, say N basis functions $\chi_i(\vec{r})$. In matrix notation, one has

$$\psi^{\text{in}}=\underline{\chi}\,\underline{C}\ , \tag{6}$$

where $\underline{C}$ is a column vector of real coefficients to be variationally determined, and χ is the row vector of basis functions. Introducing Eq. (6) in Eq. (5), we obtain the finite-volume functional to be minimized,

$$Q=\underline{C}^t(\underline{A}+b\underline{\Delta})\underline{C}\ , \tag{7}$$

where $\underline{A}$ and $\underline{\Delta}$ denote real symmetric volume and surface matrices, respectively, whose elements are

$$A_{ij}=\langle\vec{\nabla}\chi_i\,|\,\vec{\nabla}\chi_j\rangle_V+\langle\chi_i\,|\,(2\mathscr{V}-k^2)\,|\,\chi_j\rangle_V\ , \tag{8}$$

$$\Delta_{ij}=\langle\chi_i\,|\,\chi_j\rangle_\Sigma\ . \tag{9}$$

We require that Q [Eq. (7)] should be stationary with respect to the variations of $\underline{C}$ and thus obtain the homogeneous set of linear equations

$$\frac{\partial Q}{\partial C_i}=2\sum_j(A_{ij}+b\Delta_{ij})C_j=0 \tag{10}$$

or, equivalently, in matrix form

$$(\underline{A}+b\underline{\Delta})\underline{C}=0\ . \tag{11}$$

Equation (11) is the key equation of the present method.

The solution of this generalized system of eigenequations requires that the condition

$$\det(\underline{A}+b\underline{\Delta})=0 \tag{12}$$

be satisfied. This is realized for a set of eigenvalues $\{b_k\}$ that are computed first. Then solving Eq. (11) with each

b_k, successively, yields the associated set of eigenvectors $\{C_k\}$. As emphasized in the Introduction, each eigenvector *directly* defines, via Eq. (5), a solution of the Schrödinger equation for the desired energy. Thence, the problem arises of determining the number, say M, of independent energy-degenerate solutions of the system of eigenequations. At first glance, one would expect that $M=N$ since $(\underline{A}+b\underline{\Delta})$ is an $N\times N$ real symmetrical matrix. The point is that only a small number of solutions ($M \ll N$) is generally obtained. In the Appendix we give a mathematical derivation of the number M, and prove that it only depends on the structure of the surface matrix. Alternatively, on physical grounds, M can be conveniently seen as the number of eigenstates, spanned within V by the basis orbitals, that have a significant amplitude on the surface Σ.

At this point, it is worthwhile to emphasize that the consistency of the generalized system of eigenequations is exactly ensured via the compatibility condition [Eq. (12)]. This is a necessary feature of finite basis set variational calculations, and it has been proven[18] that usual Hulthen's and Kohn's methods do not properly take account of this fact.

As a final remark, it should be pointed out that the FVV wave function ψ^{in} is, by essence, approximate since the expansion [Eq. (6)] is truncated for obvious practical purposes. As a consequence, one expects that the actual variational energy E^v, that can be calculated once ψ^{in} has been determined, will slightly differ from the exact energy $E=E_0+k^2/2$ inputed in the initial global equation. In the discussion of results (Secs. III B and III C) it will appear that the fact that the difference E^v-E converges to zero constitutes a valuable probe for the convergence of the wave function expansion.

B. The continuation of variational solutions outside *V*

The variational procedure presented in Sec. II A allows for the calculation of continuum wave function in a finite volume V, provided this volume is conveniently spanned by the chosen basis functions. Of course, the partition of the molecular space into an inner and an outer region is of practical interest if all the complicated dynamical effects take place within V, while there only remain simpler long-range interactions in the external region. In this case, it is customary to propagate the internal variational solutions ψ^{in} into the asymptotic region by a convenient propagation scheme for local potential. We shall call ψ^{out} the thusly obtained continuation of ψ^{in} in the external region. Efficient techniques are now available that lead to ψ^{out} by inward numerical integration from the relevant asymptotic form. However, for the particular case of photoionization considered in this paper, the outer region interaction between the ionic core and the ejected electron can be approximated by a monopole charge term

$$\mathcal{V}^{\text{out}}=-Z/r\ , \tag{13}$$

where Z denotes the charge of the remaining ion, and $\vec{r}$ the distance of the departing electron from the origin G (e.g., the center of mass of nuclei). With this approximate outer potential, Eq. (1) becomes the Coulomb wave equation[19] whose general solutions can be cast into the following form:

$$\underline{\psi}^{\text{out}}=r^{-1}\underline{Y}(\underline{F}\,\underline{A}+\underline{G}\,\underline{B})\ . \tag{14}$$

$\underline{\psi}^{\text{out}}(\vec{r})$ and $\underline{Y}(\hat{r})$ are row vectors collecting the degenerate continuum wave functions of the given energy and the relevant spherical harmonics, respectively. $\underline{F}$ and $\underline{G}$ are diagonal matrices whose elements are the regular and irregular Coulomb functions:[19]

$$F_{ll'}=f_l(r)\delta_{ll'} \tag{15}$$

and a similar relation applies for $G_{ll'}$. The Coulomb functions are conveniently normalized in the energy scale and behave at large distances as

$$\begin{aligned} f_l(kr) &\sim \left[\frac{2Z}{k\pi}\right]^{1/2}\sin\left[kr-l\frac{\pi}{2}+\omega\right] \\ &=\mathcal{N}\sin[\theta_l(r)] \quad \text{as } r\to\infty \\ g_l(kr) &\sim \left[\frac{2Z}{k\pi}\right]^{1/2}\cos\left[kr-l\frac{\pi}{2}+\omega\right] \\ &=\mathcal{N}\cos[\theta_l(r)] \quad \text{as } r\to\infty \end{aligned} \tag{16}$$

with the Coulomb phase shift

$$\omega=\frac{Z}{k}\ln(2kr)+\arg\Gamma\left[l+1-i\frac{Z}{k}\right]\ . \tag{17}$$

In addition, it should be noted that the thusly defined functions verify the Wronskian relation[19]

$$[f_l,g_l]=\frac{df_l}{dr}g_l-f_l\frac{dg_l}{dr}=\frac{2Z}{\pi}\ . \tag{18}$$

Although the expansion of ψ^{out} [Eq. (14)] is, in principle, infinite, practical purposes impose upon us to deal with a finite number of Y_{lm} terms. This number is conveniently chosen as equal to the number M of degenerate variational solutions in the internal region. Then, the complete specification of $\underline{\psi}^{\text{out}}$ will be achieved once the $M\times M$ matrices $\underline{A}$ and $\underline{B}$ [Eq. (14)] have been determined. This is usually done by matching internal and external expressions of wave functions and derivatives at a surface boundary.[20]

Now, considering that spherical coordinates are particularly well suited to describe the outer wave function, while elliptic coordinates are computationally efficient in the inner region (see Sec. III A), we have chosen as the matching boundary, a sphere $S(G,r_0)$ contained in the ellipsoidal variational volume V. The transition between the two coordinate systems is made more transparent by expanding each internal solution [Eq. (16)] in terms of spherical harmonics, *on* the surface S. Collecting these M expansions in matrix form gives

$$\underline{\psi}^{\text{in}}=r_0^{-1}\underline{Y}\,\underline{R}(r_0)\ . \tag{19}$$

The conditions expressing the continuity of solutions and derivatives across the boundary are easily derived from Eq. (14), setting r equal to r_0, and Eq. (19). This leads to

$$\underline{F}(r_0)\underline{A}+\underline{G}(r_0)\underline{B}=\underline{R}(r_0)\ ,$$
$$\left[\frac{d\underline{F}}{dr}\right]_{r=r_0}\underline{A}+\left[\frac{d\underline{G}}{dr}\right]_{r=r_0}\underline{B}=\left[\frac{d\underline{R}}{dr}\right]_{r=r_0}\ . \tag{20}$$

Inspection of Eqs. (20) shows that one is faced with M^2 linear systems of two equations in two unknown elements of $\underline{A}$ and $\underline{B}$ matrices. Elementary algebra then leads to

$$A_{ij}=\frac{\pi}{2Z}[R_{ij}(r_0),g_i(r_0)]\ , \tag{21}$$

$$B_{ij}=-\frac{\pi}{2Z}[R_{ij}(r_0),f_i(r_0)]\ , \tag{22}$$

where the square brackets denote the Wronskian as defined in Eq. (18).

Equations (21) and (22) achieve the determination of the continuum wave functions [Eq. (14)] in the outer region. Since internal solutions [Eq. (6)] were previously obtained through the variational principle, continuum states are thence known over the entire space.

C. Physical boundary conditions and transition dipole moments

In order to extract the collisional informations (transition moments, phase shifts, angular distributions, etc.) from the variational continuum wave functions obtained in Secs. II A and II B, it is necessary to give them the standard asymptotic collisional form. For photoionization, the relevant traveling-wave solutions are defined in terms of the scattering matrix $\underline{S}$:

$$\psi^{(-)}\sim\frac{\mathscr{N}}{2ir}\underline{Y}(\underline{E}^{+}-\underline{E}^{-}\underline{S}^{*})\quad\text{as}\quad r\to\infty\ . \tag{23}$$

In Eq. (23), $\underline{E}^{\pm}$ are diagonal $M\times M$ matrices defined as

$$E_{ll'}^{\pm}=e^{\pm i\theta_l(r)}\delta_{ll'} \tag{24}$$

with the expressions of Eqs. (16) and (17) for the normalization factor $\mathscr{N}$ and the argument $\theta_l(r)$, respectively.

A convenient route to the complex wave function $\underline{\psi}^{(-)}$ is to define first, the real "standing-wave" solutions

$$\underline{\psi}^{K}\sim r^{-1}\underline{Y}(\underline{F}+\underline{G}\,\underline{K})\quad\text{as}\quad r\to\infty\ , \tag{25}$$

where $\underline{F}$ and $\underline{G}$ are the Coulomb matrices defined in Eq. (16).

By use of Euler's relations connecting $\underline{E}^{\pm}$ and the asymptotic forms of $\underline{F}$ and $\underline{G}$ [Eqs. (15) and (16)], the complex $\underline{\psi}^{(-)}$ and $\underline{S}$ matrices are easily related to the real ones, $\underline{\psi}^{K}$ and $\underline{K}$, via the well-known relations

$$\underline{\psi}^{(-)}=\underline{\psi}^{K}(\mathbb{1}+i\underline{K})^{-1} \tag{26}$$

and

$$\underline{S}=(\mathbb{1}+i\underline{K})(\mathbb{1}-i\underline{K})^{-1}\ , \tag{27}$$

the link between $\underline{\psi}^{K}$ and $\underline{\psi}^{\text{out}}$ is provided by identification of Eqs. (25) and (14). This shows that the "K normalization" induces a linear transformation in the M-dimensional set of variational solutions. More precisely, one gets

$$\underline{\psi}^{K}=\underline{\psi}^{\text{out}}\underline{A}^{-1} \tag{28}$$

and

$$\underline{K}=\underline{B}\,\underline{A}^{-1}\ . \tag{29}$$

Combining Eqs. (26)—(29) allows the expression of $\underline{\psi}^{(-)}$ and $\underline{S}$, the quantities of physical interest, in terms of quantities known from the variational process of Sec. II A:

$$\underline{\psi}^{(-)}=\underline{\psi}^{\text{out}}(\underline{A}+i\underline{B})^{-1} \tag{30}$$

and

$$\underline{S}=(\underline{A}+i\underline{B})(\underline{A}-i\underline{B})^{-1}\ . \tag{31}$$

Now diagonalizing K, or alternatively S, yields the phase shifts and the mixing coefficients which are needed to interpret the collision-theory results.

The calculation of other properties, e.g., transition dipole moments, requires the explicit knowledge of "running" solutions at small distances. By continuity, it is clear that Eq. (30) is also valid within the variational volume, provided ψ^{out} is replaced with ψ^{in}.

Now, if all the complex dipole moments related to the photoionization of the initial state ψ_0, into the M degenerate running continuum states $\psi_i^{(-)}$ are collected in the column vector

$$\underline{M}^{(-)}=\langle\underline{\psi}^{(-)}\,|\,\vec{r}\,|\,\psi_0\rangle\ . \tag{32}$$

Equation (30) and its continuation in the internal region shows that

$$(\underline{M}^{(-)})^{t}=[(\underline{A}+i\underline{B})^{-1}]^{\dagger}\underline{M}\ , \tag{33}$$

where $\underline{M}$ denotes the analog of $\underline{M}^{(-)}$ for the variational wave functions obtained in this work [Eqs. (6) and (14)], i.e.,

$$\underline{M}=\langle\underline{\psi}\,|\,\vec{r}\,|\,\psi_0\rangle\ . \tag{34}$$

The real matrix elements of the dipole operator [Eq. (34)] can be easily computed with the program that provided the integrals of Eqs. (8) and (9), and then lead to the desired complex integrals of Eq. (33).

These matrix elements are the dynamical quantities that provide the well-known formulas giving partial and total cross sections, as well as angular distributions of photoelectrons.[17] In the present work, we shall consider total cross sections only, and use for them the following formula:[3]

$$\sigma=2.6891(I+k^2/2)(\underline{M}^{(-)})^{\dagger}\underline{M}^{(-)}\ , \tag{35}$$

where σ is given in megabarns, I denotes the relevant ionization potential, and $k^2/2$ the kinetic energy of the ejected electron. Note that quantities appearing in the right-hand side of Eq. (35) are in atomic units.

III. MODEL CALCULATIONS

A. Computational aspects

The FVV theories presented in the Introduction are general and powerful formalisms. However, a major limitation for their practical use in molecular collision processes is probably of computational nature. The greatest difficulties arise in the calculation of multicentered one- and two-electron integrals, involved in the matrix elements of the $\mathscr{V}$ operator [Eq. (8)], due to the fact that integrations must be performed within a finite volume V. Recently, one of us (H.L.) modified existing algorithms[21] devoted to the integration over all space in order to compute all volume integrals (up to three collinear centers) within the ellipsoid $\xi=\xi_0$,[22] ξ being the elliptic coordinate defined by $\xi=(r_A+r_B)/R$. The corresponding integral generator program, derived from the pioneering work of Schaefer,[23] has been used in this work in order to evaluate the finite-volume integrals [Eq. (8)]. Among these integrals, it should be noted that the "grad-grad" ones [the leading terms of Eq. (8)], are of a rather unusual type. They have been computed via a specific algorithm written by one of us (H.L.). Another point to be emphasized is that the surface integrals [Eq. (9)] have been accurately computed over the ellipsoid. This means that the variational method has been *exactly* applied within the ellipsoidal volume, while in a previous work[15] we approximated it by a sphere.

In the following, we first discuss the size of the volume where the variational procedure will take place. This can be viewed as the first "parameter" to be pragmatically fixed. As a general rule, the ellipsoid must not be too large in order to be spanned by a moderate number of basis orbitals. However, this volume must be sufficient to contain all the short-range interactions. Equivalently, it can be said that most of the charge cloud of the ionic core must be confined within V. In view of this alternative, the two models (H and $H_2{}^+$) considered in this paper are very particular since they involve a single (departing) electron, and hence, no occupied shell. Nevertheless, we choose a relatively large volume, as it would be required for the treatment of heavier molecules. The ellipsoid defined by $\xi_0=10$ a.u., and a distance $R=2$ a.u. between foci, is then adopted for the two model calculations. In the case of the atomic problem, the nucleus H is situated at the center of the ellipsoid.

The second parameter to be fixed in an actual calculation is the basis set. In fact, relatively little is known about the nature and the number of basis functions required to expand continuum wave functions. However, since these functions have an oscillatory behavior, by essence, it seems worthwhile to introduce orbitals having this property, instead of the nodeless Slater[24] or Gaussian[25] types of orbitals. At this stage, the investigation on the nature of basis orbitals is greatly facilitated by the fact that our code can be provided with arbitrary orbitals. For the atomic problem, we decided to explore the possibility of using sine functions as suggested first by Kohn[8] and illustrated by Oberoi and Nesbet.[26] In the second model considered, we chose a basis set composed of Coulomb functions [Eq. (16)] associated with bound-type orbitals.

B. Photoionization of the atom H

As a preliminary test of the method, a study was made of the photoionization $1s\rightarrow Ep_0$ of the hydrogen atom for $E=0.5$ a.u. This simple system provided a convenient model of the new computational code since exact wave functions are analytically known for bound and free states. Moreover, the choice of a one-center problem eliminates, for the moment, the problems connected with the partial-wave coupling due to the asymmetry of ionic cores. As mentioned above, the continuum state Ep_0 ($E=0.5$ a.u.) is constructed as a linear combination of nucleus-centered products of sine radial functions $\sin(k_i r)$ and $Y_{10}(\hat{r})$ angular terms. Instead of trying to optimize the number and the values of k_i parameters, we choose to use grids of equally spaced values around the asymptotic value $k=\sqrt{2E}=1$. In addition, we found it useful to complete the basis set by the (bound) $2p_0$ state. In Table I results obtained with basis sets of increasing sizes are presented. In the first column, the values of the boundary term b [Eq. (4)] are reported. They exhibit a very good convergence to the exact value and show that inclusion of the $2p_0$ state significantly improves this convergence. From the same table it can be seen that actual variational energies of the computed free state, as well as photoionization cross sections, are not so well converged. This fact is particularly evident in the last two calculations (E and F) and is due to the growth of linear dependence within the basis set. Further investigations on the basis parameters would probably lead to improved results, but we reserve such a study for a future work. Anyway, it should be noted that the calculation D provides satisfactory results since absolute errors on the energy and cross section are 10^{-3} and 3×10^{-5} a.u., respectively.

In a second stage, the basis D has been used for computing continuum states over the energy range (0,1) a.u. This is made possible by the fact that basis D does not essentially depend on the energy $E=0.5$ for which it has been devised. Results are reported in Table II. The difference E^v-E, listed in the third column of this table, is of the same order of magnitude as the one obtained in Table I for a unique energy of 0.5 a.u. We conclude that the results are accurate over the full 0—1 a.u. energy range. This fact is of practical importance since the computational time required for a calculation at a given energy is quite negligible (less than 1 s on the IBM 370-168) once integrals have been obtained in the first calculation. An analogous situation is encountered in R-matrix calculations.[11]

C. Photoionization of $H_2{}^+$

The second prototype calculation we shall report in this paper concerns the photoionization of the hydrogen molecule ion from its ground state. As an example, we have studied the partial process $1\sigma_g\rightarrow E\sigma_u$ with $E=0.5$ a.u. and a bond length fixed to its equilibrium value ($R=2$ a.u.). The choice of $H_2{}^+$, the simplest molecular system, is particularly convenient for an initial study since prob-

TABLE I. Convergence of variational results for the $1s \rightarrow Ep_0$ photoionization of the atom H, as a function of the size of the basis set. Photoelectron energy is $E=0.5$ a.u. b is computed over the ellipsoid defined in the text ($\xi_0=10$ a.u.). E^v is the actual variational energy of the photoelectron. Cross section $|\langle 1s|z|Ep_0\rangle|^2$ is computed within the ellipsoid. Over all space its value is 0.115 453 a.u.

	Basis sets	k_i parameters	b	E^v (a.u.)	$\|\langle 1s\|z\|Ep_0\rangle\|^2$ (a.u.)
A	6 sines	0.3 (0.2) 1.3	0.103 939	0.509 587	0.129 604
B	$2p_0+6$ sines	set A	0.170 596	0.504 275	0.116 743
C	$2p_0+7$ sines	set $A+0.1$	0.171 282	0.499 142	0.116 949
D	$2p_0+8$ sines	set $C+1.5$	0.171 437	0.500 953	0.116 548
E	$2p_0+9$ sines	set $D+1.7$	0.171 625	0.498 826	0.116 691
F	$2p_0+10$ sines	set $E+0.05$	0.171 825	0.504 576	0.115 991
Exact[a]			0.171 839	0.5	0.116 579

[a]These values are calculated with the same integral generator code provided with Coulomb functions.

lems connected with the two-center nature of the ionic core may be investigated without considering the additional complications due to electron correlation. Another (related) attractive feature is that $H_2{}^+$ is the sole molecular species for which virtually exact wave functions are available for bound states[27] as well as for free states.[28] This means that the exact photoionization cross sections for the considered process are at our disposal[28] and can serve as reference for the present investigations.

Once the $E\sigma_u$ continuum state is obtained via the FVV method, calculation of the cross section [Eqs. (33) and (34)] require an explicit expression for the initial ground state $1\sigma_g$. In this work, instead of using the exact $1\sigma_g$ wave functions,[27] we have preferred to deal with functions in more compact forms. Three closed forms were considered and thoroughly reoptimized, namely, the linear combination of atomic orbitals (LCAO),[29] James,[30] and Guillemin-Zener[31] (GZ) ones. In order to compare these functions, we report in Table III their variational electronic energies, along with the photoionization cross sections for the $1\sigma_g \rightarrow E\sigma_u$ process, involving a numerical one-center $E\sigma_u$ continuum state obtained from the close-coupling program described elsewhere.[32] Inspection of these results first shows that the LCAO ground state, which leads to a cross section in error by a factor of 5, is definitely of no use for quantitative predictions. On the contrary, James's function provides satisfactory results. In fact, the GZ function reveals itself to be of the highest accuracy, since its energy is only 2×10^{-4} a.u. above the exact result. Moreover, it appears that the GZ cross section agrees, within at least four significant figures, with the exact one. This fact is of importance since it demonstrates, first, that the very simple GZ form can be used with confidence in photoionization process. Accordingly, this form will be used hereafter for the $1\sigma_g$ state. The second essential point is that the numerical close-coupling $E\sigma_u$ states are virtually exact. This leads us to consider as secure references the collision properties (like phase shifts) one can extract from them. For the sake of consistency, it is also useful to consider the results obtained via the numerical close-coupling method *within* the simplifying assumption of our model [Eq. (13)] and considering only two continuum states, denoted by "p" and "f" according to their main angular character. The results obtained thusly are, in fact, very close to the exact ones since cross sections and phase shifts (for "p" and "f" states, respectively) decrease from 0.014 73 Mb, 0.358 rad, and 0.105 rad to 0.014 35 Mb, 0.354 rad, and 0.103 rad under our model approximations.

TABLE II. Variational results for the $1s \rightarrow Ep_0$ photoionization of atom H for photoelectron energies within the range 0–1 a.u. Continuum states are computed over basis set D of Table I (notations and definitions as in Table I).

E (a.u.)	b	E^v-E (a.u.)	$\|z\|^2$ (a.u.)
0.0	0.5026	3×10^{-5}	
0.001	0.5198	3×10^{-5}	1.5553
0.01	0.7078	3×10^{-5}	1.4541
0.1	-0.6456	-2×10^{-4}	0.7838
0.2	0.3621	-4×10^{-4}	0.4467
0.3	5.0184	-3×10^{-4}	0.2788
0.4	-0.9221	5×10^{-4}	0.1769
0.5	0.1714	1×10^{-3}	0.1165
0.6	1.5018	6×10^{-4}	0.0789
0.7	-19.4685	3×10^{-4}	0.0524
0.8	-1.2658	-2×10^{-3}	0.0401
0.9	-0.0682	-4×10^{-3}	0.039
1.0	0.9641	-3×10^{-3}	0.0246

In order to expand the $E\sigma_u$ wave function, we chose a basis of the kind considered in a previous work,[15] namely, a mixing of long-range and short-range functions. The long-range functions are the regular and irregular Coulomb functions [Eqs. (16)] with only two azimuthal quantum numbers ($l=1,3$) since the component of the "h" ($l=5$) angular a symmetry has been found nearly negligible in the numerical calculation considered in Table III. It should be noticed that the irregular $g_1(r)$ and $g_3(r)$ functions were smoothly continued by regular functions $r \leq 1.5$ a.u. in order to eliminate their singularities at the origin. This continuation is somewhat arbitrary since the small-r form of the continuum state is taken into account by the bound-type orbitals included in the basis set. These functions were of the hydrogenlike type and also of the "p" and "f" angular symmetries.

In analogy with the atomic model calculation of Sec.

TABLE III. Comparison of various approximated states in the photoionization of $H_2^+(1\sigma_g \rightarrow E\sigma_u)$ for a photoelectron energy $E=0.5$ a.u. and an internuclear separation $R=2$ a.u.

Initial $1\sigma_g$ state		Final $E\sigma_u$ states		
Wave-function types	Energies (a.u.)	Wave-function types	States	Cross section (Mb)
LCAO[a]	$-1.086\,506$[d]	Numerical (one center)[e]	"p", "f", and "h"	0.077 57[f]
James[b]	$-1.102\,386$[d]	Numerical (one center)[e]	"p", "f", and "h"	0.014 16[f]
Guillemin-Zenner[c]	$-1.102\,443$[d]	Numerical (one center)[e]	"p" "f", and "h"	0.014 73[f]
Exact	$-1.102\,634$[g]	Exact (two centers)	Two states	0.014 73[h]

[a] Reference 29.

[b] Reference 30.

[c] Reference 31.

[d] Reoptimized by us.

[e] Computed by us with the method of Ref. 3. States were expanded up to $l=14$ at the molecular midpoint.

[f] Computed by us with the exact ionization potential of Ref. 23(a).

[g] Reference 27. The value $-1.102\,625$ a.u., reported in Ref. 27(a), is slightly less accurate.

[h] Reference 28(b).

III B, we found it useful to include the $1\sigma_u$ bound state of H_2^+ in our basis set, i.e., the main state of the relevant symmetry which essentially lies within the variational volume. As in the case of the ground state, we have optimized various closed-form wave functions. Finally, we choose the σ_u analog of the Guillemin-Zenner $1\sigma_g$ state, whose energy ($-0.665\,814$ a.u.) is equal to LCAO ones.[33] Hence, except for this function which is of two-center nature, our basis set is composed of one-center orbitals situated at the molecular midpoint.

The smallest basis set we present (basis A) is composed of 14 basis orbitals, namely, four Coulomb functions (f_1, g_1, f_3, and g_3), five functions with the Y_{10} angular symmetry ($2p$, $3p$, $4p$, $5p$, and $6p$) having all the exponent $Z=1.5$, and five Y_{30} functions, ($3f$, $4f$, $5f$, $6f$, and $7f$) with exponent $Z=2.0$. It should be noted that these exponents are again nonoptimized (as in the atomic example of Sec. III A) but simply related to the united atomic limit ($Z=2$).

Results obtained with basis A are reported in Table IV, along with the "exact" result discussed above. Although the actual energies E^v of the "p" and "f" states are of equivalent accuracy (errors are about 3×10^{-3} a.u.) it appears that the "p" wave function suffers from an inadequate representation at small distances (consider the transition moment $M^K_{\text{“}p\text{”}}$) as well as far from the nuclei (see the phase shift $\delta_{\text{“}p\text{”}}$).

Adding the bound state $1\sigma_u$ to basis A (we call B this augmented set) does not essentially change the "f" solution as could be expected from the "p" character[27(a)] of the $1\sigma_u$ state. On the other hand, one notes significant improvements for the quantities $M_{\text{“}p\text{”}}$ and $\delta_{\text{“}p\text{”}}$. Basis C contains three supplementary p orbitals ($7p$, $8p$, and $9p$). Since these functions are diffuse the "p" continuum state is essentially improved at large distance, and hence in the neighborhood of the surface Σ where the phase shift is extracted. Table IV shows that the energy, real dipole moment, and phase shift of the "p" state are correct within 5×10^{-4} a.u., 2×10^{-3} a.u., and 4×10^{-3} rad, respectively. Similarly, three additional f orbitals (basis D) do not modify the preceding "p" solutions but slightly improve the relevant continuum wave functions.

Finally, considering that the "f" state is comparatively less accurately described than the "p" state, we roughly

TABLE IV. Convergence of variational results for the $1\sigma_g \rightarrow E\sigma_u$ photoionization of H_2^+, as a function of the size of the basis set. Notations and definitions as in Table I. Photoelectron energy is $E=0.5$ a.u. and the internuclear separation is $R=2.0$ a.u.

	b		E^v (a.u.)		M^K (a.u.)			δ (rad)	
Bound basis sets[a]	"p"	"f"	"p"	"f"	"p"	"f"	σ (Mb)	"p"	"f"
A $5p+5f$[b]	−0.391	−39.2	0.4967	0.5024	−0.0357	0.0637	0.011 23	0.284	0.082
B $1\sigma_u+5p+5f$[b]	−0.334	−36.5	0.4943	0.5023	−0.0522	0.0592	0.012 89	0.311	0.083
C $1\sigma_u+8p+5f$[b]	−0.333	−36.0	0.4995	0.5023	−0.0540	0.0583	0.012 93	0.350	0.082
D $1\sigma_u+8p+8f$[b]	−0.330	−23.8	0.4994	0.5007	−0.0531	0.0597	0.013 12	0.351	0.091
E $1\sigma_u+8p+8f$[c]	−0.330	−21.9	0.4994	0.5008	−0.0515	0.0654	0.014 33	0.353	0.097
Exact[d]			0.5	0.5	−0.0520	0.0645	0.014 35	0.354	0.103

[a] Complete basis sets actually used contain, in addition, four free orbitals (f_1, g_1, f_3, and g_3) of the relevant energy (see text).

[b] Exponents of p and f orbitals are 1.5 and 2.0, respectively.

[c] Exponents of p and f orbitals are 1.5 and 2.3, respectively.

[d] These results are computed, with the method of Ref. 3, within the approximation contained in our model. They are, in fact, very close to the exact ones (see text and Table III).

optimize the common exponent of the f orbitals. This yielded to a change from $Z=2.$ (the united atom limit) to $Z=2.3$ which corresponds to a contraction of the f basis set. This basis set, with the other basis functions unchanged, is called E in Table IV. The corresponding results seem to be converged with a satisfactory accuracy although additional basis orbitals and further optimization of exponents would probably again improve the convergence.

IV. CONCLUSION

In the present work, we develop a new finite-volume variational method (FVVM) for calculating the electronic continuum wave functions involved in molecular processes like photoionization or electron collision. This FVVM is an extension of a method which has lain dormant in the literature since Kohn[8] suggested it in 1948. The FVV continuum wave functions are explicitly obtained, within a finite reaction volume V, as finite linear combinations of basis orbitals. Hence, one is able to calculate all collision observables (integrated and differential cross sections, angular distribution, phase shifts, etc.) following standard techniques.

Comparison between the FVVM and other finite-volume methods reveals that the FVV procedure is straightforward since it gives, at the required energy, the full collision result in one diagonalization of the generalized eigensystem [Eq. (11)]. As already pointed out, the eigenchannel approach[13–15] is known to be a stable procedure but requires several iterations over the eigenphase per channel and per energy (each requiring a diagonalization) to obtain the collision result. This is a rather cumbersome procedure. As stated in the Introduction, the R-matrix expansion reduces to one term and seems to give stable results if one of the eigenvalues coincides with the continuum energy.[16(b)] In this particular case, the R-matrix method and FVVM would give the same result. But a difference between the two procedures can be seen if we require a similar accuracy at a given energy: In the FVVM we introduce the energy as an input quantity and in one diagonalization of the generalized system of eigenequations we obtain all the energy-degenerate components of the inner region wave function. In the R-matrix method we obtain accurate results only at eigenvalues of the eigensystem. Zvijac, Heller, and Light[16(b)] have demonstrated that accurate results are obtained at any energy if a variational correction is added to the initial R-matrix result. Of course the same can be obtained if we change the boundary condition satisfied by the basis set, which changes the eigenvalue spectrum and allows us to span with an eigenvalue the energy spectrum of interest. Therefore, to obtain the same level of accuracy, the R-matrix theory seems to be more cumbersome than the FVVM.

Let us now compare the FVVM to methods similar in spirit (e.g., where the boundary condition is explicitly considered at some stage of the calculation) but where the calculation is performed over the full coordinate space. There are two such approaches: the (usual) full space Kohn variational method[8] giving eigenphases, and an extension of this method developed by Rudge[18] eliminating spurious resonances of Kohn's method. The origin of these spurious resonances is an incomplete (one per asymptotic channel) variational condition on the system of eigenequations coefficients corrected by Rudge. In the FVVM, all the coefficients are variationally obtained and no distinction is operated between them. Therefore the FVVM has the same stability properties as Rudge's method but in finite-volume calculation.

Let us now comment further on the two preliminary tests we have done using the FVV method, provided with finite-volume integrals computed by a convenient code.[22] These tests deal with prototype atomic and molecular one-electron systems. First, the study of the photoionization of atom H ($1s \rightarrow Ep_0$) indicates that an energy-independent set of sine orbitals gives an accurate representation of the continuum state over the full range $E(\text{a.u.}) \in (0,1)$. This is an especially attractive feature since this implies that the most costly part of the calculation, namely, the evaluation of integrals, is computed only once. In the second example, the photoionization $1\sigma_g \rightarrow E\sigma_u$ of H_2^+ is considered. Phase shifts and cross sections have been obtained by expanding the continuum states "p" and "f" with energy $E=0.5$ a.u. onto an inner-region basis set containing a mixing of bound and free orbitals. The results so obtained compare very well with the exact calculation of Bates and Öpik[28(b)] and with our single-center close-coupling calculations (see Table IV).[32] They seem as accurate as the results reported in previous works on H_2^+ by Chapman,[34] Chapman and Hayes,[35] McCurdy and Rescigno.[6]

In view of these very encouraging prototype calculations, we can reasonably expect that the method will provide results of similar accuracy for heavier molecules. Extension of the FVVM to the several-electron molecular system is straightforward within the fixed-core approximation and will be presented in a future work.

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APPENDIX

In this appendix we derive the number of independent solutions of the generalized system of eigenequations [Eq. (11)]. For this purpose, we first obtain the rank of the matrix $\underline{\Delta}$ defined in Eq. (9). Let us choose a one-electron coordinate system $\vec{u}=(u,\hat{u})$ that naturally describes the surface boundary Σ via the "radial" equation $u=u_0$. Then it is convenient to introduce relevant surface harmonics $Y_L(\hat{u})$, involving the two "angular" variables denoted by $\hat{u}$. These harmonics verify an orthonormality condition over Σ,

$$\langle Y_L \mid Y_{L'} \rangle_\Sigma = \delta_{LL'} \; . \qquad (A1)$$

Since the set $\{ Y_L, L=1,\ldots,\infty \}$ is complete, each basis orbitals can be rigorously developed on Σ, as the infinite series

$$\chi_i(\vec{u})=\sum_{L=1}^{\infty} Y_L(\hat{u})\mathscr{R}_{Li}(u_0) . \tag{A2}$$

If we suppose that none of the N basis orbitals χ_i has significant components in subspaces higher than $L=M$, the expansions (A2) can be truncated and collected in matrix form as

$$\underline{\chi}=\underline{Y}\underline{\mathscr{R}} , \tag{A3}$$

where $\underline{\chi}$ and $\underline{Y}$ are row vectors of lengths N and M, respectively. $\underline{\mathscr{R}}$ is an $M \times N$ matrix, whose columns are the components of the basis orbitals on the orthonormalized set of surface harmonics. This implies, provided there is no trivial linear dependency among the orbitals, that the matrix $\underline{\mathscr{R}}$ has the rank M:

$$\text{Rank}(\underline{\mathscr{R}})=M . \tag{A4}$$

For obtaining (A4) we have supposed that $N \geq M$, which is a necessary condition for a physically meaningful calculation. Reporting (A3) in Eq. (9) leads to

$$\underline{\Delta}=\underline{\mathscr{R}}^t\underline{\mathscr{R}} , \tag{A5}$$

where $\underline{\mathscr{R}}^t$, the transpose of $\mathscr{R}$, obviously has the rank M. Then, using the fact that $\underline{\mathscr{R}}$ and $\underline{\mathscr{R}}^t$ are $M \times N$ and $N \times M$ matrices of rank M, one easily proves[36] that

$$\text{Rank}(\underline{\Delta})=M . \tag{A6}$$

Note that this theorem gives a more precise result than the general theorem[37] on the rank of a product of arbitrary matrices stating that

$$\text{Rank}(\underline{A}\,\underline{B}) \leq \min\{\text{Rank}(\underline{A}),\text{Rank}(\underline{B})\} \tag{A7}$$

if $\underline{A}\,\underline{B}$ exists.

Now, returning to the generalized system of eigenequations [Eq. (11)] we can rewrite it as

$$(\underline{A}^{-1}\underline{\Delta})\underline{C}=-b^{-1}\underline{C} , \tag{A8}$$

where we again assume that there is no linear dependency within the basis set, which implies that $\underline{A}$ is invertible and that

$$\text{Rank}(\underline{A})=\text{Rank}(\underline{A}^{-1})=N . \tag{A9}$$

Equation (A8) is clearly a standard eigenvalue problem whose number of independent solutions is precisely equal to the rank of $(\underline{A}^{-1}\underline{\Delta})$.[38] By use of the theorem (A7) and the results (A6) and (A9), it follows that

$$\text{Rank}(\underline{A}^{-1}\underline{\Delta}) \leq M \tag{A10}$$

so that the generalized eigenproblem [Eq. (11)] has no more than M eigensolutions.

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