Adiabatic description of nonadiabatic isotopic asymmetry effects. The dipole moment of HD

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A new method is proposed for describing the effects of the asymmetry in those electronic properties of a molecule which are induced by the isotopic asymmetry of the nuclear core when this core consists of different isotopes of the same chemical element. Whereas in the traditional approach the computations of the corrections to the adiabatic wave function of the molecule are laborious, in the new approach the isotopic asymmetry of the electronic properties fits into the framework of the adiabatic approximation. For this purpose use is made of the fact that the accuracy of the adiabatic approximation depends on the specific choice of the dynamic variables describing the "fast" and "slow" subsystems in the molecule. It is shown that in the case of diatomic isotopically asymmetric molecules the coordinates can be chosen such that all the asymmetry effects will be included in the potential energy. As a result, the adiabatic approximation can be used, and this simplifies greatly the theory of the isotopic asymmetry of the electronic properties. The new approach is illustrated with the molecules HD and HD$^+$. In the case of HD the mean value of the component of the dipole moment along the line joining the nuclei and the dipole moments determining the intensities of the rotational and vibrational-rotational transitions are computed. In the case of the one-electron molecule HD$^+$ a connection is established between the isotopic asymmetry effects and the physical characteristics (the electric polarizability, the quadrupole moment, the diamagnetic susceptibility, and the change that occurs in the nuclear magnetic screening in an electric field) of the homonuclear molecular ion H_2^+. The displacement of the center of the electron cloud from the center of the nuclear core in HD$^+$ is computed.

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A special place is occupied in the theory of molecules by molecules whose nuclei are made up of different isotopes of the same chemical element. As was pointed out by Wick,[1] such molecules, e.g., HD, are not strictly homonuclear: the difference between the nuclear masses leads to a situation in which the dynamics of the electron interaction with the various nuclei are different. The asymmetry in the nuclear masses produces an asymmetry in the electronic properties: a molecule that is not strictly homonuclear possesses a nonzero electric dipole moment and, as a result, a rotational and a vibrational-rotational spectrum, the possibility of the observation of which was predicted by Wick[1] and independently by Ginzburg.[2] This prediction was experimentally confirmed by Herzberg[3] and other authors.[4-8] The first theoretical estimations of the dipole moment and the intensities of the vibrational-rotational transitions for HD were carried out by Shirokov,[9] Wu,[10] and Faĭn.[11] The publication of new experimental data and the development of the computational capabilities of the theory in the past decade have brought about an upsurge in interest in the properties of molecules that are not strictly homonuclear. In particular, calculations of the dipole moment and the intensities of the vibrational-rotational[12-19] and forbidden electronic[20] transitions have been carried out for the HD molecule.

In all the above-cited theoretical papers the isotopic asymmetry of the electronic properties of HD is interpreted as a nonadiabatic effect stemming from those terms in the molecule's kinetic-energy operator which are antisymmetric under interchange of the nuclei.

Here we propose a new approach that allows us to take into account within the framework of the adiabatic approximation the effects of the isotopic asymmetry in the electronic properties of molecules that are not strictly homonuclear. This simplifies the theory appreciably, and broadens the region of its practical applicability without lowering the level of accuracy.

We proceed from the fact that the accuracy of the adiabatic approximation in the description of the isotopic-asymmetry effects significantly depends on the choice of the coordinates describing the "fast" and "slow" subsystems. For the special coordinates chosen below, the isotopic asymmetry effects are described by the potential-energy operator up to terms of the order of $\varkappa^4$ inclusively, where $\varkappa$ is the Born–Oppenheimer parameter, and the isotopic asymmetry of the kinetic-energy operator is of the order of $\varkappa^8$ (instead of the $\varkappa^4$ for the normally used relative coordinates). Since $\varkappa^4 \sim 10^{-3}-10^{-4}$, the effects of the isotopic asymmetry of the electronic properties of molecules that are not strictly homonuclear can be computed with the chosen-subsystem coordinates within the framework of the adiabatic approximation without any allowance for the difficult-to-compute nonadiabatic corrections. The relative computational errors here are $\varkappa^3 \lesssim 0.5\%$.

Let us elucidate the foregoing in the particular case of a diatomic n-electron molecule AB whose nuclei have the same charge $q_A = q_B = q$, but different masses $M_A \neq M_B$. The Hamiltonian of the molecule depends, after the separation of the motion of the center of mass, on $3(n+1)$ relative coordinates, i.e., on $n+1$ three-dimensional vectors determining the relative disposition of the n electrons and the two nuclei and the orientation of this disposition in space. Let us choose the relative coordinates in the following form:

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$$\begin{aligned}\boldsymbol{\xi}&=\frac{M_B}{M_B'}\mathbf{R}_B-\frac{M_A}{M_A'}\mathbf{R}_A+\left(\frac{1}{2M_B'}-\frac{1}{2M_A'}\right)\sum_{j=1}^{n}\mathbf{r}_{j,\mathrm{el}},\\ \boldsymbol{\rho}_j&=\mathbf{r}_{j,\mathrm{el}}-\left(\frac{1}{4M_A'}+\frac{1}{4M_B'}\right)\sum_{i=1}^{n}\mathbf{r}_{i,\mathrm{el}}-\frac{M_A}{2M_A'}\mathbf{R}_A-\frac{M_B}{2M_B'}\mathbf{R}_B.\end{aligned}\tag{1}$$

Here $\mathbf{R}_A$, $\mathbf{R}_B$, and $\mathbf{r}_{j,\mathrm{el}}$ respectively denote the radius vectors of the nucleus A, the nucleus B, and the j-th electron in the laboratory system $(j=1,2,3,\ldots,n)$. We use the atomic system of units in which $|e|=\hbar=m=1$, so that the nuclear masses M_A and M_B are measured in units of the electron mass. For the sake of brevity we use the notation: $M_A'=M_A+n/2$, $M_B'=M_B+n/2$. In the coordinates (1), the energy operator for the molecule has the following form:

$$\begin{aligned}H=&-\frac{1}{2\mu_1}\sum_{j=1}^{n}\Delta_{\rho_j}-\frac{1}{2\mu_2}\sum_{i,j}{}'\nabla_{\rho_i}\nabla_{\rho_j}-\frac{1}{2\mu_3}\Delta_{\xi}\\&+\frac{1}{2}\sum_{i,j}{}'|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j|^{-1}+q^2\left|\left(1+\frac{n}{4\mu}\right)\boldsymbol{\xi}+\frac{1}{2\mu_0}\sum_{i=1}^{n}\boldsymbol{\rho}_i\right|^{-1}\\&-q\sum_{j=1}^{n}\left|\boldsymbol{\rho}_j+\frac{1}{2}\boldsymbol{\xi}+\frac{n}{2M_A}\left[\frac{1}{2}\boldsymbol{\xi}+\left(\sum_{i=1}^{n}\boldsymbol{\rho}_i\right)/n\right]\right|^{-1}\\&-q\sum_{j=1}^{n}\left|\boldsymbol{\rho}_j-\frac{1}{2}\boldsymbol{\xi}+\frac{n}{2M_B}\left[-\frac{1}{2}\boldsymbol{\xi}+\left(\sum_{i=1}^{n}\boldsymbol{\rho}_i\right)/n\right]\right|^{-1}.\end{aligned}\tag{2}$$

Here we have introduced the following notation for the particle-mass-dependent coefficients:

$$\begin{gathered}\mu^{-1}=M_A^{-1}+M_B^{-1},\quad \mu_0^{-1}=M_A^{-1}-M_B^{-1},\\ \mu_1^{-1}=1+\frac{M_A}{4(M_A')^2}+\frac{M_B}{4(M_B')^2}-\frac{1}{2M_A'}-\frac{1}{2M_B'}+\frac{n}{16(M_A')^2}+\frac{n}{16(M_B')^2}\\ +\frac{n}{8M_A'M_B'},\\ \mu_2^{-1}=\mu_1^{-1}-1,\quad \mu_3^{-1}=\frac{M_A}{(M_A')^2}+\frac{M_B}{(M_B')^2}+\frac{n}{4}\left(\frac{1}{M_A'}-\frac{1}{M_B'}\right)^2.\end{gathered}\tag{3}$$

Let us introduce the Born–Oppenheimer parameter $\varkappa=(\mu_1/\mu_3)^{1/4}$. It can be seen from (3) that $\mu_1^{-1}\sim 1$, while μ^{-1}, μ_0^{-1}, μ_2^{-1}, and μ_3^{-1} are of the order of $\varkappa^4$.

It is important to note that in the Hamiltonian (2) the kinetic energy of the motion in the ξ coordinate (which, as $\varkappa\to 0$, is the analog of the relative coordinate $\mathbf{R}_B-\mathbf{R}_A$ of the nuclei) is strictly separated from the kinetic energy of the motion in the ρ_j coordinates (which are the analogs of the electron coordinates). At the same time, the kinetic energy operator expressed in terms of the traditional relative coordinates contains in the electronic and nuclear coordinates a cross term that leads to the nonadiabatic mixing of the adiabatic states of opposite parity and to the appearance of a corresponding contribution to the isotopic asymmetry of the electronic properties (see, for example, Refs. 1, 10, 12–20). The absence of a similar term in our kinetic-energy operator allows us to take account of the isotopic asymmetry within the framework of the adiabatic approximation.

Let us carry out the adiabatic approximation for the eigenfunctions of the operator (2), assuming ξ to be the coordinate of the slow subsystem and the set $\boldsymbol{\rho}_j$ to be the coordinates of the fast subsystem. In this approximation the wave function of the molecule has the form

$$\Psi(\boldsymbol{\rho}_j,\boldsymbol{\xi})=\varphi(\boldsymbol{\rho}_j,\boldsymbol{\xi})\chi(\boldsymbol{\xi}),\tag{4}$$

where the adiabatic wave functions of the fast, $\varphi(\boldsymbol{\rho}_j,\xi)$, and slow, $\chi(\xi)$, subsystems are determined from the equations

$$\begin{aligned}\Bigg\{&-\frac{1}{2\mu_1}\sum_{j=1}^{n}\Delta_{\rho_j}-\frac{1}{2\mu_2}\sum_{i,j}^{n}{}'\nabla_{\rho_i}\nabla_{\rho_j}+\frac{1}{2}\sum_{i,j}^{n}{}'|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j|^{-1}\\&+q^2\left|\left(1+\frac{n}{4\mu}\right)\boldsymbol{\xi}+\frac{1}{2\mu_0}\sum_{i=1}^{n}\boldsymbol{\rho}_i\right|^{-1}-q\sum_{j=1}^{n}\Bigg|\boldsymbol{\rho}_j+\frac{1}{2}\boldsymbol{\xi}\\&+\frac{n}{2M_A}\left(\frac{1}{2}\boldsymbol{\xi}+\frac{1}{n}\sum_{i=1}^{n}\boldsymbol{\rho}_i\right)\Bigg|^{-1}-q\sum_{j=1}^{n}\Bigg|\boldsymbol{\rho}_j-\frac{1}{2}\boldsymbol{\xi}\\&+\frac{n}{2M_B}\left(-\frac{1}{2}\boldsymbol{\xi}+\frac{1}{n}\sum_{i=1}^{n}\boldsymbol{\rho}_i\right)\Bigg|^{-1}\Bigg\}\varphi(\boldsymbol{\rho}_j,\boldsymbol{\xi})=W(\boldsymbol{\xi})\varphi(\boldsymbol{\rho}_j,\boldsymbol{\xi}),\end{aligned}\tag{5}$$

$$\left[-\frac{1}{2\mu_3}\Delta_{\xi}+W(\boldsymbol{\xi})\right]\chi(\boldsymbol{\xi})=E\chi(\boldsymbol{\xi}).\tag{6}$$

The deviation of the obtained adiabatic wave function from the exact eigenfunction of the energy operator is due primarily to the nonrigorous allowance for the operator $-\Delta_\xi/2\mu_3$. The resulting error in the allowance for the isotopic asymmetry effects is determined by the asymmetry of the indicated operator with respect to interchange of the nuclei A and B. It can easily be verified with the aid of the formula (1) that the interchange of $\mathbf{R}_A$ and $\mathbf{R}_B$ transforms the operator Δ_ξ into the operator $\Delta_\xi+O(\varkappa^4)$. Therefore, the contribution of the operator $-\Delta_\xi/2\mu_3$ to the isotopic asymmetry of the electronic properties is of the order of $O(\varkappa^8)$ and can be neglected, so that we need to take into account only the isotopic asymmetry of the potential energy in (2), an asymmetry which is of the order of $O(\varkappa^4)$. The contribution of the nonadiabatic corrections stems primarily from the terms of the form $-\chi(\xi)\Delta_\xi\varphi(\rho,\xi)/2\mu_3$ and $-(\nabla_\xi\varphi(\rho,\xi),\nabla_\xi\chi(\xi))/\mu_3$, which were dropped from Eqs. (5) and (6), and gives rise to a computational error of the order of $O(\varkappa^7)$. Therefore, the adiabatic approximation indeed adequately takes account of the isotopic asymmetry effects.

Let us separate in the potential energy in Eq. (5) the terms that are even and odd under inversion of the vector ξ:

$$V=V_e(\boldsymbol{\rho}_j,\boldsymbol{\xi})+V_o(\boldsymbol{\rho}_j,\boldsymbol{\xi});\tag{7}$$

$$V_e=[V(\boldsymbol{\rho}_j,\boldsymbol{\xi})+V(\boldsymbol{\rho}_j,-\boldsymbol{\xi})]/2,\quad V_o=[V(\boldsymbol{\rho}_j,\boldsymbol{\xi})-V(\boldsymbol{\rho}_j,-\boldsymbol{\xi})]/2.\tag{8}$$

Expanding the potential-energy operator in a series in the multipoles (in doing so we assume that the mean value of the ratio $n|\boldsymbol{\rho}|/2\mu_0|\xi|\sim\varkappa^4$), we obtain

$$V_e=-q\sum_{j=1}^{n}r_{jA}^{-1}-q\sum_{j=1}^{n}r_{jB}^{-1}+\frac{1}{2}\sum_{i,j}^{n}{}'r_{ij}^{-1}+q^2\xi^{-1}+O(\varkappa^4),\tag{9}$$

$$V_o=\frac{q}{4\mu_0}\sum_{i,j}^{n}\left\{\frac{(\mathbf{r}_{iA},\mathbf{r}_{jA})}{r_{jA}^3}-\frac{(\mathbf{r}_{iB},\mathbf{r}_{jB})}{r_{jB}^3}\right\}-\frac{q^2}{2\mu_0}\sum_{i=1}^{n}\frac{z_i}{\xi^2}+O(\varkappa^8).\tag{10}$$

Here we have introduced the following notation:

$$\begin{gathered}\xi=|\boldsymbol{\xi}|,\quad z_j=(\boldsymbol{\rho}_j,\boldsymbol{\xi})/\xi,\quad \mathbf{r}_{ij}=\boldsymbol{\rho}_i-\boldsymbol{\rho}_j,\\ \mathbf{r}_{jA}=\boldsymbol{\rho}_j+{}^1/{}_2\boldsymbol{\xi},\quad \mathbf{r}_{jB}=\boldsymbol{\rho}_j-{}^1/{}_2\boldsymbol{\xi}.\end{gathered}\tag{11}$$

It is evident from (2) that $\mathbf{r}_{jA}$ and $\mathbf{r}_{jB}$ represent to within terms of the order $\varkappa^4$ the radius vectors of the j-th electrons relative to the nuclei A and B, while

$\mathbf{r}_{ij}$ is exactly equal to the difference between the radius vectors of the i-th and j-th electrons.

The fast-subsystem wave function φ, which is determined by Eq. (5), can also be represented in the form of a sum of functions, $\varphi_e + \varphi_0$, the first of which preserves, while the second changes, its sign when the vector ξ is inverted. In accordance with the structure of the potential energy, $\varphi_e \sim \varkappa^0$ and $\varphi_0 \sim \varkappa^4$.

The electric dipole moment of the molecule is given by the operator

$$\hat{D}=q(\mathbf{R}_A+\mathbf{R}_B)-\sum_{j=1}^{n}\mathbf{r}_{j,\,\mathrm{el}}$$

and does not depend on the choice of the origin, provided the molecule is neutral (when $n=2q$). The component of the dipole-moment operator along the line joining the nuclei is equal to

$$\hat{D}_{\parallel}=\mathbf{D}\frac{\mathbf{R}_B-\mathbf{R}_A}{|\mathbf{R}_B-\mathbf{R}_A|}=\sum_{j=1}^{n}z_j+\frac{n^2}{8\mu_0}\xi$$
$$+\frac{1}{2\mu_0\xi}\sum_{i,j=1}^{n}[(\rho_i,\rho_j)-z_iz_j]+O(\varkappa^8). \tag{12}$$

Averaging $\hat{D}_{\parallel}$ over the wave function of the fast subsystem, we obtain the dipole moment of the molecule along the line joining the nuclei:

$$D_{\parallel}=2\langle\varphi_e|\sum_{j=1}^{n}z_j|\varphi_o\rangle_\rho+\frac{1}{2\mu_0}\Big[\frac{n^2}{4}\xi$$
$$+\frac{1}{\xi}\langle\varphi_e|\,\Big|\sum_{j=1}^{n}\rho_j\Big|^2-\Big(\sum_{j=1}^{n}z_j\Big)^2|\varphi_e\rangle_\rho\Big]+O(\varkappa^7). \tag{13}$$

The symbol $\langle\ \rangle_\rho$ denotes integration over the coordinates of the fast subsystem. We can, without altering the order of magnitude of the error ($\varkappa^8$), replace the function φ_e in the right side of (13) by the function satisfying the equation

$$[H_0-W_0(\xi)]\varphi_0=0, \tag{14}$$

where H_0 is the energy operator for a homonuclear molecule with fixed nuclei:

$$H_0=-\frac{1}{2}\sum_{j=1}^{n}\Delta_{\rho_j}+\frac{1}{2}\sum_{i,j}^{n}{}'\,|\rho_i-\rho_j|^{-1}+q^2\xi^{-1}$$
$$-q\sum_{j=1}^{n}\Big[\Big|\rho_j+\frac{1}{2}\xi\Big|^{-1}+\Big|\rho_j-\frac{1}{2}\xi\Big|^{-1}\Big]. \tag{15}$$

Similarly, the function φ_0 can be replaced by the solution of the first-order perturbation theory equation:

$$[H_0-W_0(\xi)]\varphi_1=(\langle V_O\rangle_\rho-V_O)\varphi_0. \tag{16}$$

Let us introduce a function φ_z that describes the polarization of the electron shell of the homonuclear molecule with fixed nuclei in a uniform field:

$$[H_0-W_0(\xi)]\varphi_z=-\sum_{j=1}^{n}z_j\varphi_0. \tag{17}$$

Replacing in (13) φ_e by φ_0 and φ_0 by φ_1, and using the identity

$$\langle\varphi_0|\sum_{j=1}^{n}z_j|\varphi_1\rangle_\rho=\langle\varphi_0|V_O|\varphi_z\rangle_\rho, \tag{18}$$

which follows from Eqs. (16) and (17), we obtain for the mean value of the dipole moment component along the $A-B$ line the expression

$$D_{\parallel}(R)=\frac{1}{2\mu_0}\Big\{q\langle\varphi_0|\sum_{i,j}\Big[\frac{(\mathbf{r}_{iA},\mathbf{r}_{jA})}{r_{iA}^3}-\frac{(\mathbf{r}_{iB},\mathbf{r}_{jB})}{r_{iB}^3}\Big]|\varphi_z\rangle_\rho$$
$$-\frac{2q^2}{\xi^2}\langle\varphi_0|\sum_{i=1}^{n}z_i|\varphi_z\rangle_\rho+\frac{n^2}{4}\xi$$
$$+\frac{1}{\xi}\langle\varphi_0|\,\Big|\sum_{i=1}^{n}\rho_i\Big|^2-\Big(\sum_{i=1}^{n}z_i\Big)^2|\varphi_0\rangle_\rho\Big\}+O(\varkappa^7). \tag{19}$$

Here R denotes the internuclear distance: $R=|R_B-R_A|=\xi+O(\varkappa^4)$. It can be seen from (19) that the dipole moment along the $A-B$ line is proportional to the quantity $\mu_0^{-1}=M_A^{-1}-M_B^{-1}$, which characterizes the mass asymmetry of the nuclear core, and which can be expressed in terms of the matrix elements of the operators computed with the unperturbed adiabatic electronic wave function ϕ_0 of the homonuclear molecule and the correction function φ_z describing the polarization of the electron shell of the homonuclear molecule in a uniform longitudinal electric field. Let us emphasize that in our approach the "axis" of the molecule is oriented along the vector ξ. It follows from (1) that

$$\mathbf{R}_B-\mathbf{R}_A=\frac{1}{2\mu_0}\sum_{j=1}^{n}\rho_j+\Big(1+\frac{n}{4\mu}\Big)\xi. \tag{20}$$

Hence it is clear that the direction of the vector $\mathbf{R}_B-\mathbf{R}_A$ does not coincide with the direction of the vector ξ. In our procedure for the adiabatic separation of the variables, $\mathbf{R}_B-\mathbf{R}_A$ is not the coordinate of the slow subsystem, but is a "mixture" of the fast coordinates ρ_j and the slow coordinate ξ. Therefore, the quantity $D_{\parallel}(R)$ cannot be regarded as the dipole moment component along the axis of the molecule.

Let us now turn to the electric dipole moment responsible for the dipole rotational and vibrational-rotational transitions in a not-strictly homonuclear, isotopically-asymmetric molecule. For our method of adiabatic separation of the variables, the orientation of the molecule in space is determined by the direction of the vector ξ, the coordinate of the slow subsystem, and not by the direction of the vector $\mathbf{R}_B-\mathbf{R}_A$; for the latter, as can be seen from (20), is a "mixture" of the coordinates of the fast and slow subsystems. Accordingly, we can make the molecule wave function (4) more specific by introducing the vibrational wave function $f_v(\xi)$ and the spherical harmonic describing the rotational state:

$$\Psi_{vJM}(\rho_j,\xi)=\varphi(\rho_j,\xi)f_v(\xi)Y_{JM}(\theta,\Phi). \tag{21}$$

The angles θ and Φ in (21) determine the orientation of the vector ξ in the laboratory system. Let us construct the matrix element of the neutral-molecule dipole-moment operator

$$\hat{\mathbf{D}}=\frac{n}{2}(\mathbf{R}_B+\mathbf{R}_A)-\sum_{j=1}^{n}\mathbf{r}_{j,\,\mathrm{el}}=-\frac{n^2}{8\mu_0}\xi-\Big(1+\frac{n}{4\mu}\Big)\sum_{j=1}^{n}\rho_j \tag{22}$$

for the transition $vJM-v'J'M'$ between vibrational-rotational levels of one and the same electronic state. Integrating the expression over $\boldsymbol{\rho}_j$ and $\boldsymbol{\xi}$, as well as over the angles θ and Φ, we obtain

$$|\langle v'J'M'|D|vJM\rangle|=\delta_{M,M'}\left\{\delta_{J',J+1}\left[\frac{J'^2-M'^2}{(2J+1)(2J'+1)}\right]^{1/2}+\delta_{J',J-1}\left[\frac{J^2-M^2}{(2J+1)(2J'+1)}\right]^{1/2}\right\}\int\limits_0^\infty \xi^2\,d\xi f_{v'}(\xi)f_v(\xi)D(\xi)+O(\varkappa^7). \tag{23}$$

Here the function

$$D(\xi)=\langle\mathbf{D}(\boldsymbol{\rho}_j,\boldsymbol{\xi}),\boldsymbol{\xi}/\xi\rangle_\rho \tag{24}$$

is the mean value of the component of the dipole moment operator (22) along the direction of the vector $\boldsymbol{\xi}$ as computed with the wave function φ through the integration over the coordinates of the fast subsystem. It follows from symmetry considerations that the vector's mean value $\langle\mathbf{D}\rangle_\rho$ is oriented along $\boldsymbol{\xi}$. By performing transformations similar to those carried out in the derivation of the formula (19), we can reduce (24) to the form

$$D(\xi)=\frac{1}{2\mu_0}\left\{\frac{n}{2}\langle\varphi_0|\sum_{i,j}\left[\frac{(\mathbf{r}_{iA},\mathbf{r}_{jA})}{r_{iA}^3}-\frac{(\mathbf{r}_{iB},\mathbf{r}_{jB})}{r_{iB}^3}\right]|\varphi_z\rangle_\rho-\frac{n^2}{2\xi^2}\langle\varphi_0|\sum_{j=1}^n z_j|\varphi_z\rangle_\rho+\frac{n^2}{4}\xi\right\}+O(\varkappa^7). \tag{25}$$

Knowledge of the function $D(\xi)$ allows us to compute using the formula (23), the matrix elements of the vibrational-rotational and purely rotational transitions for a not-strictly homonuclear, isotopically-asymmetric diatomic molecule. Here we should emphasize the significant difference between the functions $D(\xi)$ and $D_\parallel(\xi)$, (19): the first function gives the probabilities of the transitions that are allowed owing to the isotopic asymmetry, while the second indicates the extent to which the mean value of the sum of the components of the electron radius vectors along the internuclear axis deviates from the geometric center of the nuclear core. Let us note in this connection that in Kolos and Wolniewicz's first papers[14,16,17] a quantity corresponding to our $D_\parallel$, (19), was assumed to be responsible for the dipole moment of the vibrational-rotational transition in the HD molecule, and only later[15,17-19] were the so-called transverse corrections $D_\perp$ to the dipole moment, corrections which in the final analysis lead to the correct theoretical function D, computed. In these papers all the computations were carried out in "traditional" relative coordinates of the form

$$\mathbf{R}=\mathbf{R}_B-\mathbf{R}_A \text{ and } \mathbf{r}_j=\mathbf{r}_{j,\,el}-(\mathbf{R}_A+\mathbf{R}_B)/2,$$

in terms of which the isotopic-asymmetry effects are essentially nonadiabatic, and necessitate laborious computations of the perturbation of the adiabatic states by an operator containing a cross product of derivatives with respect to $\mathbf{R}$ and $\mathbf{r}_j$.

Our approach, which is based on the adiabatic approximation with the use of the specially chosen relative coordinates (1), is appreciably simpler: it allows us to clearly distinguish between the physical meanings of the functions $D_\parallel$ and D, and provides simple recipes for their computation with the formulas (19) and (25). Here the formula (25) for the transition dipole moment D is even simpler than the formula (19) for the quantity $D_\parallel$. In the nonadiabatic theory,[15-19] this same quantity D for, say, the HD molecule is computed as a sum of nonadiabatic contributions from the excited Σ_u states (these contributions give $D_\parallel$) and Π_u-state contributions, which give the correction for the "transverse" dipole moment $D_\perp$. Determining $D_\perp$, and comparing the formulas (19) and (25), we obtain the following expression for the contribution of the transverse dipole moment to the transition dipole moment:

$$D_\perp=D-D_\parallel=-\frac{1}{2\mu_0\xi}\langle\varphi_0|\,\Big|\sum_{j=1}^n\boldsymbol{\rho}_j\Big|^2-\Big(\sum_{j=1}^n z_j\Big)^2|\varphi_0\rangle_\rho. \tag{26}$$

It can be seen from this that the computation of $D_\perp$ reduces simply to the computation of the mathematical expectation of the operator

$$\Big|\sum_{j=1}^n\boldsymbol{\rho}_j\Big|^2-\Big(\sum_{j=1}^n z_j\Big)^2$$

in the unperturbed electronic wave function of the homonuclear molecule.

Let us now illustrate our theory by applying it to the HD molecule. In Table I we present the results of the computations, performed by us with the formulas (19) and (25), of the dipole moments $D_\parallel$ and D for the HD molecule as functions of the internuclear distance R. As the unperturbed wave function, we used a refined Weinbaum function[21]; the correction function φ_z was determined with the aid of a ten-parameter linear variational procedure. A comparison of our adiabatic calculations with the most exact published many-parameter calculations performed within the framework of the nonadiabatic approach[18] indicates a fairly good agreement; the discrepancy is primarily due to the rather approximate character of the Weinbaum function: it does not take account of the correlation of the electrons in the direction perpendicular to the axis of the molecule, and only partially takes account of the correlation in the longitudinal direction.

In conclusion, let us note that for $n=q=1$ the formula (19) can be used to compute the displacement $\delta_\parallel$ of the center of the electron cloud from the center of the nulcear core of the one-electron HD$^+$ molecule. After simple transformations, we obtain for this displacement the expression

TABLE I. Dependence of the transition dipole moment D and the dipole moment $D_\parallel$ along the line joining the nuclei on the internuclear distance R in the HD molecule (in a.u.).

R	$D\cdot10^4$, adiabatic approach [formula (25)]	$D\cdot10^4$, nonadiabatic approach [Ref. (18)]	$D_\parallel\cdot10^4$, adiabatic approach [formula (19)]	$D_\parallel\cdot10^4$, nonadiabatic approach [Ref. (18)]
1,0	4,84	4.300	8,11	7,565
1.2	4,13	3,661	7.13	6.629
1,3	3,93	3.447	6.81	6.299
1.4	3,74	3.293	6.53	6,043
1.5	3,59	3.167	6,37	5.826
1,6	3.51	3.054	6.14	5.631
1.8	3,39	2.908	5.84	5.342

TABLE II. Displacement of the center of the electron cloud of the molecular ion HD$^+$ relative to the center of the nuclear core along the H—D line (in a.u.).

R	$\delta_\parallel \cdot 10^4$	R	$\delta_\parallel \cdot 10^4$	R	$\delta_\parallel \cdot 10^4$
1.0	3.585	2.8	9.778	4.6	47,36
1,2	3.699	3.0	11.47	4.8	57,24
1,4	3,960	3.2	13,53	5.0	69.30
1.6	4.345	3.4	16.02	5,2	84.07
1,8	4.852	3.6	19.04	5.4	102,0
2,0	5,487	3.8	22,71	5.6	124.0
2.2	6,269	4.0	27.18	5.8	150,9
2.4	7.222	4.2	32.63	6.0	183.7
2.6	8,378	4.4	39.26		

$$\delta_\parallel = \frac{1}{2\mu_0}\left\{\frac{R}{4} + \frac{\alpha_\parallel(R)}{R^2} + \frac{2Q(R)}{3R} - \frac{4\chi_d(R)}{\gamma^2 R} + \frac{3}{2\gamma}\frac{d}{dE}(\sigma_{dA} - \sigma_{dB})\right\} + O(\varkappa^7). \tag{27}$$

The right-hand side contains observable physical characteristics of the molecular ion H_2^+: $\alpha_\parallel$ is the transverse polarizability; Q, the electronic contribution to the quadrupole moment; χ_d, the mean diamagnetic part of the susceptibility; $d\sigma_{dA}/dE$, the derivative of the diamagnetic-screening constant for the nucleus A with respect to the longitudinal-electric-field intensity; and γ, the fine structure constant. The results of the computations of the displacement of the center of the electron cloud along the H-D line, performed for HD$^+$ with the use of the formula (27) and Sherstyuk and Yakovleva's[22,23] accurate theoretical values for the physical characteristics of H_2^+, are presented in Table II.

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