Relativistic photoeffect in the H_2 molecule

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The photoionization cross section of the H_2 molecule is calculated for knocked-out electrons with relativistic energies up to 1 MeV. The cross section is summed over all vibrational states of the H_2^+ ion. A relativistic plane wave was employed as the ejected electron wave function. The ground state wave function for the H_2 molecule is set up in an approximation which is a relativistic extension of the Heitler-London method. The photoionization differential cross section of a molecule fixed in space, calculated without taking into account nuclear oscillations, is oscillatory for all knock-out electron angles. Allowance for the vibrational motion of the molecule nuclei with increasing photon energy conceals the oscillations, which remain detectable only in a restricted angular range in which $(\mathbf{k}-\mathbf{q}, \mathbf{R}_0^0) \sim 0$, where $\mathbf{k}$ and $\mathbf{q}$ are the photon and photoelectron wave vectors and $\mathbf{R}_0$ is the internuclear distance. At $E_{ph} > 1000$ eV, the effect of the nuclear vibrations on the total photoeffect cross section is negligible. It is found that almost throughout the whole range considered the probability for H_2^+ ion formation in the first excited state is five times smaller than that for the ground state. The nonadditivity in the total photoeffect cross section is estimated and it is shown that with increasing photon energy the molecular cross section does not tend to the sum of the atomic cross sections. The accuracy of the plane-wave approximation is verified for the H atom.

1. FORMULATION OF PROBLEMS

Much experimental material has been accumulated by now on the photoionization of molecules in the gas phase[1,2]. The available material on photoionization of valence electrons of molecules, however, pertains to the threshold photon-energy region and to the region adjacent to it. There is undisputed interest in research on the behavior of the photoionization cross section with increasing quantum energy, up to the x-ray and γ-ray bands. Whereas the molecular bond can be disregarded in the case of photoionization from the inner shells of the atoms making up the molecule, this can no longer be done in the case of valence electrons. The coupling of the valence electrons in the atoms is of the same order as the magnitude of the intermolecular interactions. The distribution of the electron density of the valence electrons in the molecule differs significantly from the distribution in isolated atoms. The latter should affect the cross section of the photoeffect regardless of the energy of the incident quantum.

We have previously[3] considered the nonrelativistic photoeffect on the H_2 molecule. It turned out that the dependence of the cross section on the photoelectron emission angle relative to the molecular axis has a strongly pronounced oscillatory character due to interference phenomena. An oscillatory term is contained also in the total cross section, and the number of oscillations increases with increasing photoelectron energy. An investigation of the behavior of the cross section of the photoeffect with further increase of the photon energy called for a transition to the relativistic region.

In the present paper we consider the photoionization at relativistic energies of the knocked-out electron. We choose as the model system the H_2 molecule. Insofar as we know, no one has performed theoretical calculations of the relativistic photoeffect on molecules.

In the first approximation in the interaction with the radiation, the relativistic cross section for photoionization into an element of solid angle $d\Omega$ can be represented in the form[1)]

$$\frac{d\sigma}{d\Omega}=\frac{\varepsilon q\alpha V}{2\pi\omega}\sum_{\substack{\text{fin}\\ \text{state}}}|\langle\Psi_{\text{fin}}|\hat{F}|\Psi_{\text{init}}\rangle|^2, \tag{1}$$

$$\hat{F}=\sum_i\hat{f}_i=\sum_i(\boldsymbol{\alpha}_i\mathbf{e})\exp(i\mathbf{k}\mathbf{r}_i), \tag{2}$$

Ψ_{init} and Ψ_{fin} are the wave functions describing the initial and final states of the system. The cross section is summed over all the possible final states. The summation over i is over all the electrons of the system; ω, $\mathbf{k}$ and $\mathbf{e}$ are the frequency, wave vector, and polarization vector of the photon; $\mathbf{q}$ and ϵ are the momentum and total energy of the knocked-out electrons; α is the fine-structure constant; α_i is the Dirac matrix of the i-th electron; V is the volume of the system.

The Hamiltonian of the molecule can be represented in the c.m.s. in the form of a sum of two terms

$$\hat{H}=\hat{T}+\hat{H}_0, \tag{3}$$

where $\hat{T}$ is the operator of the kinetic energy of the nuclei and $\hat{H}_0$ includes the kinetic energy of the electrons and the energy of the interaction between all particles.

The motion of the nuclei can always be regarded as nonrelativistic, while the motion of the electrons will be considered to be relativistic. The calculation will be carried out with accuracy to $1/c^2$, which corresponds to an accuracy $1/c$, i.e., to the first power of α, for the function. In this approximation, the Hamiltonian $\hat{H}_0$ for the H_2 molecule can be represented, in analogy with the Breit Hamiltonian for two particles, in the form

$$\hat{H}_0=\hat{H}_a(r_1)+\hat{H}_b(r_2)+\hat{V}, \tag{4}$$

where $\hat{H}_a(r)$ is the Dirac Hamiltonian for an electron in the field of nucleus a, and $\hat{V}$ is the operator of the interaction between the two hydrogen atoms. Since the wave functions are constructed in zero order in the interaction $\hat{V}$, the concrete form of the operator $\hat{V}$ is immaterial, and all that matters is that it be symmetrical with respect to permutation of the nuclei (since the nuclei are identical).

On going from atoms to molecules, we face the need for taking into account the vibrational motion of the nuclei. It is interesting to note that allowance for the vibrations is important not only near the threshold of the photoeffect, as has been customarily assumed to date, but also in the shorter-wavelength region. The influence of the vibrational motion of the nuclei becomes most acutely pronounced in the differential cross section, which is not averaged over the rotation of the molecules. The point is that the cross section of the molecular photoeffect contains an oscillating factor that depends on the ratio R/λ_e, where R is the interatomic distance and λ_e is the de Broglie wavelength of the knocked-out electron. With increasing photon energy, the wavelength of the knocked-out electron becomes of the same order of or less than the amplitude of the nuclear vibrations. Therefore the deviation of the internuclear distance from equilibrium, as a result of the nuclear vibrations, affects the character of the oscillations substantially.

We construct the wave function of the initial states in an approximation that is the relativistic generalization of the Heitler-London method. The need for constructing a relativistic wave function for the initial state that is not relativistic is brought about by the relativism of the final state. If we were to assume that the wave function of the initial state is nonrelativistic, we would lose terms that are important in the nonrelativistic energy region (cf. the analogous situation in the case of the relativistic photoeffect on the H atom[4]). The final-state wave functions were taken in the form of the product of a relativistic plane wave by a molecular orbital of the ground or excited state of the H_2^+ ion. The molecular orbital of H_2^+, like the ground-state function of H_2, is made up of relativistic 1s-orbitals. The accuracy with which the plane wave is approximated in our energy band can be estimated with the H atom as an example. In the Appendix we present such estimates for a large energy interval.

2. CONSTRUCTION OF THE WAVE FUNCTIONS

In the construction of the wave functions of the H_2 molecule and of the H_2^+ ion, we start from the Born-Oppenheimer approximation according to which the wave function of the molecule can be represented in the form of an electronic wave function $\Phi(r, R)$ that depends on the nuclear coordinates as parameters multiplied by the wave functions $\chi(R)$ that describe the motion of the nuclei. Calculations by Kolos et al. (see[5]) have shown that the Born-Oppenheimer approximation holds quite well even for so light a molecule as H_2. The deviation of the H_2 dissociation energy calculated in the Born-Oppenheimer approximation from the experimental value does not exceed the experimental error ($\sim 10^{-3}\%$).

We assume that the H_2 molecule is initially in the electronic ground state and in a nuclear-motion state characterized by the set of quantum numbers:

$$\Psi_{\text{init}} = \Phi_0(r, R)\chi_{0\lambda}(R). \tag{5}$$

The electron wave function satisfies the equation

$$\hat{H}_0(r, R)\Phi_0(r, R) = E_0(R)\Phi_0(r, R), \tag{6}$$

where the Hamiltonian is given by expression (4). The wave function $\chi_{0\lambda}(R)$ describes the motion of the nuclei and satisfies the Schrödinger equation with potential energy $E_0(R)$

$$[\hat{T} + E_0(R)]\chi_{0\lambda}(R) = E_{0\lambda}\chi_{0\lambda}(R). \tag{7}$$

The motion of the nuclei breaks up into oscillations relative to the equilibrium position and rotations of the molecule as a whole. The wave function of the motion of the nuclei takes in this case the form of a product of the vibrational wave function $\Lambda_{0v}(Q)$ by the rotational wave function

$$\Theta_{MK}^{J}(\vartheta) = [(2J+1)/8\pi^2]^{1/2} D_{MK}^{J}(\vartheta),$$

where $D_{MK}^{J}(\vartheta)$ are generalized spherical functions, see[6],

$$\chi_{0\lambda}(R) = \Lambda_{0v}(Q)[(2J+1)/8\pi^2]^{1/2} D_{MK}^{J}(\vartheta), \tag{8}$$

where v numbers the vibrational levels, Q is the normal coordinate and coincides in this case with the deviation of the internuclear distance from the equilibrium value, M is the projection of the angular momentum J on the z axis in the lab, K is the projection of the angular momentum J on the molecule axis, and ϑ is the aggregate of the three Euler angles.

We construct the electronic wave function of the ground state of the H_2 molecule in the zeroth approximation in the interaction of the H atoms. In the nonrelativistic case, this approximation corresponds to the well-known Heitler-London mechanism. The electronic ground state function can be easily obtained in the Heitler-London method from the requirement that it describe a state with total electron spin S = 0. In the relativistic case the spin is not conserved, but to construct the correct zeroth-approximation function we can use the symmetry of the Hamiltonian (4) with respect to spatial transformations.

We start from the products of the Slater relativistic 1s functions for the atoms a and b:

$$\psi_{a\mu}(1)\psi_{b\nu}(2), \quad \mu, \nu = 1, 2. \tag{9}$$

The functions $\psi_{a\mu}$ differ from the solutions of the Dirac equation for the H atom in that the argument of the exponential contains the effective charge η. The value of η is determined by optimizing the energy of the ground state of H_2 in the nonrelativistic approximation, and is assumed in the present calculation to equal 1.2. Since $\alpha\eta \ll 1$, the functions $\psi_{a\mu}$ can be represented in the form (cf.[7]):

$$\psi_{a\mu} = (1 - {}^1/_2 i\alpha(\alpha\nabla))\varphi_a u_\mu, \tag{10}$$

where $\varphi_a = (\eta^3/\pi)^{1/2}\exp(-\eta r_a)$, and u_μ are bispinors given by

$$u_\mu = \begin{pmatrix} w_\mu \\ 0 \end{pmatrix}, \quad w_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad w_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{11}$$

Since the electronic wave function should be antisymmetrical with respect to permutations of the electrons, the products (9) must be antisymmetrized. They can be used to construct four determinants. To make up correct zeroth-approximation linear combinations we take into account the fact that the Hamiltonian $\hat{H}_0$ is invariant against the operations of the point group $D_{\infty h}$. Since the functions are constructed from 1s-orbitals, it suffices to symmetrize them with respect to inversion. This leads to three non-normalized functions with symmetry Σ_u:

$$\det|\psi_{a1}\psi_{b1}|, \ \det|\psi_{a2}\psi_{b2}|, \ \det|\psi_{a1}\psi_{b2}| - \det|\psi_{b1}\psi_{a2}|, \tag{12}$$

and one function with symmetry Σ_g:

$$\det|\psi_{a1}\psi_{b2}| + \det|\psi_{b1}\psi_{a2}|. \tag{13}$$

The electronic ground state of the H_2 molecule is described by the function (13). It is easy to show that the normalized function (13) can be represented in the form

$$\begin{gathered}\Phi_0 = N_0[1 - {}^1/_2 i\alpha(\boldsymbol{\alpha}_1\nabla_1)][1 - {}^1/_2 i\boldsymbol{\alpha}_2\nabla_2)] \\ \times[\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)][u_1(1)u_2(2) - u_1(2)u_2(1)],\end{gathered} \tag{14}$$

$N_0 = (1 + s_{ab}^2)^{1/2}$, where s_{ab} is the overlap integral of the orbitals $\psi_{a\mu}$ and $\psi_{b\mu}$. It is clear from (14) that in the nonrelativistic limit Φ_0 goes over into a Heitler-London function that describes a state with a total electron spin S = 0.

The electronic states of the ion H_2^+, just as the electronic states of H_0, will be made up of the relativistic 1s-functions (10). Altogether we can make up two types of independent relativistic molecular orbitals:

$$\tau_{n\nu} = [2(1 \pm s_{ab})]^{1/2}(\psi_{a\nu} \pm \psi_{b\nu}). \tag{15}$$

The orbitals corresponding to the upper sign describe the electronic ground state of H_2^+, while those corresponding to the lower sign describe the excited repulsion state.

We describe the knocked-out electron by a relativistic plane wave that can be represented in a form similar to (10):

$$\xi_{q\gamma} = \left(1 - i\frac{\alpha}{1+\alpha^2\varepsilon}(\boldsymbol{\alpha}\nabla)\right)v_{\mathbf{q}}(\mathbf{r})u_\gamma, \tag{16}$$

$$v_{\mathbf{q}}(\mathbf{r}) = [(1+\alpha^2\varepsilon)/2\alpha^2\varepsilon V]^{1/2}\exp(i\mathbf{qr}). \tag{17}$$

The products of the single-electron functions (15) and (16) can be used to construct four normalized[2)] and antisymmetrical electronic functions of the final state of the system H_2^+ + e:

$$\Phi_n^{\gamma\nu} = \frac{1}{\sqrt{2}}\det|\tau_{n\nu}\xi_{q\gamma}|, \qquad \nu,\gamma = 1, 2. \tag{18}$$

The complete wave functions of the final state are obtained by multiplying the electronic wave function (18) by the function $\chi_{n\kappa}(R)$ that describes the nuclear motion in the ion H_2^+:

$$\Psi_{\text{fin}} = \Phi_n^{\gamma\nu}(r, R)\chi_{n\kappa}(R). \tag{19}$$

3. CALCULATION OF THE CROSS SECTION

The calculation for the differential cross section (1) of the photoeffect contains a sum over the final states of the system. The final state is described by a set of quantum numbers characterizing the electronic, rotational-vibrational, and polarization state of the system. We shall consider henceforth the partial cross section of the photoeffect with formation of an H_2^+ ion in a fixed electronic state. The rotational-vibrational state is not fixed, and we assume that the photoeffect can cause the ion to be in any rotational-vibrational state compatible with the conservation laws. Owing to the large energy of the electron knocked out from the molecule, this energy can be regarded as independent of the energy of the rotational-vibrational sublevels, so that it is possible to obtain readily the sum over all the final rotational-vibrational sublevels.

Substituting in (1) the expressions (5) and (19) for the wave functions of the initial and final states, and using the completeness of the system of functions describing the nuclear motion, we obtain

$$\begin{aligned}\frac{d\sigma_{n0}{}^{\lambda}}{d\Omega} &= \frac{\alpha\varepsilon qV}{2\pi\omega}\sum_{\substack{\text{fin}\\\text{state}}}|\langle\Psi_{\text{fin}}|\hat{F}|\Psi_{\text{init}}\rangle|^2 \\ &= \frac{\alpha\varepsilon qV}{2\pi\omega}\sum_{\gamma,\nu=1}^{2}\sum_{\kappa}|\langle\Phi_n{}^{\gamma\nu}(r,R)\chi_{n\kappa}(R)|\hat{F}|\Phi_0(r,R)\chi_{0\lambda}(r,R)\rangle|^2 \\ &= \frac{\alpha\varepsilon qV}{2\pi\omega}\sum_{\gamma,\nu=1}\langle\chi_{0\lambda}(R)||\mathscr{M}_{n0}{}^{\gamma\nu}(R)|^2|\chi_{0\lambda}(R)\rangle,\end{aligned} \tag{20}$$

where

$$\mathscr{M}_{n\,0}^{\gamma\nu}(R) = \langle\Phi_n^{\gamma\nu}(r, R)|\hat{F}|\Phi_0(r, R)\rangle \tag{21}$$

is the electronic matrix element and depends on the nuclear coordinates as parameters, while λ describes the aggregate of the quantum numbers v, J, M, and K.

We substitute in (20) an expression for the wave functions $\chi_{0\lambda}$ (see (8)). Putting

$$\frac{d\sigma_{n0}{}^{v}(\vartheta)}{d\Omega} = \frac{\alpha\varepsilon qV}{2\pi\omega}\left\langle\Lambda_{0v}(Q)\,\middle|\,\sum_{\gamma,\nu=1}^{2}|\mathscr{M}_{n0}{}^{\gamma\nu}(Q,\vartheta)|^2\,\middle|\,\Lambda_{0v}(Q)\right\rangle, \tag{22}$$

we obtain

$$\frac{d\sigma_{n0}^{vJMK}}{d\Omega} = \frac{2J+1}{8\pi^2}\left\langle D_{MK}{}^{J}(\vartheta)\,\middle|\,\frac{d\sigma_{n0}{}^{v}(\vartheta)}{d\Omega}\,\middle|\,D_{MK}{}^{J}(\vartheta)\right\rangle. \tag{23}$$

Expression (22) is the partial cross section for the photoionization of a molecule from the electron-vibrational level 0v, not averaged over the rotations of the molecule. The subscript n designates the electronic state of the H_2^+ ion.

The measured quantity, however, is the cross section averaged over all the initial rotational-vibrational states of the system. We denote by w(vJMK) the probability of populating the rotational-vibrational levels. In the adiabatic approximation, the rotational and vibrational motions can be regarded with good accuracy as independent, and we can represent w(vJMK) in the form

$$w(vJMK) = w(v)w(JMK), \tag{24}$$

where $w(JMK) = (2J+1)^{-1}w(JK)$ owing to the degeneracy with respect to M. The probabilities are normalized by the natural conditions

$$\sum_v w(v) = 1, \quad \sum_{JMK} w(JMK) = \sum_{JK} w(JK) = 1. \tag{25}$$

We shall assume the temperature to be not too high, so as to excite only the lower vibrational states. Then the vibrations can be regarded as harmonic and

$$w(v) = \exp\left\{-\frac{\hbar\omega_0}{kT}v\right\}\left(1 - \exp\left\{-\frac{\hbar\omega_0}{kT}\right\}\right), \tag{26}$$

where ω_0 is the frequency of the zero-point oscillations of H_2.

We average the cross section (23) over the rotational and vibrational initial states:

$$\begin{aligned}\frac{\overline{d\sigma_{n0}}}{d\Omega} &= \sum_{vJMK} w(vJMK)\frac{2J+1}{8\pi^2}\left\langle D_{MK}{}^{J}(\vartheta)\,\middle|\,\frac{d\sigma_{n0}{}^{v}(\vartheta)}{d\Omega}\,\middle|\,D_{MK}{}^{J}(\vartheta)\right\rangle \\ &= \sum_v w(v)\int\frac{d\sigma_{n0}{}^{v}(\vartheta)}{d\Omega}\frac{d\vartheta}{8\pi^2}.\end{aligned} \tag{27}$$

In the derivation of (27) we used the orthogonality relation of the generalized spherical functions (see[6]):

$$\sum_M D_{MK}^{*J}(\vartheta)D_{MK'}^{J}(\vartheta) = \delta_{KK'}. \tag{28}$$

It follows from (27) that for averaging the cross section over the rotational states it suffices to integrate the non-averaged cross section, divided by $8\pi^2$, over the Euler angles. Although this result was obtained here for molecules of the symmetrical-top type, it is valid for molecules of arbitrary type (cf.[8]).

Our next task is to calculate in succession the quantities (21), (22), and (27). For convenience in the calculations, we express the electronic function of the initial state (14) in the form

$$\Phi_0 = N_0 \sum_{\mu=1}^{2} (-1)^{\mu+1} \{\psi_{a\mu}(1)\psi_{b,3-\mu}(2) - \psi_{a\mu}(2)\psi_{b,3-\mu}(1)\}. \tag{29}$$

We substitute in (21) the expressions (18) and (29) for the wave functions:

$$\begin{aligned}\mathscr{M}_{n0}^{\gamma\nu} = -\sqrt{2} N_0 \sum_{\mu=1}^{2} (-1)^{\mu} \{&\langle\xi_{q\gamma}|\hat{f}|\psi_{a\mu}\rangle \langle\tau_{n\nu}|\psi_{b,3-\mu}\rangle \\ &+ \langle\xi_{q\gamma}|\hat{f}|\psi_{b\mu}\rangle \langle\tau_{n\nu}|\psi_{a,3-\mu}\rangle - \langle\tau_{n\nu}|\hat{f}|\psi_{a\mu}\rangle \langle\xi_{q\gamma}|\psi_{b,3-\mu}\rangle \\ &- \langle\tau_{n\nu}|\hat{f}|\psi_{b\mu}\rangle \langle\xi_{q\gamma}|\psi_{a,3-\mu}\rangle\}.\end{aligned} \tag{30}$$

We assume that the plane wave $\xi_{q\gamma}$ is orthogonal to the atomic orbitals. This is equivalent to discarding the last two terms in (30). This approximation, as shown by our calculations, is justified, since the contribution of the discarded terms to the total photoionization cross section does not exceed 3% at the photon energy 100 eV and decreases rapidly with increasing energy of the latter.

The wave function $\xi_{q\gamma}$ and the operator $\hat{f}$ are specified in a coordinate system connected with the mass center of the molecule, while the functions $\psi_{a\mu}$ and $\psi_{b\mu}$ are centered at the nuclei a and b, respectively. To calculate the integrals, it is convenient to refer all the functions to a single center:

$$\begin{aligned}\langle\xi_{q\gamma}|\hat{f}|\psi_{a\mu}\rangle &= \langle\xi_{q\gamma}|\hat{f}|\psi_{\mu}\rangle \exp\{i(\mathbf{k}-\mathbf{q},\ \mathbf{R}_a)\}, \\ \langle\xi_{q\gamma}|\hat{f}|\psi_{b\mu}\rangle &= \langle\xi_{q\gamma}|\hat{f}|\psi_{\mu}\rangle \exp\{i(\mathbf{k}-\mathbf{q},\ \mathbf{R}_b)\},\end{aligned} \tag{31}$$

where $\mathbf{R}_a$ and $\mathbf{R}_b$ are vectors drawn from the mass center to the nuclei.

The initial matrix element (30) used in the calculations takes the form

$$\mathscr{M}_{n0}^{\gamma\nu} = (-1)^{\nu+1} \langle\xi_{q\gamma}|f|\psi_{3-\nu}\rangle G_n, \tag{32}$$

where

$$G_n = (1 \pm s_{ab})^{1/2} N_0 [\exp\{i(\mathbf{k}-\mathbf{q},\ \mathbf{R}_b)\} \pm \exp\{i(\mathbf{k}-\mathbf{q},\ \mathbf{R}_a)\}]. \tag{33}$$

The plus sign in (33) describes ionization with formation of an H_2^+ ion in the ground state, while the minus describes ionization with formation of H_2^+ in a repulsion electronic state.

We substitute (10) and (16) in (32) and recognize that products of the type $u_\gamma^+(\boldsymbol{\alpha}\cdot\mathbf{a}_1)\ldots(\boldsymbol{\alpha}\cdot\mathbf{a}_n)u_\mu$, where $\mathbf{a}_i$ is an arbitrary vector that vanishes if the number of $\boldsymbol{\alpha}$ matrices is odd. We obtain

$$\begin{aligned}\mathscr{M}_{n0}^{\gamma\nu} &= (-1)^{\nu+1} G_n \frac{2^3\eta^{5/2}\sqrt{\pi}}{\sqrt{V}(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^2} \left(\frac{1+\alpha^2\varepsilon}{2\varepsilon}\right)^{1/2} \cdot \\ &\times u_\gamma^+ \left[-\frac{1}{2}(\alpha\mathbf{e})(\alpha, \mathbf{k}-\mathbf{q}) + \frac{1}{1+\alpha^2\varepsilon}(\alpha\mathbf{q})(\alpha\mathbf{e})\right] u_{3-\nu}.\end{aligned} \tag{34}$$

We substitute further in (34) the explicit form of the bispinors u_γ (11). Taking the matrices $\boldsymbol{\alpha}$ in the standard representation:

$$\alpha \equiv \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix},$$

where $\boldsymbol{\sigma}$ are Pauli matrices, we obtain ultimately

$$\begin{aligned}\mathscr{M}_{n0}^{\gamma\nu} = \left(\frac{2^7\pi\eta^5}{V\varepsilon(1+\alpha^2\varepsilon)}\right)^{1/2} \frac{(-1)^{\nu+1}G_n}{(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^2} \Big\{ &(\mathbf{eq})\delta_{\gamma,3-\nu} \\ &- \frac{1+\alpha^2\varepsilon}{4} w_\gamma^+(\sigma\mathbf{e}) \left(\sigma, \mathbf{k} + \frac{1-\alpha^2\varepsilon}{1+\alpha^2\varepsilon}\mathbf{q}\right) w_{3-\nu}\Big\}.\end{aligned} \tag{35}$$

We sum the square of the modulus of the matrix element (35) over the final polarization states of the electrons. After rather cumbersome manipulations, we obtain

$$\begin{aligned}\sum_{\gamma,\nu=1}^{2} |\mathscr{M}_{n0}^{\gamma\nu}|^2 &= \frac{2^6(1\pm s_{ab})\pi\eta^5(1\pm\cos(\mathbf{k}-\mathbf{q}, \mathbf{R}_{ab}))}{V\varepsilon(1+s_{ab}^2)(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^4} \\ &\times \left[(\mathbf{eq})^2 + \frac{1+\alpha^2\varepsilon}{8}\left(\mathbf{k} + \frac{1-\alpha^2\varepsilon}{1+\alpha^2\varepsilon}\mathbf{q}\right)^2\right].\end{aligned} \tag{36}$$

It is convenient to use in the summation the following relations:

$$\sum_{\gamma=1}^{2} w_\gamma w_\gamma^+ = 1,\ (\sigma\mathbf{A})(\sigma\mathbf{B}) = (\mathbf{AB}) + i(\sigma[\mathbf{A}\times\mathbf{B}]),\ \sum_{\gamma=1}^{2} w_\gamma^+(\sigma\mathbf{A})w_\gamma = 0, \tag{37}$$

where **A** and **B** are arbitrary vector operators that commute with the matrices $\boldsymbol{\sigma}$.

A differential cross section, not averaged over the rotations, is obtained for the photoionization of the H_2 molecule by integrating (22) over the vibrational coordinates. We confine ourselves to consideration of photoionization from the lower vibrational levels, and therefore choose as the wave functions Λ_{0v} the harmonic-oscillator wave functions

$$\Lambda_{0v} = \left(\frac{a}{\sqrt{\pi}\, v!\, 2^v}\right)^{1/2} \exp\left\{-\frac{1}{2}a^2Q^2\right\} H_v(aQ), \tag{38}$$

where $H_v(x)$ is a Hermite polynomial, $a = (M\omega_0/2)^{1/2}$, M is the proton mass, and $\omega_0 = 1.98 \times 10^{-2}$ is the frequency of the zero-point vibrations of the H_2 nuclei; $Q = R_{ab} - R_0$ is the normal coordinate describing the deviation of the nuclei from the equilibrium distance R_0.

We substitute (36) and (38) in (22). After a number of transformations we arrive at a differential cross section, not averaged over the molecule orientations, for the photoionization from the electron-vibrational level 0v:

$$\begin{aligned}\frac{d\sigma_{n0}^v}{d\Omega} &= \frac{2^5\eta^5\alpha(1\pm s_{ab})q}{(1+s_{ab}^2)\omega(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^4} \Big\{1 \pm \cos(\mathbf{k}-\mathbf{q}, \mathbf{R}_0) \\ &\times \exp\left[-\frac{(\mathbf{k}-\mathbf{q}, \mathbf{R}_0)^2}{4a^2R_0^2}\right] L_v\left[\frac{(\mathbf{k}-\mathbf{q}, \mathbf{R}_0)^2}{2a^2R_0^2}\right]\Big\} \\ &\times \left[(\mathbf{eq})^2 + \frac{1+\alpha^2\varepsilon}{8}\left(\mathbf{k} + \frac{1-\alpha^2\varepsilon}{1+\alpha^2\varepsilon}\mathbf{q}\right)^2\right],\end{aligned} \tag{39}$$

where $L_v(x)$ is a Laguerre polynomial.

The cross section averaged over the initial rotational and vibrational states is obtained when (39) is substituted in (27), and is equal to

$$\begin{aligned}\frac{\overline{d\sigma_{n0}}}{d\Omega} &= \frac{2^5\eta^5\alpha(1\pm s_{ab})q}{(1+s_{ab}^2)\omega(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^4} \left((\mathbf{eq})^2 + \frac{1+\alpha^2\varepsilon}{8}\left(\mathbf{k} + \frac{1-\alpha^2\varepsilon}{1+\alpha^2\varepsilon}\mathbf{q}\right)^2\right) \\ &\times \sum_v w(v) \left(1 \pm \frac{\sqrt{2}a}{|\mathbf{k}-\mathbf{q}|} \int_0^X dx \cos(\sqrt{2}aR_0x) e^{-x^2/2} L_v(x^2)\right).\end{aligned} \tag{40}$$

The quantity $X = |\mathbf{k}-\mathbf{q}|/\sqrt{2}a$, the upper limit of the integral in (40), increases with increasing energy of the incident photon. At $E_{ph} = 4 \times 10^3$ eV we have $X > 10$ and since the integrand contains an exponential function, the upper limit of the integral can be replaced by ∞ with good accuracy. The cross section (40) is then transformed into

$$\begin{aligned}\frac{\overline{d\sigma_{n0}}}{d\Omega} &= \frac{2^5\eta^5\alpha(1\pm s_{ab})q}{(1+s_{ab}^2)\omega(\eta^2+|\mathbf{k}-\mathbf{q}|^2)^4} \left((\mathbf{eq})^2 + \frac{1+\alpha^2\varepsilon}{8}\left(\mathbf{k} + \frac{1-\alpha^2\varepsilon}{1+\alpha^2\varepsilon}\mathbf{q}\right)^2\right) \\ &\times \sum_v w(v) (1 \pm [2^v v!|\mathbf{k}-\mathbf{q}|]^{-1} \sqrt{\pi} a \exp(-a^2R_0^2) H_v^2(aR_0)).\end{aligned} \tag{41}$$

4. DISCUSSION OF RESULTS

A calculation of the nonrelativistic differential photoionization cross section of the H_2 molecule[3] has shown that the photoelectron angular distribution not averaged over the molecule rotations has sharply pronounced maxima and minima, the number of which increases with increasing photoelectron energy. The calculation presented in this paper has made it possible to investigate this effect with further increase of the photon energy and with allowance for the vibrations of the nuclei.

Figure 1 shows the differential photoionization cross sections of the H_2 molecule at two values of the photon energy, calculated with allowance for the nuclear vibrations (formula (39)) and without allowance for the vibrations (the expression for the cross section is obtained in this case from (39) by replacing the exponential and the Laguerre polynomial by unity). The cross sections were calculated as functions of the angle θ between the photon wave vector **k** and the photoelectron vector **q**. It was assumed in the calculation that the vector **q** lies in the plane of the vectors **k** (z axis) and e (x axis), while the molecule axis is directed along the vector **k**.

An analysis of the curves show that at relatively low photon energies (up to 1000 eV) the vibrations of the nuclei influence little the angular dependences of the differential cross section (cf. the curves in Figs. 1a and 1b). The reason is that the product of the exponential by the Laguerre polynomial in (39) differs little from unity at these energies in the entire range of photoelectron emission angles. With increasing photon energy, allowance for the nuclear vibrations alters significantly the oscillatory picture (see the curves in Figs. 1c and 1d). The point is that at large photon energies the product of the exponential by the Laguerre polynomial turns out to be close to unity not in the entire range of variation of the angle θ, but only in a limited range of angles in which $|(\mathbf{k}-\mathbf{q}, \mathbf{R}_0)| \ll 1$. For the case considered by us (the molecule axis is directed along **k**) this is equivalent to the equality $\cos\theta \sim k/q$. Since $q = (k^2 + 2k/\alpha)^{1/2}$ at large k, it follows that

$$\cos\theta \sim (1 + 2/\alpha k)^{-1/2}. \qquad (42)$$

With increasing photon energy E_{ph}, the angle interval in which the oscillations are observed contracts and, as follows from (42), shifts towards smaller angles, as is clearly seen from Fig. 2. The maximum of the cross section also shifts with increasing E_{ph} toward smaller angles, i.e., in the direction of the vector **k**. This shift is well known from the theory of the relativistic photoeffect on atoms. Averaging of the molecule cross section over the rotations leads to a vanishing of the oscillations. The relativistic shift of the maximum, of course, still remains (see Fig. 3).

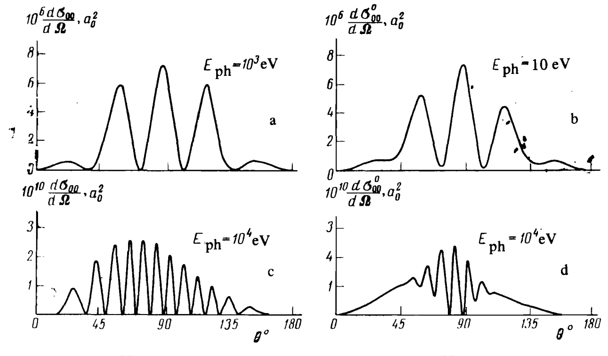

FIG. 1. Differential cross section of the photoeffect of the molecule H_2, not averaged over the rotational states: a and c are the cross sections calculated without allowance for the nuclear vibrations, b and d—with allowance for the nuclear vibrations.

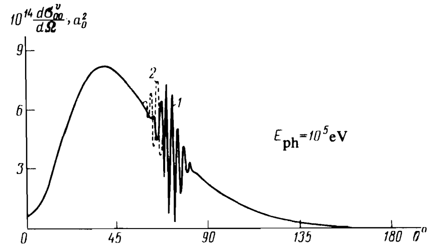

FIG. 2. Differential cross section of the molecule H_2, not averaged over the rotational states: 1—the H_2 molecule is in the vibrational ground state (v = 0), 2—in the first-excited vibrational state (v = 1).

The total cross section of the photoeffect is obtained by integrating (40) over all the photoelectric emission angles. We have calculated the following cases: (a) the H_2^+ ion is produced in the electronic ground state (cross section σ_{00}); (b) the H_2^+ ion is produced in the first excited state, which is repulsive (cross section σ_{10}). The total cross sections were calculated under the assumption that the molecular-gas temperature does not exceed 1000° K. This limitation has made it possible to retain only the term with v = 0 in the sum over v in (40), and the relative error in the cross section did not exceed 10^{-3}.

The obtained cross sections are listed in the table. As seen from the table, the probability of production of the H_2^+ ion in a repulsion state is almost one-fifth as large as in the ground state over the entire energy range.

To assess the influence of the vibrations of the nuclei on the total cross section of the photoeffect, we have also calculated the photoeffect cross sections without allowance for the vibrational motion of the nuclei. The result of the calculations, in the form of the ratio of the cross sections as a function of the photon energy, is shown in Fig. 4. We see that at photon energies exceeding 1000 eV the vibrations of the nuclei exert practically no influence on the behavior of the cross sections; at photon energies less than 1000 eV, failure to take the vibrations of the nuclei into account leads to cross-section errors that reach 30%.

It is of interest to compare our values of the photoionization cross sections of the H_2 molecule with the values obtained under the assumption that the molecular cross sections are additive (see the fifth column of the table). The atomic photoionization cross sections σ_H were calculated by us by formula (43) for photon energies $E_{ph} < 10^4$ eV and by formula (44) for $E_{ph} > 10^4$ eV

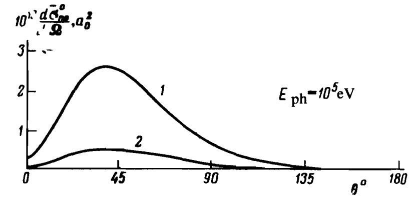

FIG. 3. Differential cross section of the photoeffect of the molecule H_2, averaged over the rotational states: 1—the H_2^+ ion is produced in the ground electronic state (n = 0), 2—in the first excited state (n = 1).

E_{ph}, eV	$\bar{\sigma}_{00}$, a.u.	$\bar{\sigma}_{10}$, a.u.	$\frac{\bar{\sigma}_{10}}{\bar{\sigma}_{00}}$	$2\sigma_H$, a.u.	$\frac{\bar{\sigma}_{00}}{2\sigma_H}$	$\frac{\bar{\sigma}_{00}+\bar{\sigma}_{10}}{2\sigma_H}$
$1\cdot10^2$	0.(2)30	0.(2)10	0.33	0.(2)19	1.57	2.11
$2\cdot10^2$	0.(3)32	0.(3)10	0.31	0.(3)23	1.43	1.83
$3\cdot10^2$	0.(4)97	0.(4)22	0.23	0.(4)62	1.51	1.92
$4\cdot10^2$	0.(4)39	0.(4)74	0.19	0.(4)24	1.62	1.93
$5\cdot10^2$	0.(4)18	0.(5)34	0.19	0.(4)11	1.49	1.94
$6\cdot10^2$	0.(5)91	0.(5)19	0.21	0.(5)61	1.49	1.64
$7\cdot10^2$	0.(5)52	0.(5)12	0.23	0.(5)36	1.45	1.77
$8\cdot10^2$	0.(5)32	0.(6)73	0.23	0.(5)23	1.43	1.71
$9\cdot10^2$	0.(5)22	0.(6)48	0.22	0.(5)15	1.46	1.79
$1\cdot10^3$	0.(5)15	0.(6)33	0.22	0.(5)11	1.35	1.66
$5\cdot10^3$	0.(8)58	0.(8)12	0.20	0.(8)40	1.45	1.75
$1\cdot10^4$	0.(9)51	0.(9)10	0.20	0.(9)36	1.42	1.69
$5\cdot10^4$	0.(11)20	0.(12)40	0.20	0.(11)14	1.43	1.71
$1\cdot10^5$	0.(12)20	0.(13)40	0.20	0.(12)14	1.43	1.71
$5\cdot10^5$	0.(14)16	0.(15)31	0.20	0.(14)10	1.45	1.73
$1\cdot10^6$	0.(15)29	0.(16)59	0.20	0.(15)21	1.38	1.66

NOTE: 0.4(97) means 0.000097

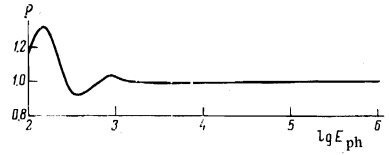

FIG. 4. Ratio ρ of the cross section of the photoeffect of the H_2 molecule, calculated without allowance for the vibrations of the nuclei, to the corresponding cross section calculated with allowance for the vibrations of the nuclei, as a function of the photon energy E_{ph} (in eV); the H_2^+ ion is produced in the ground state.

(see the Appendix). The sixth column of the table gives the ratio of the cross section for H_2-molecule photoionization with production of H_2^+ in the ground electronic state to double the cross section of the H atom. As seen from the presented data, there is no additivity in the entire considered range of energies. This deviation from additivity is due to the change in the shape of the electron cloud of the atoms as a result of the chemical bond, and should become manifest in the case of photoeffects on valence shells and other molecules.

The total cross section of the molecular photoeffect is a sum of partial cross sections $\bar{\sigma}_{n0}$, each of which corresponds to production of an H_2^+ ion in one of the excited electronic states. Allowance for the contribution of these partial cross sections leads to an increase of the non-additivity (see the last column of the table).

In conclusion, the authors thank L. P. Pitaevskiĭ, V. G. Plotnikov, and M. A. Kozhushner for useful discussions of a number of problems touched upon in the present paper.

APPENDIX

Estimate of the plane-wave approximation for the knocked-out electron in the case of photionization of the hydrogen atom

The only quantum-mechanical systems for which exact expressions are available for the photoionization cross sections is the hydrogen atom. It is therefore a natural object for testing the plane-wave approximation.

In the nonrelativistic region, the cross section for the photoionization of the H atom is described by the Stobbe formula, and in the relativistic region by the Sauter formula, see [4]. In the nonrelativistic limit, the Sauter formula does not go over into the Stobbe formula, since Sauter has neglected in his derivation the ionization potential of the atom in comparison with the photon energy, and has also assumed that the photoelectron velocity $v \sim 1/\alpha$. It is therefore necessary to use both formulas in the calculation of the photoionization cross section in the energy range from threshold to relativistic.

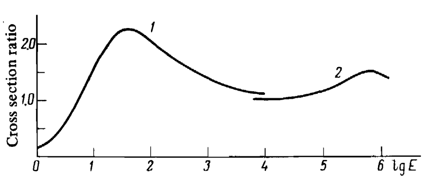

FIG. 5. Estimate of the plane-wave approximation in the case of the photoeffect on the H atom; E is in eV (explanation in the text).

It is easy to show that in the plane-wave approximation the following expressions hold for the photoionization cross sections of the H atom:

$$\sigma^{\text{nonrel}}_{\text{pl. wave}} = 2^3\pi\alpha(2E)^{5/2}/(E+1/2)^5, \tag{43}$$

$$\sigma^{\text{rel}}_{\text{pl. wave}} = 2\pi\alpha^8\frac{(\gamma^2-1)^{5/2}}{(\gamma-1)^5}\left(\frac{4}{3}+\frac{\gamma(\gamma-1)}{\gamma+1}\right), \tag{44}$$

where E is the kinetic energy of the knocked-out electron, and $\gamma = [1-(\alpha v)^2]^{-1/2}$. At $\alpha v \ll 1$, formula (44) goes over into (43) if one neglects in the latter the ion ization potential $I = 1/2$ in comparison with E.

We have calculated the photoionization cross sections by means of formulas (43) and (44) and by using the formulas of Stobbe and Sauter. Figure 5 shows the ratios $\sigma^{\text{nonrel}}_{\text{pl. wave}}/\sigma_{\text{Stobbe}}$ (curve 1) and $\sigma^{\text{rel}}_{\text{pl. wave}}/\sigma_{\text{Sauter}}$ (curve 2). As expected, the influence of the Coulomb field of the nucleus is most significant near the threshold and decreases with increasing energy of the knocked-out electron. With further increase of the energy, however, the influence of the Coulomb field, in spite of the widely held opinion, again becomes appreciable. The error of the plane-wave approximation reaches ~50% at $E = 6.6 \times 10^5$. The error then decreases again, and a transition to the limit in the case $\gamma \gg 1$ shows that formula (43) coincides with Sauter's formula, i.e., the plane-wave approximation is practically exact.

Thus, our estimates show that the plane-wave approximation holds satisfactorily at knocked-out electron energies from 5 to 100 kV, where the error does not exceed 50%, and is exact in the ultrarelativistic region.

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[1] We use atomic units in this article.

[2] The functions (18) are normalized accurate to terms ~ 1/V.

[1] F. I. Vilesov, Usp. Fiz. Nauk 81, 669 (1963) [Sov. Phys.-Uspekhi 6, 888 (1964)]; Adv. Photochem. 2, 385 (1964).
[2] F. I. Vilesov and S. N. Lopatin, Vestnik LGU, No. 4 (1970).
[3] I. G. Kaplan and A. P. Markin, Dokl. Akad. Nauk SSSR 184, 66 (1969) [Sov. Phys.-Doklady 14, 36 (1969)].
[4] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskiĭ, Relyativistskaya kvantovaya mekhanika (Relativistic Quantum Mechanics), Part 1, Nauka, 1968.

[5] W. Kolos, Adv. Quant. Chem. **5**, 99 (1970); J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. **12**, 3 (1967).

[6] A. S. Davydov, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963.

[7] A. I. Akhiezer and V. B. Berestetskiĭ, Kvantovaya élektrodinamika (Quantum Electrodynamics), Nauka, 1969.

[8] F. H. Read and G. L. Whiterod, Proc. Roy. Soc. **82**, 434 (1963).

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