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# Electronic and nuclear motion and their couplings in the presence of a magnetic field

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We investigate the performance of an adiabatic separation of electronic and nuclear motion in the presence of a magnetic field and find that the diagonal term of the nonadiabatic coupling elements *must* be added to the nuclear equation of motion in the Born-Oppenheimer approximation. As an alternative to the Born-Oppenheimer approximation we introduce the so-called screened Born-Oppenheimer approximation which is particularly suited to describe the adiabatic separation of electronic and nuclear degrees of freedom in a magnetic field. A new interpretation of the well-known gauge-centering phases is given. Furthermore, we provide a qualitative discussion of some of the effects of the off-diagonal nonadiabatic coupling elements.

## I. INTRODUCTION

The existence of strong magnetic fields near compact cosmic objects[1] like white dwarf stars and neutron stars has motivated many studies on the properties of matter in strong fields.[2-10] Most of the investigations are on the behavior of the H atom in strong homogeneous magnetic fields. The ground as well as many excited states of the H atom in such strong fields are therefore known to a high accuracy.[11-15] In order to study the physics of the intermediate- and high-field region at *laboratory magnetic field strengths* two possibilities have been used. The first one is to investigate the behavior of excitons or excitonic molecules in a semiconductor. Because of their small effective masses and the large dielectric constants, typical strong-field effects can appear already at laboratory magnetic field strengths.[16] The second possibility is to study highly excited atoms[17,18] (Rydberg atoms) at laboratory magnetic field strengths. This possibility is of special interest, because it allows an experimental as well as theoretical investigation of the transition of a quantum system from regularity to irregularity,[19-21] as indicated, e.g., by the distribution of energy levels.

In contrast to the numerous investigations on atoms in magnetic fields, especially on the hydrogen atom, the knowledge of the properties of molecules in strong magnetic fields is rather rare. There exist a few works on the structure and properties of the $H_2{}^+$ ion[22-34] and much less information on many-electron molecules.[35-58] Nevertheless, the existing knowledge on molecules in a homogeneous strong magnetic field indicates a richness of new phenomena. Examples are the contraction of the bond length, the increase in binding energy, or the hindered rotation of the molecular axis against the magnetic field direction, which leads in the high-field limit, for example, for the $H_2'{}^+$ ion, to the dissociation of the molecule.[34]

The above-mentioned arguments show that not only the electronic structure but also the molecular dynamics is severely altered by the presence of a strong magnetic field. In this paper we want to investigate whether some of the commonly used concepts and approximations of molecular dynamics are still valid and useful if a magnetic field is present or whether they have to be altered or even abandoned. Starting with the Hamiltonian in Cartesian coordinates one first separates the center-of-mass motion of the molecule from its internal motion. For neutral molecules in a homogeneous magnetic field, there exists a constant of motion, the total pseudomomentum,[39] which allows a pseudoseparation of the center of mass motion. In this case the dependency of the Hamiltonian on the center of mass can be reduced to a Stark term arising due to the electric field induced by the center-of-mass motion.[40] The pseudoseparation as well as the influence of the Stark term on the spectrum was discussed to some extent in the literature.[39-43] In the case of ions there exist only few investigations on the center-of-mass motion of *atomic* ions.[44-46]

One of the most important foundations of molecular physics, the validity of which was presumed in all the above-mentioned studies on molecules in a magnetic field, is the Born-Oppenheimer approximation.[47] However, so far there exist no investigations on the validity of the Born-Oppenheimer approximation if a magnetic field is present.

Before we consider the problems associated with the Born-Oppenheimer approximation in the presence of a magnetic field, we want to make some brief remarks on the zero-field case. It is well known that the Born-Oppenheimer adiabatic approximation[48] provides very good approximate molecular spectra and wave functions if the electronic energy-level spacings are large compared with typical spacings associated with the nuclear motion. The inclusion of the mass-correction terms (due to the finite nuclear masses) and the diagonal term of the nonadiabatic couplings in the adiabatic approximation scheme then causes only small and, for most practical calculations, negligible corrections.[60] Only for the case that the electronic states are close in energy it is necessary to abandon the Born-Oppenheimer approximation and to include the nonadiabatic couplings of the electronic states which are involved. A prominent example is the well-known Jahn-Teller effect.[49,50] The latter is a special case of the so-called conical intersection situations,[51] which appear for the exact degeneracy of some electronic states of a polyatomic molecule.

In the case of the presence of a magnetic field the situation is much more complicated. It is clear that no kind of adiabatic approximation can be valid over the whole range of magnetic field strengths. For the case of the $H_2{}^+$ ion, it has been shown[30,34] that in the very-high-field region the zero-point energy of the hindered rotation approaches the order of magnitude of the Coulomb binding energy and therefore any kind of adiabatic approximation breaks down. This breakdown also takes place in the case of neutral molecules. Apart from it, there exist some other serious problems which make the applicability of an adiabatic approximation *a priori* questionable. For example, the nuclear equation of motion in the Born-Oppenheimer adiabatic approximation treats—as we shall see—the nuclei as "naked" charges, i.e., it does not describe the effect of the screening of the magnetic field by the electrons.[52] This screening should be almost complete in the weak-field case for the dissociation of the molecule into neutral atoms. Because of the exactness of the fully coupled nuclear equations of motion, the missing screening must be contained in the nonadiabatic couplings.

A problem related to that of the missing screening is the gauge dependency of electronic potential surfaces in practical approximate calculations. To *reduce* this gauge dependency[53] one has to take care of the *correct gauge centering*[54–58] of the functions, used to build up the molecular wave function. This can, in general, be done by multiplying the functions by a magnetic-field-dependent phase factor.

The above-mentioned difficulties in the performance of a Born-Oppenheimer separation in the presence of a magnetic field were already partially investigated in a previous paper[52] of the authors for the special case of a homonuclear diatomic molecule, which is, as will be shown later on, much simpler than the general case. In the following sections we want to proceed as follows. In Sec. II we carry out the pseudoseparation of the center-of-mass motion of an arbitrary neutral molecule. In Sec. III we make an adiabatic ansatz for the total wave function of a heteronuclear diatomic molecule and derive the electronic Hamiltonian, nonadiabatic coupling elements and nuclear equations of motion. The formulas for the case of an arbitrary molecule are given in the Appendix. In Sec. IV we investigate the problem of the missing screening which appears in the nuclear equation of motion in the Born-Oppenheimer approximation. We show the importance of the diagonal term of the nonadiabatic coupling elements and are thereby led to the *screened* Born-Oppenheimer approximation. In Sec. V we briefly discuss the special case of a homonuclear diatomic molecule. In Sec. VI we obtain a new interpretation of the gauge-centering phases by investigating the separate center-of-mass motions of the atoms of a homonuclear diatomic molecule. Furthermore, we discuss some of the effects of the off-diagonal nonadiabatic coupling elements.

## II. PSEUDOSEPARATION OF THE CENTER OF MASS

Our starting point is the nonrelativistic Hamiltonian for a neutral molecule in a homogeneous magnetic field in Cartesian coordinates

$$\mathcal{H}'_c=\sum_i \frac{1}{2m}[\mathbf{p}'_i-e\,\mathbf{A}(\mathbf{r}'_i)]^2+\sum_\alpha \frac{1}{2M_\alpha}[\mathbf{p}'_\alpha+eZ_\alpha\,\mathbf{A}(\mathbf{r}'_\alpha)]^2 + V'(\{\mathbf{r}'_i\};\{\mathbf{r}'_\alpha\}) \,, \tag{2.1}$$

where we have neglected the rather trivial interaction of the spin with the magnetic field. Throughout the paper Greek indices are used for the nuclei and Latin ones for the electrons. The symbols $m$, $e$, $\mathbf{r}'_i$, $\mathbf{p}'_i$, and $\mathbf{A}(\mathbf{r}'_i)$ denote the mass, charge, position vector, canonical conjugated momentum, and vector potential for the $i$th electron, respectively. $M_\alpha$, $Z_\alpha$, $\mathbf{r}'_\alpha$, $\mathbf{p}'_\alpha$, and $\mathbf{A}(\mathbf{r}'_\alpha)$ denote the mass, nuclear charge number, position vector, canonical conjugated momentum, and vector potential for the $\alpha$th nucleus, respectively. $V'$ contains all the Coulomb interaction terms. The Hamiltonian (2.1) has a constant of motion,[39,41] the total pseudomomentum $\hat{\mathbf{k}}$

$$\hat{\mathbf{k}}=\sum_i [\mathbf{p}'_i-e\,\mathbf{A}(\mathbf{r}'_i)+e\mathbf{B}\times\mathbf{r}'_i] + \sum_\alpha [\mathbf{p}'_\alpha+eZ_\alpha\,\mathbf{A}(\mathbf{r}'_\alpha)-eZ_\alpha\mathbf{B}\times\mathbf{r}'_\alpha] \,, \tag{2.2a}$$

$$[\mathcal{H}'_c,\hat{\mathbf{k}}]=0 \,, \tag{2.2b}$$

where $\mathbf{B}$ is the magnetic field strength. For convenience we will adopt in the following the symmetric gauge for the vector potential $\mathbf{A}(\mathbf{r})=\frac{1}{2}\mathbf{B}\times\mathbf{r}$. Nevertheless, all our formulas can be translated directly to the more general case of the mixed gauge,[29,59] which also obeys the Coulomb-gauge condition $\nabla\cdot\mathbf{A}=0$.

In our case of a neutral molecule the components of $\mathbf{k}$ can be made sharp simultaneously, i.e., they obey the commutation relations $\hat{\mathbf{k}}\times\hat{\mathbf{k}}=0$. In the zero-field case $\hat{\mathbf{k}}$ becomes identical with the conserved total momentum of the molecule.

In order to take advantage of the constant of motion $\hat{\mathbf{k}}$ for the pseudoseparation of the center of mass, we transform the Hamiltonian (2.1) to a coordinate system which contains the center-of-mass coordinate and $(n-1)$ remaining internal coordinates.[42,43] As internal coordinates we choose $(n-1)$ relative coordinates to the center of mass of nuclei (CMN). This internal coordinate system is especially appropriate for the subsequent performance of an adiabatic separation, i.e., it enables us to identify the relative velocities of the nuclei. Furthermore, it has the advantage that it does not lead to terms in the Hamiltonian which involve mixed electronic and nuclear momenta.[60] The Hamiltonian (2.1) in this coordinate system reads as follows:

$$\mathcal{H}'=\sum_i \frac{1}{2m}\left[\mathbf{p}_i+\frac{m}{M}\mathbf{P}_s-\frac{e}{2}\mathbf{B}\times\left[\mathbf{r}_i+\mathbf{R}_s-\frac{m}{M}\sum_j \mathbf{r}_j\right]\right]^2$$
$$+\sum_\alpha{}' \frac{1}{2M_\alpha}\left[\mathbf{p}_\alpha-\frac{M_\alpha}{M_0}\left[\sum_i \mathbf{p}_i+\sum_\alpha{}'\mathbf{p}_\alpha\right]+\frac{M_\alpha}{M}\mathbf{P}_s+\frac{e}{2}Z_\alpha\mathbf{B}\times\left[\mathbf{r}_\alpha+\mathbf{R}_s-\frac{m}{M}\sum_i \mathbf{r}_i\right]\right]^2$$
$$+\frac{1}{2M_n}\left[\frac{M_n}{M}\mathbf{P}_s-\frac{M_n}{M_0}\left[\sum_i \mathbf{p}_i+\sum_\alpha{}'\mathbf{p}_\alpha\right]+\frac{e}{2}Z_n\mathbf{B}\times\left[\mathbf{R}_s-\frac{m}{M}\sum_i \mathbf{r}_i-\frac{1}{M_n}\sum_\alpha{}' M_\alpha\mathbf{r}_\alpha\right]\right]^2+V(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\ , \qquad (2.3)$$

where $M$ is the total mass of the molecule and $M_0$ the total mass of the nuclei. $\mathbf{R}_s$ and $\mathbf{P}_s$ are the center-of-mass coordinate and its canonical conjugated momentum, respectively. $M_n$ and $Z_n$ are the mass and nuclear-charge number of that nucleus, the relative position of which has been excluded from the internal coordinate system. The primed sum indicates summation over all nuclei except that denoted by $n$.

The total pseudomomentum reads in this coordinate system

$$\hat{\mathbf{k}}=\mathbf{P}_s+\frac{e}{2}\mathbf{B}\times\sum_i \mathbf{r}_i-\frac{e}{2}\frac{1}{M_n}\mathbf{B}\times\sum_\alpha{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\ , \qquad (2.4)$$

where

$$\mathcal{M}_\alpha=(Z_\alpha M_n-Z_n M_\alpha)\ . \qquad (2.5)$$

The eigenfunctions of the Hamiltonian (2.3) can be chosen as simultaneous eigenfunctions of $\hat{\mathbf{k}}$ with eigenvalue $\mathbf{k}$. They take on the following appearance:

$$\Psi(\mathbf{R}_s;\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})=U\psi(\mathbf{k};\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\ , \qquad (2.6)$$

with

$$U=\exp\left\{+i\left[\mathbf{k}-\frac{e}{2}\mathbf{B}\times\left[\sum_i \mathbf{r}_i-\frac{1}{M_N}\sum_\alpha{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\right]\right]\cdot\mathbf{R}_s\right\}\ . \qquad (2.7)$$

It is therefore possible to eliminate the center-of-mass coordinate from the Hamiltonian (2.3) by a unitary transformation

$$\mathcal{H}=U^{-1}\mathcal{H}'U\ . \qquad (2.8)$$

The unitary transformation $U$ replaces the canonical conjugated momentum of the center-of-mass coordinate by the eigenvalue $\mathbf{k}$ of $\hat{\mathbf{k}}$. The Hamiltonian $\mathcal{H}$ can, after some lengthy algebra, be rearranged to a rather simple form which is particularly suited for investigating the performance of an adiabatic separation. The resulting Hamiltonian takes on the following appearance:

$$\mathcal{H}=\frac{1}{2M}\mathbf{k}^2-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\left[\sum_i \mathbf{r}_i-\frac{1}{M_n}\sum_a{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\right]+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i+\frac{e}{2}\frac{m}{MM_n}\mathbf{B}\times\sum_a{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\right]^2$$
$$+\frac{1}{2M_0}\left[\sum_i \mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i \mathbf{r}_i-\frac{e}{2}\frac{M_0}{M_n}\left[\frac{1}{M}+\frac{1}{M_0}\right]\mathbf{B}\times\sum_a{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\right]^2+\sum_a{}'\frac{1}{2M_\alpha}\left[\mathbf{p}_\alpha+\frac{e}{2}Z_\alpha\mathbf{B}\times\mathbf{r}_\alpha-\frac{e}{2}\frac{m}{M}Z_\alpha\mathbf{B}\times\sum_i \mathbf{r}_i\right]$$
$$-\frac{1}{2M_0}\left[\sum_a{}'\mathbf{p}_\alpha+\frac{e}{2}\frac{1}{M_n}\mathbf{B}\times\sum_a{}'\mathcal{M}_\alpha\mathbf{r}_\alpha-\frac{e}{2}\frac{m}{M}Z\mathbf{B}\times\sum_i \mathbf{r}_i\right]^2$$
$$+\frac{e^2}{8}\frac{Z_n^2}{M_n}\left[\frac{1}{M_n}\mathbf{B}\times\sum_a{}' M_\alpha\mathbf{r}_\alpha+\frac{m}{M}\mathbf{B}\times\sum_i \mathbf{r}_i\right]^2+V(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\ , \qquad (2.9)$$

where $Z$ is the total-nuclear-charge number. The Hamiltonian (2.9) depends only parametrically via the pseudomomentum $\mathbf{k}$ on the center-of-mass motion. As can be seen from Eq. (2.9) the only consequence of the center-of-mass motion is, apart from the trivial constant kinetic energy term, the appearance of a Stark effect due to a motional electric field [see second term on the right-hand side (rhs) of Eq. (2.9)]. In the zero-field case this Stark effect disappears, i.e., we have no coupling of the center of mass to the internal degrees of freedom.

The Hamiltonian (2.9) contains a series of mass-correction terms for the electronic and nuclear motion. These corrections terms (due to the finite nuclear masses) can be divided into the following two types: the specific-mass corrections, i.e., mass-polarization terms, which provide additional couplings of the motion of different particles, and the normal-mass corrections, which can be taken exactly into account (for the nomenclature of the mass correction terms in the absence of a magnetic field see, for instance, Ref. 60 or 61). In the zero-field case the normal mass corrections are due to reduced masses. In our case of the Hamiltonian (2.9) this type of corrections are contained in the second and fourth quadratic term for the electronic and nuclear motion, respectively. In Sec. IV we will discuss new normal-mass corrections which appear in the Hamiltonian (2.9) and are *not* present in the zero-field case. The specific-mass corrections or mass-polarization terms which involve the momenta or coordinates of *different* electrons are also included in the second quadratic term of Eq. (2.9).

For an arbitrary molecule we have all types of mass-correction terms in the Hamiltonian (2.9), except those which include mixed electronic and nuclear momenta. The latter do not appear because of the special choice of our internal coordinate system. We remark that no further essential simplification of the mass-correction terms can be achieved by choosing another reference point (defined by the nuclei) for the internal coordinate system. For the special case of a diatomic homonuclear molecule the Hamiltonian (2.9) reduces to a form which contains no mass-correction terms involving mixed electronic and nuclear degrees of freedom.[52] This case will be discussed separately in Sec. V.

In Sec. III we make an adiabatic ansatz for the wave function of a heteronuclear diatomic molecule in a magnetic field and present its electronic Hamiltonian, nonadiabatic couplings and nuclear equation of motion. The electronic Hamiltonian, nonadiabatic couplings, and nuclear equation of motion for an *arbitrary* molecule are given in the Appendix.

## III. ADIABATIC SEPARATION IN THE PRESENCE OF A MAGNETIC FIELD

There is one physical picture which is common to all adiabatic approximations for molecules. It is the picture that the Coulomb forces cause electronic velocities which are much larger than the nuclear velocities and therefore, from the point of view of the electrons, the nuclei can in a first approximation be regarded as fixed in space. In order to separate the electronic and nuclear motion we have to establish the electronic Hamiltonian for fixed nuclei. Usually one starts from the Hamiltonian (2.1) in a space-fixed laboratory coordinate system and defines the electronic Hamiltonian by assuming infinitely heavy, fixed nuclei. In the following we will call this electronic Hamiltonian the fixed-nuclei electronic Hamiltonian. The corresponding electronic energy is a good approximation in many cases, but has an inherent weakness in the treatment of the motion of the center of mass. It is known[62] that correction terms due to finite nuclear masses are of particular importance in the presence of a magnetic field (see Sec. IV). Their order of magnitude becomes in the very-high-field region comparable with the Coulomb binding energy and they are no more negligible.

In order to obtain a correct treatment of the center of mass and to include the mass-correction terms in the electronic Hamiltonian we will in the following apply the adiabatic separation to the Hamiltonian (2.9) which is expressed in the center of mass of nuclei coordinate system.[60] The resulting electronic Hamiltonian will coincide in the infinite-nuclear-mass limit with the above-mentioned fixed-nuclei electronic Hamiltonian. We will call it the "mass-corrected electronic Hamiltonian." For the sake of clarity we will in this section specialize to a heteronuclear diatomic molecule and present the formulas for a general polyatomic system in the Appendix. As a first step in our calculation we rewrite the Hamiltonian (2.9) to give the following simpler form for the diatomic molecule

$$\begin{aligned}\mathcal{H}= {} & \frac{1}{2M}\mathbf{k}^2-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\left[\sum_i \mathbf{r}_i-\frac{1}{M_0}\mathcal{M}\mathbf{R}\right]+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i+\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2\\ & +\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i-\frac{e}{2}\left[\frac{1}{M}+\frac{1}{M_0}\right]\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2\\ & +\frac{M_0}{2M_1M_2}\left[\mathbf{P}+\frac{e}{2}\cdot\frac{1}{M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}-\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2+V(\{\mathbf{r}_i\};\mathbf{R})\ ,\end{aligned}\tag{3.1}$$

with

$$\mathcal{M}=Z_1M_2-Z_2M_1\ ,$$

where $Z_1$ and $M_1$, and $Z_2$ and $M_2$ denote the nuclear-charge numbers and masses of the two nuclei, respectively. **R** is now the *relative* coordinate of the two nuclei and **P** its canonical conjugated momentum.

In order to obtain the mass-corrected electronic Hamiltonian we have to set the *nuclear relative velocities* in the total Hamiltonian (3.1) equal to zero. In the zero-field case and using our internal coordinate system this is equivalent to setting the canonical conjugated momentum of the relative coordinate of the nuclei equal to zero. In the magnetic-field case one has to calculate the equations of motion for the nuclear coordinates

$$\dot{\mathbf{R}}=\frac{1}{i}[\mathbf{R},\mathcal{H}']\ ,\tag{3.2}$$

with $\mathcal{H}'$ being the total Hamiltonian of the system given in Eq. (2.3). Setting $\dot{\mathbf{R}}=0$ in Eq. (3.2) is equivalent to requiring

$$\dot{\mathcal{R}}=U^{-1}\dot{\mathbf{R}}U=\frac{1}{i}[\mathbf{R},\mathcal{H}]=0\ ,\tag{3.3}$$

with $\mathcal{H}$ from Eq. (3.1) and $U$ from Eq. (2.7). The commutator (3.3) yields the following condition:

$$\begin{aligned}&\mathbf{P}+\frac{e}{2}\frac{1}{M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}-\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\\ &\quad=0\ .\end{aligned}\tag{3.4}$$

From Eq. (3.4) it is clear that the third quadratic term in the Hamiltonian (3.1) is related to the relative kinetic energy of the nuclei. Using condition (3.4) we arrive at the following *mass-corrected* electronic Hamiltonian

$$\mathcal{H}_{\mathrm{el}}=-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\left[\sum_i\mathbf{r}_i-\frac{1}{M_0}\mathcal{M}\mathbf{R}\right]+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i+\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2$$

$$+\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i-\frac{e}{2}\left[\frac{1}{M}+\frac{1}{M_0}\right]\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2+V(\{\mathbf{r}_i\};\mathbf{R})\ . \qquad (3.5)$$

The first term on the rhs of Eq. (3.5) contains the coupling of the pseudomomentum to the internal degrees of freedom. We have included the coupling of the pseudomomentum to the nuclear degrees of freedom in the *electronic* Hamiltonian in order to obtain the correct **k**-dependent behavior of the electronic energy in the dissociation limit of the molecule (see also Sec. VI). This coupling disappears for the special case of a homonuclear molecule (see Sec. V). There are three kinds of mass corrections included in Eq. (3.5). They are the following:

(i) The mass-correction term $[em/(2MM_0)]\mathcal{M}\mathbf{B}\times\mathbf{R}$ which is contained explicitly in the first and implicitly in the second quadratic term of $\mathcal{H}_{\mathrm{el}}$. This term shifts the gauge origin from the origin of the coordinate system. As we shall show in Sec. IV this term can and *must* be taken *exactly* into account in order to obtain a well-defined mass-corrected electronic potential surface. It is therefore of particular importance.

(ii) Exact corrections due to reduced masses which are included in the second quadratic term of $\mathcal{H}_{\mathrm{el}}$.

(iii) Dynamical corrections due to mass-polarization terms (i.e., terms which involve, for example, the momenta of different electrons) which are also contained in the second quadratic term of the Hamiltonian (3.5).

We remark that in order to obtain the *mass-corrected* electronic Hamiltonian it was essential to set the *nuclear relative velocities* equal to zero and not the canonical conjugated momentum **P** of the nuclei. Otherwise one would obtain an ill-defined mass-corrected electronic Hamiltonian, the expectation value of which contains terms which *diverge* as the internuclear distance goes to infinity.

As a next step we expand the total wave function $\psi$ in a series of products of electronic and nuclear functions

$$\psi(\{\mathbf{r}_i\};\mathbf{k};\mathbf{R})=\sum_{j'}\phi_{j'}(\{\mathbf{r}_i\};\mathbf{k};\mathbf{R})\chi_{j'}(\mathbf{k};\mathbf{R})\ . \qquad (3.6)$$

The functions $\phi_{j'}$, which depend parametrically on the pseudomomentum **k** and on the nuclear coordinates, are eigenfunctions of the mass-corrected electronic Schrödinger equation

$$\mathcal{H}_{\mathrm{el}}\phi_j(\{\mathbf{r}_i\};\mathbf{k};\mathbf{R})=\varepsilon_j(\mathbf{k};\mathbf{R})\phi_j(\{\mathbf{r}_i\};\mathbf{k};\mathbf{R})\ . \qquad (3.7)$$

Substituting Eq. (3.6) in the total Schrödinger equation $\mathcal{H}\psi=E\psi$, multiplying by $\phi_j^*(\{\mathbf{r}_i\};\mathbf{k};\mathbf{R})$, and integrating over the coordinates of the electrons, we find the set of nuclear equations of motion

$$\left[\frac{M_0}{2M_1M_2}\left[\mathbf{P}+\frac{e}{2M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\mathbf{R})-E\right]\chi_j+\sum_{j'}\Lambda_{jj'}\chi_{j'}=0\ , \qquad (3.8)$$

where $E$ is the total energy. The first term of Eq. (3.8) contains the paramagnetic ($\propto B$) and diamagnetic ($\propto B^2$) part of the nuclear motion. The second term is the trivial kinetic energy term of the pseudomomentum. The *nonadiabatic* coupling elements are given by

$$\Lambda_{jj'}=\frac{M_0}{2M_1M_2}\left\langle\phi_j\left|\left[\mathbf{P}-\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2\right|\phi_{j'}\right\rangle+\frac{M_0}{M_1M_2}\left\langle\phi_j\left|\left[\mathbf{P}-\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\right]\right|\phi_{j'}\right\rangle\times\left[\mathbf{P}+\frac{e}{2M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]\ , \qquad (3.9)$$

where the integration is over the electronic coordinates only and where the operators in the scalar product in Eq. (3.9) act only on the electronic wave function $\phi_{j'}$.

The Born-Oppenheimer adiabatic approximation is obtained from Eq. (3.8) in analogy to the zero-magnetic-field case[48] by neglecting all the nonadiabatic coupling elements $\Lambda_{jj'}$. The corresponding nuclear equation of motion reads

$$\left[\frac{M_0}{2M_1M_2}\left[\mathbf{P}+\frac{e}{2M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\mathbf{R})-E\right]\chi_j=0\ . \qquad (3.10)$$

In this approximation the nuclear equation of motion is restricted to perform on the single electronic potential surface $\varepsilon_j(\mathbf{k};\mathbf{R})$ which, in contrast to the zero-field case, still depends on the center-of-mass motion. An equation similar to Eq. (3.10) for $\mathbf{k}=0$ was used in the literature for the calculation of the rovibrational spectrum of the $H_2^+$ ion in a strong magnetic field.[31,32]

We now briefly want to discuss the nonadiabatic coupling elements (3.9). The first matrix element on the rhs of Eq. (3.9) gives in the zero-field case the matrix element of the nuclear relative kinetic energy and the second term gives the derivative coupling, which contains explicitly the nuclear momentum operator **P**. The nonadiabatic coupling elements (3.9) contain several terms which depend explicitly on the magnetic field strength. In addition, the matrix elements (3.9) depend implicitly, via the electronic wave functions $\{\phi_j\}$, on the magnetic field strength. The nonadiabatic coupling elements $\Lambda_{jj'}$, and with it the quality of the adiabatic approximation will therefore, in general, be very sensitive to the order of magnitude of the magnetic field strength. In particular, in the case of electronic-level degeneracy, or near degeneracy, the magnetic field could play an important role. The symmetry lowering due to the presence of a magnetic field now allows electronic states to couple which did not couple in the zero-field case (see also Sec. VII).

Finally, we remark that the nonadiabatic coupling terms of Eq. (3.9) which explicitly depend on the electronic coordinates via the term $\mathbf{B}\times\sum_i \mathbf{r}_i$ are by a factor $m/M$ smaller ($\propto m/M^2$) than those involving only nuclear degrees of freedom ($\propto 1/M$). In Sec. IV we investigate in some detail the nuclear equation of motion (3.8).

## IV. IMPORTANCE OF THE DIAGONAL TERM OF THE NONADIABATIC COUPLINGS AND THE SCREENED BORN-OPPENHEIMER APPROXIMATION

### A. Importance of the diagonal term of the nonadiabatic couplings

In the following we again specialize to the case of a heteronuclear diatomic molecule. For the sake of simplicity we neglect the effects of the pseudomomentum $\mathbf{k}$, i.e., we assume $\mathbf{k}=0$ (the case $\mathbf{k}\neq 0$ is discussed in Sec. VI). The nuclear equation in the Born-Oppenheimer approximation, which is obtained from Eq. (3.10) by setting $\mathbf{k}$ equal to zero, then reads as follows:

$$\left[\frac{M_0}{2M_1M_2}\left[\mathbf{P}+\frac{e}{2M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]^2 +\varepsilon_j(\mathbf{R})-E\right]\chi_j=0 . \quad (4.1)$$

Equation (4.1) contains all the magnetic-field-dependent terms of the relative motion of the nuclei. It therefore treats the nuclei as "naked" charges in a magnetic field and cannot describe the effect of the *screening* of the nuclear charge by the electrons against the magnetic field. This screening is of particular importance for the dissociation of the molecule into neutral atoms, i.e., AB→A+B. In this case the electronic energy $\varepsilon_j(\mathbf{R})$ becomes a $\mathbf{R}$-independent number and Eq. (4.1) shows the relative motion of two charged nuclei in a magnetic field. *In reality* the nuclear charges are screened by the electrons and paramagnetic and diamagnetic terms should not appear in the nuclear equation of motion. In the dissociation limit we have two neutral atoms each of which is moving with its own conserved pseudomomentum (see Sec. VI). Hence one should arrive at a virtually free nuclear equation of motion.

Because of the exactness of the fully coupled equations of motion (3.8) the missing screening must be contained in the nonadiabatic coupling elements. In order to investigate this problem we investigate the electronic wave function of the molecule in the dissociation limit. The simplest choice of a dissociative electronic wave function would be an eigenfunction $\phi_0$ of the electronic Hamiltonian in the infinite-nuclear-mass limit, i.e., to the Hamiltonian

$$\frac{1}{2m}\sum_i\left(\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i\right)^2+V(\{\mathbf{r}_i\};\mathbf{R}) . \quad (4.2)$$

However, the expectation value of the mass-correction terms calculated with $\phi_0$ diverge at a large internuclear distance $|\mathbf{R}|$. This can be seen by calculating the electronic energy with the wave function $\phi_0$ and the mass-corrected electronic Hamiltonian (3.5) for $\mathbf{k}=0$. The reason for these divergencies is the mass-correction term $[em/(2MM_0)]\mathcal{M}\mathbf{B}\times\mathbf{R}$ of the first quadratic term on the rhs of Eq. (3.5). It centers the gauge of the Hamiltonian away from the origin of our coordinate system. This term is also implicitly contained in the second quadratic term of $\mathcal{H}_{\text{el}}$ in Eq. (3.5). We therefore *must* choose an eigenfunction $\phi$ to the electronic Hamiltonian

$$\overline{\mathcal{H}}_{\text{el}}=\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i+\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2 +V(\{\mathbf{r}_i\};\mathbf{R}) , \quad (4.3)$$

in order to obtain a well-defined electronic energy. We note that we cannot establish a dissociative molecular eigenfunction of the full electronic Hamiltonian (3.5). However, the mass-correction terms not included in $\overline{\mathcal{H}}_{\text{el}}$ contribute only corrections which in the following are taken into account by perturbation theory. Our electronic wave function $\phi$ which is an eigenfunction of $\overline{\mathcal{H}}_{\text{el}}$ takes on the following appearance:

$$\phi=\mathcal{N}\mathfrak{U}[\mathcal{P}\varphi_{1A}(\{\mathbf{r}_i\};\{\mathbf{s}_i\};\mathbf{R})\varphi_{2B}(\{\mathbf{r}_j\};\{\mathbf{s}_j\};\mathbf{R})] , \quad (4.4)$$

where $\mathcal{N}$ is a normalization constant and where $\mathfrak{U}$ is the antisymmetrization operator. The electrons with position vectors $\{\mathbf{r}_i\}$ and $\{\mathbf{r}_j\}$, and spin variables $\{\mathbf{s}_i\}$ and $\{\mathbf{s}_j\}$ are located at the nucleus $A$ and $B$, respectively. $\varphi_{1A}$ and $\varphi_{2B}$ are electronic atomic functions [for details see Eq. (4.6)]. $\mathcal{P}$ is the phase factor

$$\mathcal{P}=\exp\left[-i\frac{e}{2}\frac{m}{MM_0}\mathcal{M}(\mathbf{B}\times\mathbf{R})\cdot\left[\sum_i\mathbf{r}_i+\sum_j\mathbf{r}_j\right]\right] . \quad (4.5)$$

$\mathcal{P}$ must be included in order to ensure that $\phi$ is an eigenfunction of the Hamiltonian $\overline{\mathcal{H}}_{\text{el}}$ in Eq. (4.3). By commuting $\mathcal{P}$ with $\overline{\mathcal{H}}_{\text{el}}$ one shifts the gauge center in the Hamiltonian $\overline{\mathcal{H}}_{\text{el}}$ and obtains the electronic Hamiltonian in the infinite-nuclear-mass limit.

In order to specify the atomic functions $\varphi_{1A}$ and $\varphi_{2B}$ we must take care of the gauge degrees of freedom. The gauge dependency of the electronic expectation values computed within an incomplete basis set is a very-well-known problem.[53-59] It was recognized very early[55] that in order to obtain approximate gauge-invariant energy expectation values one must provide the correct gauge centering[55-59] of the localized functions used to build up the molecular electronic wave function. In our case this means that, in addition to the phase $\mathcal{P}$, the atomic functions $\varphi_{1A}$ and $\varphi_{2B}$ also contain phases which provide the gauge centering on the nuclei $A$ and $B$, respectively. The functions $\varphi_{1A}$ and $\varphi_{2B}$ therefore have the following structure:

$$\begin{aligned}\varphi_{1A}&=\exp\left[+i\frac{e}{2}\frac{M_2}{M_0}(\mathbf{B}\times\mathbf{R})\cdot\sum_i \mathbf{r}_i\right]\\&\quad\times\varphi_1\left[\left[\mathbf{r}_i-\frac{M_2}{M_0}\mathbf{R}\right];\{\mathbf{s}_i\}\right],\\ \varphi_{2B}&=\exp\left[-i\frac{e}{2}\frac{M_1}{M_0}(\mathbf{B}\times\mathbf{R})\cdot\sum_j \mathbf{r}_j\right]\\&\quad\times\varphi_2\left[\left[\mathbf{r}_j+\frac{M_1}{M_0}\mathbf{R}\right];\{\mathbf{s}_j\}\right],\end{aligned}\tag{4.6}$$

where the functions $\varphi_1$ and $\varphi_2$ are eigenfunctions of the atomic electronic Hamiltonians without mass corrections, i.e., eigenfunctions to

$$\sum_l \frac{1}{2m}\left[\mathbf{p}_l-\frac{e}{2}\mathbf{B}\times\mathbf{r}_l\right]^2+V(\{\mathbf{r}_l\})\ .\tag{4.7}$$

In formula (4.7) the nucleus of the atom $A,B$ is chosen as the origin of the electronic coordinates $\{\mathbf{r}_l\}$.

Having specified our dissociative wave function $\phi$ we return to our original problem of the missing screening. We have calculated the electronic energy $\varepsilon$, i.e., the expectation value of the Hamiltonian (3.5), for $\mathbf{k}=\mathbf{0}$ with our dissociative wave function $\phi$ and the diagonal term $\Lambda_d$ of the nonadiabatic couplings (3.9). The results are

$$\begin{aligned}\varepsilon&=\langle\phi|\mathcal{H}_{\rm el}\,(\mathbf{k}=\mathbf{0})|\phi\rangle=E_A+E_B-\mathcal{C}\ ,\\ \Lambda_d&=-\frac{e}{2}(M_0M_1M_2)^{-1}(Z_1M_2^2+Z_2M_1^2)(\mathbf{B}\times\mathbf{R})\cdot\mathbf{P}\\&\quad-\frac{e^2}{8}(M_0^3M_1M_2)^{-1}(Z_1M_2^2+Z_2M_1^2)^2(\mathbf{B}\times\mathbf{R})^2+\mathcal{C}\ ,\end{aligned}\tag{4.8}$$

where the trivial Zeeman spin terms have been omitted. $E_A$ and $E_B$ are the energies of the atom $A,B$ in the presence of a magnetic field. The energetic contributions of the *atomic* mass-correction terms are contained in the energies $E_A$ and $E_B$ up to a first-order perturbation theory with respect to the functions $\varphi_1$ and $\varphi_2$. $\mathcal{C}$ is an irrelevant *atomic* constant which cancels if the electronic energy $\varepsilon$ and the diagonal term $\Lambda_d$ of the nonadiabatic couplings are inserted into the nuclear equation of motion

$$\begin{aligned}\mathcal{C}=&\frac{M_2}{2M_1M_0}\left\langle\varphi_1\left|\left[\sum_l\left[\mathbf{p}_l+\frac{e}{2}\mathbf{B}\times\mathbf{r}_l\right]\right]^2\right|\varphi_1\right\rangle\\&+\frac{M_1}{2M_2M_0}\left\langle\varphi_2\left|\left[\sum_l\left[\mathbf{p}_l+\frac{e}{2}\mathbf{B}\times\mathbf{r}_l\right]\right]^2\right|\varphi_2\right\rangle,\end{aligned}\tag{4.9}$$

with the notation of Eq. (4.7). [The reader should note that within this section the summation index $l$ labels the electronic coordinates (momenta) which have the nucleus of the corresponding atom as the origin of the coordinate system, whereas the indices $i$ and $j$ label electronic coordinates (momenta) which are referred to the molecular center of mass of nuclei.]

The most important feature of $\Lambda_d$ in Eq. (4.8) is that its first and second term are the negative counterparts of the paramagnetic ($\propto B$) and diamagnetic ($\propto B^2$) terms occurring in the nuclear equation of motion (3.8). Inserting Eq. (4.8) into the nuclear equation of motion (3.8) (for $\mathbf{k}=\mathbf{0}$) and neglecting only the off-diagonal nonadiabatic coupling elements or equivalently adding $\Lambda_d$ to $\varepsilon_j=\varepsilon$ in Eq. (4.1) provides the following equation of motion:

$$\left[\frac{M_0}{2M_1M_2}\mathbf{P}^2+E_A+E_B-E\right]\chi=0\ .\tag{4.10}$$

From Eq. (4.10) one immediately realizes the effect of a complete screening of the nuclear charge against the magnetic field, i.e., the disappearance of the paramagnetic and diamagnetic terms in the nuclear equation of motion. As can be seen from Eq. (4.8) the screening is contained in the diagonal terms of the nonadiabatic couplings. In order to obtain the correct free nuclear equation of motion for the dissociation limit it is therefore *necessary* to include the diagonal term of the nonadiabatic coupling elements. This statement is independent of the region of the magnetic field strength, i.e., it applies also for weak magnetic fields, since the diagonal term $\Lambda_d$ can be made arbitrarily large for large internuclear distances. In the general case, i.e., also far from dissociation, the inclusion of the diagonal term becomes more important for increasing magnetic field strength.

We remark that in the zero-field case and for real electronic wave functions the diagonal term of the nonadiabatic couplings is simply the expectation value of the nuclear kinetic energy operator and its inclusion in the adiabatic approximation scheme is known as a Born-Huang adiabatic approximation.[48] In the presence of a magnetic field the wave functions are, in general, complex and we therefore have all types of diagonal nonadiabatic coupling terms, especially derivative coupling terms. In fact, the derivative coupling terms cause the canceling of the paramagnetic ($\propto \mathbf{B}$) terms in the nuclear equation of motion.

We conclude with the statement that a meaningful description of nuclear dynamics in the presence of a magnetic field is only possible under inclusion of the diagonal term of the nonadiabatic coupling elements. The inclusion of the diagonal terms provides not only a modification of the adiabatic approximation, as it does in the zero-field case, but also dynamical corrections due to the presence of the derivative diagonal coupling term.

### B. Screened Born-Oppenheimer approximation

In Sec. III we presented the nonadiabatic couplings and nuclear equations of motion for a heteronuclear diatomic molecule. We obtain the nuclear equations of motion in the Born-Oppenheimer approximation from the fully coupled nuclear equations of motion by neglecting the nonadiabatic coupling elements. In the zero-field case and for our internal coordinate system this neglect is equivalent to the assumption that

$$\mathbf{P}|\phi_j\rangle=\frac{1}{i}\left|\frac{\partial}{\partial\mathbf{R}}\phi_j\right\rangle=0 \tag{4.11}$$

holds. Equation (4.11) is the usual assumption to derive the Born-Oppenheimer approximation in the absence of an external field. There are now two possibilities to generalize the condition (4.11) to the case of the presence of a magnetic field. The first possibility was implicitly used in Sec. III and reads as follows:

$$\left[\mathbf{P}-\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\right]|\phi_j\rangle=0\ . \tag{4.12}$$

Equation (4.12) is motivated by the fact that $|\phi_j\rangle$ contains the phase $\mathcal{P}$ from Eq. (4.5) and therefore Eq. (4.12) is equivalent to the following condition:

$$\mathbf{P}|\phi_{0j}\rangle=0\ , \tag{4.13}$$

with $\phi_j=\mathcal{P}\phi_{0j}$. Equation (4.13) is the analogue of condition (4.11) for the case of the presence of a magnetic field. For a *homonuclear* diatomic molecule, we have $\mathcal{P}\equiv1$ and our condition (4.12) becomes identical with the condition (4.11) of the zero-field case. Using Eq. (4.12) in the fully coupled nuclear equations of motion (3.8) we arrive at the nuclear equations of motion in the Born-Oppenheimer approximation (3.10). The latter were used in the literature[31,32] for the special case of the $H_2{}^+$ ion to calculate its rovibrational spectrum in a strong magnetic field. In this approximation scheme the diagonal terms of the nonadiabatic couplings contain, as shown in Sec. IV A, the screening of the nuclear charges against the magnetic field and therefore must be included in the nuclear equation of motion.

An alternative possibility to derive the nuclear equation of motion in an adiabatic approximation is motivated by the fact that we have had to set the nuclear relative velocities equal to zero in order to obtain a well-defined electronic Hamiltonian from the total Hamiltonian of the molecule. Since the electronic wave functions are calculated for fixed nuclear relative coordinate it suggests itself to use the condition

$$\dot{\mathfrak{R}}|\phi_j\rangle=0 \tag{4.14}$$

instead of Eqs. (4.12) and (4.13), where $\dot{\mathfrak{R}}$ is given by Eq. (3.3). In the zero-field case we have $\dot{\mathfrak{R}}=\dot{\mathbf{R}}=(M_0/M_1M_2)\mathbf{P}$, i.e., the canonical conjugated momentum is equal to the nuclear relative velocity and the condition (4.14) becomes identical with (4.11). In the presence of a magnetic field Eq. (4.14) is equivalent to the condition

$$\mathbf{P}|\phi_j\rangle=\left[-\frac{e}{2}\frac{1}{M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}+\frac{e}{2}\frac{m}{MM_0}\mathcal{M}\mathbf{B}\times\sum_i\mathbf{r}_i\right]|\phi_j\rangle\ . \tag{4.15}$$

The second term on the rhs of Eq. (4.15) again cancels if we use the fact that $\phi_j$ contains the phase $\mathcal{P}$

$$\mathbf{P}|\phi_{0j}\rangle=\left[-\frac{e}{2}\frac{1}{M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]|\phi_{0j}\rangle\ . \tag{4.16}$$

The electronic wave functions $\phi_{0j}$ still are strongly dependent on the internuclear distance. Only in the dissociation limit of the molecule into atoms this dependency is well known and described by the gauge-centering phases given in Sec. IV A [see Eq. (4.6)]. Apart from these gauge phases the electronic wave function shows a smooth behavior with respect to the internuclear distance. Hence Eq. (4.15) is the mathematical formulation that the electronic wave function, apart from all gauge phases is taken to be independent of $\mathbf{R}$.

Equation (4.14) provides a new kind of adiabatic approximation which we call the *screened* Born-Oppenheimer approximation. The nuclear equation of motion in the screened Born-Oppenheimer approach which results from the condition (4.14) reads as follows:

$$\left[\frac{M_0}{2M_1M_2}\mathbf{P}^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\mathbf{R})-E\right]\chi_j+\sum_{j'}\Lambda^S_{jj'}\chi_{j'}=0\ . \tag{4.17}$$

The screened Born-Oppenheimer approximation is obtained by ignoring all nonadiabatic coupling terms $\Lambda^S_{jj'}$. The paramagnetic and diamagnetic terms of the nuclear equation of motion in the Born-Oppenheimer approximation (3.10) are not present in the screened Born-Oppenheimer approximation (4.17). They are now included in the diagonal term of the nonadiabatic coupling elements. The nonadiabatic coupling elements which appear in the fully coupled nuclear equations of motion are now given by the appealing expressions

$$\Lambda^S_{jj'}=\frac{M_1M_2}{2M_0}\langle\phi_j|\dot{\mathfrak{R}}^2|\phi_{j'}\rangle+\langle\phi_j|\dot{\mathfrak{R}}|\phi_{j'}\rangle\cdot\mathbf{P}\ , \tag{4.18}$$

with

$$\dot{\mathfrak{R}}=\frac{M_0}{M_1M_2}\mathbf{P}+\frac{e}{2}(M_1M_2M_0)^{-1}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}-\frac{e}{2}\frac{m\mathcal{M}}{MM_1M_2}\mathbf{B}\times\sum_i\mathbf{r}_i\ .$$

The screened Born-Oppenheimer approximation has the advantage that its nuclear equation of motion (4.17) is well behaved in the dissociation limit of the molecule into atoms. In analogy to the zero-field case the diagonal term of the nonadiabatic couplings $\Lambda^S_{jj'}$ then provides only small corrections to the nuclear equation of motion (4.17) in the dissociation limit. For the general case, i.e., also far from dissociation, it is left to future investigations to find out to which extent the screening of the nuclear charges takes place. This will clarify the importance of the diagonal terms of the nonadiabatic couplings in the different approximation schemes.

Finally, we remark that the off-diagonal elements of the nonadiabatic coupling terms are identical in both of the two approaches, i.e., $\Lambda_{jj'}=\Lambda^S_{jj'}$ for $j\neq j'$. Moreover, the nuclear equations of motion which we obtain by adding the diagonal terms of the nonadiabatic couplings $\Lambda_{jj}$ to the nuclear equation of motion *in the Born-Oppenheimer approximation* or alternatively by adding the diagonal terms $\Lambda^S_{jj}$ to the nuclear equation of motion in the *screened* Born-Oppenheimer approximation are identical.

## V. A SPECIAL CASE: THE HOMONUCLEAR DIATOMIC MOLECULE

The total Hamiltonian for a homonuclear diatomic molecule which can be obtained from Eq. (3.1) by assuming equal nuclear charges and nuclear masses of the two atoms simplifies to

$$\mathcal{H}=\frac{1}{2M}\mathbf{k}^2-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\sum_i \mathbf{r}_i+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i\right]^2+\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2+\frac{2}{M_0}\left[\mathbf{P}+\frac{eZ}{4}\mathbf{B}\times\mathbf{R}\right]^2+V(\{\mathbf{r}_i\};\mathbf{R})\ , \qquad (5.1)$$

where $Z$ is the nuclear charge number of the nuclei. The Hamiltonian (5.1) is much simpler than in the heteronuclear case. It contains, in particular, no mass-correction terms which include mixed electronic and nuclear degrees of freedom. Furthermore, there exists no coupling of the pseudomomentum to the nuclear degrees of freedom. The mass-corrected electronic Hamiltonian, which can be obtained from Eq. (3.5) by setting $\mathcal{M}$ equal to zero, reads

$$\mathcal{H}_{\text{el}}=-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\sum_i \mathbf{r}_i+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i\right]^2+\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2+V(\{\mathbf{r}_i\};\mathbf{R})\ , \qquad (5.2)$$

and the nuclear equation of motion, which results from Eq. (3.8), reads

$$\left[\frac{2}{M_0}\left[\mathbf{P}+\frac{eZ}{4}\mathbf{B}\times\mathbf{R}\right]^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\mathbf{R})-E\right]\chi_j+\sum_{j'}\Lambda_{jj'}\chi_{j'}=0\ , \qquad (5.3)$$

with the nonadiabatic coupling elements

$$\Lambda_{jj'}=\frac{2}{M_0}\left[\langle\phi_j|\mathbf{P}^2|\phi_{j'}\rangle+2\langle\phi_j|\mathbf{P}|\phi_{j'}\rangle\mathbf{P}+\frac{e}{2}Z\mathbf{B}\times\mathbf{R}\cdot\langle\phi_j|\mathbf{P}|\phi_{j'}\rangle\right]\ . \qquad (5.4)$$

Apart from the nonadiabatic couplings also present in the zero-field case, we have for a homonuclear diatomic molecule only one additional explicit magnetic-field-dependent coupling term [last term in Eq. (5.4)]. This term vanishes if the molecular axis is parallel to the magnetic field direction, which is the equilibrium position of, for example, the $H_2{}^+$ ion in the presence of a magnetic field. However the first two terms of Eq. (5.4) depend implicitly via the wave functions $\{\phi_j\}$ on the magnetic field strength and we therefore expect the nonadiabatic coupling terms to depend considerably on the magnetic field strength.

The problem of the missing screening is resolved analogously to the heteronuclear case. The electronic energy $\epsilon$ and the diagonal term $\Lambda_d$ of the nonadiabatic couplings read in the dissociation limit of the molecule into neutral atoms $A_2 \rightarrow A + A$ as follows:

$$\varepsilon=2E_A+\mathcal{C}\ ,$$

$$\Lambda_d=-eZ\frac{1}{M_0}(\mathbf{B}\times\mathbf{R})\cdot\mathbf{P}-e^2Z^2\frac{1}{8M_0}(\mathbf{B}\times\mathbf{R})^2-\mathcal{C}\ . \qquad (5.5)$$

We again see that the explicit magnetic-field-dependent parts of $\Lambda$ in Eq. (5.5) are the negative counterparts of the paramagnetic and diamagnetic term in the nuclear equation of motion (5.3). The screening of the nuclear charges is therefore contained in the diagonal term of the nonadiabatic couplings. We remark that the screening of the paramagnetic ($\propto B$) term arises from the derivative coupling term [second term in Eq. (5.4)], which is equal to zero in the zero-field case, whereas the screening of the diamagnetic term ($\propto B^2$) comes partially from the coupling terms of the zero-field case and partially from the additional explicit magnetic field-dependent coupling term [first and third term in Eq. (5.4), respectively]. Again the same conclusions hold as they were already drawn for the case of a heteronuclear molecule in Sec. IV A.

Finally, we present the nuclear equation of motion in the screened Born-Oppenheimer approximation and the corresponding nonadiabatic coupling elements $\Lambda^S_{jj'}$. The latter can be obtained from Eq. (4.18) and read

$$\Lambda^S_{jj'}=\frac{2}{M_0}\left\langle\phi_j\middle|\left[\mathbf{P}+\frac{eZ}{4}\mathbf{B}\times\mathbf{R}\right]^2\middle|\phi_{j'}\right\rangle+\frac{4}{M_0}\left\langle\phi_j\middle|\left[\mathbf{P}+\frac{eZ}{4}\mathbf{B}\times\mathbf{R}\right]\middle|\phi_{j'}\right\rangle\mathbf{P}\ . \qquad (5.6)$$

The nuclear equation of motion takes on the following appearance:

$$\left[\frac{2}{M_0}\mathbf{P}^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\mathbf{R})-E\right]\chi_j=0\ . \qquad (5.7)$$

As already discussed in Sec. IV B the advantage of the nuclear equation of motion in the screened Born-Oppenheimer approximation is its correct behavior in the dissociation limit of the molecule into atoms. The diagonal term of the nonadiabatic coupling elements (5.6) then, in general, provides only small corrections to the total energy $E$.

## VI. ATOMIC PSEUDOMOMENTA GAUGE-CENTERING PHASES, AND OFF-DIAGONAL NONADIABATIC COUPLINGS

In Sec. V we investigated the case of vanishing pseudomomentum $\mathbf{k}$. In this section we will provide a brief discussion of some aspects of the case of nonvanishing pseudomomentum for a *homonuclear diatomic molecule.* In the following $\mathbf{k}$ denotes the total pseudomomentum of the neutral molecule and $\mathbf{k}_A$ and $\mathbf{k}_B$ denote the pseudomomenta of the atoms $A$ and $B$, respectively. In the dissociation limit of the molecule into neutral atoms we have no interaction between the two atoms and as a consequence there exist two constants of motion: the atomic pseudomomenta $\mathbf{k}_A$ and $\mathbf{k}_B$. They obey the following commutation relations:

$$[\hat{\mathbf{k}}_A,\mathcal{H}_A]=[\hat{\mathbf{k}}_B,\mathcal{H}_B]=[\hat{\mathbf{k}}_A,\mathcal{H}_B]=[\hat{\mathbf{k}}_B,\mathcal{H}_A]=0\ , \tag{6.1}$$

where $\mathcal{H}_A$ and $\mathcal{H}_B$ are the atomic Hamiltonians for the atoms $A$ and $B$. The electronic and nuclear equations of motion for the molecule in an adiabatic approximation contain *no* information about the individual atomic pseudomomenta $\mathbf{k}_A$ and $\mathbf{k}_B$; only the sum $\mathbf{k}=\mathbf{k}_A+\mathbf{k}_B$ enters. The same statement holds if we take the dynamical corrections, due to the diagonal term of the nonadiabatic couplings, into account. The effects of the atomic pseudomomenta must therefore be contained in the *off-diagonal* nonadiabatic coupling elements. Nevertheless, it is possible to understand some of the effects of the atomic pseudomomenta in a qualitative way by the following simple considerations.

In our pseudoseparation of the center of mass of the molecule in Sec. II we have separated the phase

$$\exp\left[+i\left[\mathbf{k}-\frac{e}{2}\mathbf{B}\times\sum_l \mathbf{r}_l\right]\cdot\mathbf{R}_S\right] \tag{6.2}$$

from our total molecular wave function [see Eqs. (2.6) and (2.7)]. In Eq. (6.2) $\mathbf{R}_S$ denotes the center-of-mass coordinate of the molecule and $\{\mathbf{r}_l\}$ the electronic relative coordinates to the center of mass of nuclei. Since we discuss the case of well-separated atoms we have $\mathbf{k}=\mathbf{k}_A+\mathbf{k}_B$ with conserved pseudomomenta $\mathbf{k}_A$ and $\mathbf{k}_B$. Analogously, the phases which can be eliminated from the total atomic wave functions are of the form

$$\begin{gathered}\exp\left[+i\left[\mathbf{k}_A-\frac{e}{2}\mathbf{B}\times\sum_i \mathbf{r}_{Ai}\right]\cdot\mathbf{R}_{S_A}\right]\ ,\\ \exp\left[+i\left[\mathbf{k}_B-\frac{e}{2}\mathbf{B}\times\sum_j \mathbf{r}_{Bj}\right]\cdot\mathbf{R}_{S_B}\right]\ ,\end{gathered} \tag{6.3}$$

where $\mathbf{R}_{S_A}$ and $\mathbf{R}_{S_B}$ are the center-of-mass coordinates of the atoms $A$ and $B$, respectively. $\{\mathbf{r}_{Ai}\}$ and $\{\mathbf{r}_{Bj}\}$ are the electronic relative coordinates to the nuclei of the atoms $A$ and $B$, respectively. The phase $\mathcal{P}_T$ which transforms the molecular phase (6.2) to the atomic ones (6.3) reads in molecular coordinates as follows:

$$\begin{aligned}\mathcal{P}_T=\exp&\left\{+i(\mathbf{k}_A-\mathbf{k}_B)\cdot\left[\frac{m}{M}\left[\sum_i \mathbf{r}_i-\sum_j \mathbf{r}_j\right]+\frac{M_0}{2M}\mathbf{R}\right]\right\}\\ &\times\exp\left[-i\frac{e}{4}\mathbf{B}\times\left[\sum_i \mathbf{r}_i-\sum_j \mathbf{r}_j\right]\cdot\mathbf{R}\right]\ ,\end{aligned} \tag{6.4}$$

where $\mathbf{R}$ is the relative coordinate of the two nuclei and $\{\mathbf{r}_i\}$ and $\{\mathbf{r}_j\}$ denote the relative coordinates of the electrons, which are located at the nucleus $A$ and $B$, respectively, to the center of mass of nuclei. The second part of the phase (6.4) is nothing other than the gauge phases discussed in connection with Eq. (4.6) in Sec. IV A. They shift the gauge origin from the origin of the coordinate system to the nuclei of the atoms. We therefore conclude that for a molecule in the dissociation limit, the gauge-centering phases [second part of the phase (6.4)] are closely related to the separate center-of-mass motions of the atoms in the molecule. This might be also valid far from dissociation, although the atomic pseudomomenta are in this case no longer conserved quantities. We remark that, although we have shown it only for the special case of a homonuclear diatomic molecule, the preceding statement holds also for an arbitrary molecule. In the case of a heteronuclear diatomic molecule the corresponding phase to $\mathcal{P}_T$ in Eq. (6.4) also contains the phase $\mathcal{P}$ from Eq. (4.5).

From the phase (6.4) it can be seen that if one neglects its first part one implicitly assumes the equality of the atomic pseudomomenta, i.e., $\mathbf{k}_A=\mathbf{k}_B$. The first part of the phase (6.4) may be useful to fix the boundary conditions $\mathbf{k}_A$ and $\mathbf{k}_B$ in, for example, describing collision experiments. If we include it in our dissociative wave function (4.4) we obtain the *total wave function*

$$\varphi_T=\mathcal{N}\mathfrak{U}[\mathcal{P}_T\varphi_0(\{\mathbf{r}_i-\mathbf{R}/2\};\{\mathbf{s}_i\})\varphi_0(\{\mathbf{r}_j+\mathbf{R}/2\};\{\mathbf{s}_j\})]\ , \tag{6.5}$$

with $\mathcal{P}_T$ from Eq. (6.4). The total energy calculated with the total wave function (6.5) by using the electronic Hamiltonian (5.2) and the diagonal term $\Lambda_d$ [see Eq. (5.5)] of the nonadiabatic coupling elements reads as follows:

$$E=\frac{1}{M}\mathbf{k}_A^2+\frac{1}{M}\mathbf{k}_B^2+2E_A\ . \tag{6.6}$$

The energy $E$ now contains the correct $\mathbf{k}_A$ and $\mathbf{k}_B$ dependencies which we would not obtain if we would have ignored the $(\mathbf{k}_A-\mathbf{k}_B)$-dependent part of the phase $\mathcal{P}_T$ in Eq. (6.5). Turning to the Born-Oppenheimer approximation (with diagonal corrections or screened) the nuclear equation of motion (4.10) or (4.17) replaces the first part of the phase $\mathcal{P}_T$ by the free wave $\exp(i\mathbf{P}\cdot\mathbf{R})$ with $\mathbf{P}^2=(M_0/4M)(\mathbf{k}_A-\mathbf{k}_B)^2$. The difference between the two phases is due to the neglect of the off-diagonal couplings.

Finally, we briefly discuss the interrelation between the off-diagonal nonadiabatic matrix elements and the atomic pseudomomenta. It is well-known that in the zero-field case the off-diagonal nonadiabatic coupling elements can be made arbitrarily large by increasing the relative velocity of the collision partners. Since we have separated the center-of-mass motion before performing an adiabatic separation we expect the off-diagonal nonadiabatic coupling elements not to be very sensitive to the magnitude of the pseudomomentum **k**. However, the relative velocities may be large in the case of collisions, i.e., we may have large $|\mathbf{k}_A - \mathbf{k}_B|$. Such a situation increases the magnitude of the nonadiabatic coupling terms. For bound states it is the large amplitude motion which increases the off-diagonal nonadiabatic coupling elements and therefore restricts the range of validity of the approximation scheme.

## VII. SUMMARY AND CONCLUSIONS

In order to obtain a correct treatment of the center-of-mass motion we performed, as a first step, the pseudoseparation of the center of mass for an arbitrary neutral molecule in a homogeneous magnetic field. The existence of a constant of motion, the pseudomomentum **k**, enabled us to reduce the center-of-mass dependency of the Hamiltonian to a motional Stark effect.

As an internal coordinate system we chose the relative coordinates to the *center of mass of nuclei* which is especially adapted to an adiabatic approximation. We remark that another choice of the reference point (defined by the nuclei) of the internal coordinate system would not lead to essential simplifications of the formulas. Our resulting Hamiltonian contains series of paramagnetic ($\propto B$) and diamagnetic ($\propto B^2$) terms involving nuclear and electronic degrees of freedom. Nevertheless, we succeeded in rearranging the Hamiltonian in a unique manner so it takes on a rather simple form. This form enabled us to identify the specific (mass-polarization) and exact normal-mass-correction terms (reduced masses, gauge-centering corrections). This identification is of particular importance in a magnetic field. We have seen that the mass corrections which shift merely the gauge origin in the electronic part of the Hamiltonian can and must be included exactly in any calculation which takes mass corrections into account. Otherwise one would obtain divergences in the limit of infinitely separated atoms. Furthermore it is known[62] that corrections due to reduced masses and mass-polarization terms play an important role in the high-field region (see below).

With our total molecular Hamiltonian we performed an adiabatic separation of the electronic and nuclear degrees of freedom. In order to obtain a mass-corrected electronic Hamiltonian which is well behaved in the dissociation limit of the molecule into atoms it was essential to set the nuclear relative velocities equal to zero. As further results we derived the nonadiabatic coupling elements and the equation of motion for the nuclei.

A serious problem arises for the nuclear equation of motion in the Born-Oppenheimer adiabatic approximation. The screening of the nuclear charges by the electrons against the magnetic field is missing. The nuclei appear as naked charges whereas in reality they are screened. We have resolved this problem by investigating the diagonal term of the nonadiabatic coupling elements in the dissociation limit of the molecule into neutral atoms. The diagonal terms of the nonadiabatic couplings contain the screening of the nuclear charges and therefore *must* be included in the adiabatic approximation scheme in order to obtain a reasonable description of nuclear dynamics in the presence of a magnetic field. Because of the complexity of the wave functions, the derivative coupling terms now also contribute to the diagonal of the nonadiabatic coupling elements. In contrast to the zero-field case it is therefore not sufficient to perform a Born-Oppenheimer or Born-Huang[48] adiabatic approximation.

We finally introduced the *screened* Born-Oppenheimer approximation which provides the correct free nuclear equation of motion in the dissociation limit of the molecule. The diagonal term of the nonadiabatic coupling elements now contains the paramagnetic and diamagnetic terms of the nuclear equation of motion in the Born-Oppenheimer approximation. In analogy to the zero-field case, the diagonal term of the nonadiabatic couplings then provides only small corrections to the nuclear equation of motion in the dissociation limit. For bound states it is left to future investigations to determine how complete the screening is and to compare the importance of the diagonal term of the nonadiabatic couplings in the different approximation schemes.

A problem which will be also the subject of future investigations is the restriction of the range of validity of the adiabatic approximation scheme by the explicit and implicit magnetic field dependences of the off-diagonal nonadiabatic coupling elements. Nevertheless, some qualitative remarks can already be given here.

As already mentioned, it is known[61] that mass corrections play an important role in the very-high-field region where their energetic contribution becomes comparable with the Coulomb binding energy of the molecule. Since the off-diagonal nonadiabatic coupling elements contain, in general, the higher-order mass corrections they are not expected to be any more negligible in the very-high-field region. Another case of nonadiabatic effects is due to the symmetry lowering in the presence of a magnetic field. Electronic states which are, because of their different spatial symmetry, not allowed to couple in the zero-field case may now couple. Their energies may, therefore, no longer be allowed to cross each other as a function of the internuclear distance. In this case already a weak magnetic field may suffice to introduce relevant nonadiabatic effects. For stronger fields the energy levels are shifted substantially by the increase of binding energy and the interaction terms of the spins with the magnetic field. On the one hand energy levels which are well separated in the zero-field case may come closely together and interact. On the other hand near degeneracies or degeneracies may be resolved by separating the involved energy levels. Another point which will substantially modify the potential energy surfaces and the nonadiabatic coupling elements is the increase of the relevant number of degrees of freedom in the presence of a magnetic field. For a diatomic molecule we have already *two* relevant nuclear degrees of freedom: the internuclear distance and the angle between the molecular axis and the magnetic field.

Finally, we mention that the electronic Hamiltonian as well as the nonadiabatic coupling elements contain the effect of an antiscreening, i.e., polarization of the molecule. The origin of this polarization are the Stark effects occurring explicitly in the electronic Hamiltonian and implicitly in the nonadiabatic coupling elements by their dependencies on the separate centre of mass motions of the atoms. This antiscreening is, however, only of relevance for extremely strong magnetic fields.

*Note added in proof.* The importance of the phase $\mathcal{P}$ [see Eq. (4.5)] for the wave function of a heteronuclear diatomic molecule was discussed extensively in Sec. IV. In Sec. VI we showed the physical significance of this phase. For the sake of completeness we give here the Hamiltonian (3.1) of the heteronuclear diatomic molecule in its unitarity equivalent (and simpler) form

$$\begin{aligned}\mathcal{P}^{-1}\mathcal{H}\mathcal{P}=&\frac{1}{2M}\mathbf{k}^2-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\left[\sum_i\mathbf{r}_i-\frac{1}{M_0}\mathcal{M}\mathbf{R}\right]+\sum_i\frac{1}{2M}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i\right]^2\\&+\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i-\frac{e}{M_0}\mathcal{M}\mathbf{B}\times\mathbf{R}\right]^2\\&+\frac{M_0}{2M_1M_2}\left[\mathbf{P}+\frac{e}{2}\frac{1}{M_0^2}(Z_1M_2^2+Z_2M_1^2)\mathbf{B}\times\mathbf{R}\right]^2+V(\{\mathbf{r}_i\};\mathbf{R})\ .\end{aligned}$$

A similar unitary transformation holds for the case of an arbitrary molecule.

## APPENDIX: THE EQUATIONS OF MOTION FOR AN ARBITRARY MOLECULE

For the case of an arbitrary molecule we obtain the mass-corrected electronic Hamiltonian from the total Hamiltonian (2.9) by setting equal to zero all relative velocities of the nuclei. The corresponding equations of motion for the nuclear relative coordinates are

$$\dot{\mathbf{r}}_\alpha=\frac{1}{i}[\mathbf{r}_\alpha,\mathcal{H}']\ , \tag{A1}$$

with $\mathcal{H}'$ from Eq. (2.3). $\dot{\mathbf{r}}_\alpha=0$ (for all $\alpha$) then implies

$$\dot{\mathbf{r}}_\alpha=\frac{1}{i}[\mathbf{r}_\alpha,\mathcal{H}]=0\ , \tag{A2}$$

with $\mathcal{H}$ from Eq. (2.9). The commutator (A2) is equal to the condition

$$\begin{aligned}\dot{\mathbf{r}}_\alpha=&\frac{1}{M_\alpha}\mathbf{p}_\alpha-\frac{1}{M_0}\left[\sum_\beta{}'\,\mathbf{p}_\beta\right]+\frac{e}{2}\frac{Z_\alpha}{M_\alpha}(\mathbf{B}\times\mathbf{r}_\alpha)\\&-\frac{e}{2}\frac{1}{M_0M_n}\sum_\beta{}'\,(\mathbf{B}\times\mathcal{M}_\beta\mathbf{r}_\beta)\\&+\frac{e}{2}\frac{m}{MM_0M_\alpha}(ZM_\alpha-Z_\alpha M_0)\left[\mathbf{B}\times\sum_i\mathbf{r}_i\right]=0\ ,\end{aligned} \tag{A3}$$

where $Z$ is the total nuclear-charge number. $Z_\alpha$ and $M_\alpha$ are the nuclear-charge number and mass of the individual nuclei, respectively. $\mathbf{p}_\alpha$ is the canonical conjugated momentum of the nuclear relative coordinate $\mathbf{r}_\alpha$. Furthermore, we have used the abbreviation $\mathcal{M}_\beta=(Z_\beta M_n-Z_nM_\beta)$ [see Eq. (2.5)].

Using conditions (A3) in the total Hamiltonian (2.9) we obtain the following mass-corrected electronic Hamiltonian

$$\begin{aligned}\mathcal{H}_{\mathrm{el}}=&-\frac{e}{M}(\mathbf{k}\times\mathbf{B})\cdot\left[\sum_i\mathbf{r}_i-\frac{1}{M_n}\sum_\alpha{}'\,\mathcal{M}_\alpha\mathbf{r}_\alpha\right]+\sum_i\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{2}\mathbf{B}\times\mathbf{r}_i+\frac{e}{2}\frac{m}{MM_n}\mathbf{B}\times\sum_\alpha{}'\,\mathcal{M}_\alpha\mathbf{r}_\alpha\right]^2\\&+\frac{1}{2M_0}\left[\sum_i\mathbf{p}_i+\frac{e}{2}\mathbf{B}\times\sum_i\mathbf{r}_i-\frac{e}{2}\frac{M_0}{M_n}\left[\frac{1}{M}+\frac{1}{M_0}\right]\mathbf{B}\times\sum_\alpha{}'\,\mathcal{M}_\alpha\mathbf{r}_\alpha\right]^2+V(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\ .\end{aligned} \tag{A4}$$

The resulting nuclear equation of motion (see Sec. IV A) takes on the following appearance:

$$\begin{aligned}&\left[\sum_\alpha{}'\,\frac{1}{2M_\alpha}\left[\mathbf{p}_\alpha+\frac{e}{2}Z_\alpha\mathbf{B}\times\mathbf{r}_\alpha\right]^2-\frac{1}{2M_0}\left[\sum_\alpha{}'\,\mathbf{p}_\alpha+\frac{e}{2M_n}\mathbf{B}\times\sum_\alpha{}'\,\mathcal{M}_\alpha\mathbf{r}_\alpha\right]^2+\frac{e^2}{8}\frac{Z_n^2}{M_n^3}\left[\mathbf{B}\times\sum_\alpha{}'\,M_\alpha\mathbf{r}_\alpha\right]^2\right.\\&\qquad\left.+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\{\mathbf{r}_\alpha\})-E\right]\chi_j(\mathbf{k};\{\mathbf{r}_\alpha\})+\sum_{j'}\Lambda_{jj'}\chi_{j'}(\mathbf{k};\{\mathbf{r}_\alpha\})=0\end{aligned} \tag{A5}$$

with the nonadiabatic coupling elements $\Lambda_{jj'}$ given by

$$\begin{aligned}\Lambda_{jj'}=&\sum_{\alpha}{}'\frac{1}{2M_\alpha}\left\langle\phi_j\left|\left[\mathbf{p}_\alpha-\frac{e}{2}\frac{m}{M}Z_\alpha\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2\right|\phi_{j'}\right\rangle-\frac{1}{2M_0}\left\langle\phi_j\left|\left[\sum_\alpha{}'\mathbf{p}_\alpha-\frac{e}{2}\frac{m}{M}Z\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2\right|\phi_{j'}\right\rangle\\&+\frac{e^2}{8}\frac{Z_n^2m^2}{M_nM^2}\left\langle\phi_j\left|\left[\mathbf{B}\times\sum_i\mathbf{r}_i\right]^2\right|\phi_{j'}\right\rangle+\sum_\alpha{}'\frac{1}{M_\alpha}\left\langle\phi_j\left|\left[\mathbf{p}_\alpha-\frac{e}{2}\frac{m}{M}Z_\alpha\mathbf{B}\times\sum_i\mathbf{r}_i\right]\right|\phi_{j'}\right\rangle\left[\mathbf{p}_\alpha+\frac{e}{2}Z_\alpha\mathbf{B}\times\mathbf{r}_\alpha\right]\\&-\frac{1}{M_0}\left\langle\phi_j\left|\left[\sum_\alpha{}'\mathbf{p}_\alpha-\frac{e}{2}\frac{m}{M}Z\mathbf{B}\times\sum_i\mathbf{r}_i\right]\right|\phi_{j'}\right\rangle\cdot\left[\sum_\alpha{}'\mathbf{p}_\alpha+\frac{e}{2M_n}\mathbf{B}\times\sum_\alpha{}'\mathcal{M}_\alpha\mathbf{r}_\alpha\right]\\&+\frac{e^2}{4}\frac{Z_n^2m}{M_n^2M}\left[\mathbf{B}\times\sum_\alpha{}'M_\alpha\mathbf{r}_\alpha\right]\cdot\left\langle\phi_j\left|\left[\mathbf{B}\times\sum_i\mathbf{r}_i\right]\right|\phi_{j'}\right\rangle\ .\end{aligned}\tag{A6}$$

The integration in the matrix elements is over the electronic coordinates only and $\langle\phi_j|\mathbf{p}_\alpha|\phi_{j'}\rangle$ means $\langle\phi_j|\mathbf{p}_\alpha\phi_{j'}\rangle$, etc.

Finally, we present the nonadiabatic couplings belonging to the screened Born-Oppenheimer approach,

$$\begin{aligned}\Lambda_{jj'}^S=&\sum_\alpha{}'\frac{M_\alpha}{2}\left\langle\phi_j\left|\left[\dot{\mathbf{r}}_\alpha+\frac{1}{M_n}\sum_\beta{}'M_\beta\dot{\mathbf{r}}_\beta\right]^2\right|\phi_{j'}\right\rangle\\&-\frac{M_0}{2M_n^2}\left\langle\phi_j\left|\left[\sum_\beta{}'M_\beta\dot{\mathbf{r}}_\beta\right]^2\right|\phi_{j'}\right\rangle+\sum_\alpha{}'\left\langle\phi_j\left|\left[\dot{\mathbf{r}}_\alpha+\frac{1}{M_n}\sum_\beta{}'M_\beta\dot{\mathbf{r}}_\beta\right]\right|\phi_{j'}\right\rangle\mathbf{p}_\alpha-\frac{1}{M_n}\left\langle\phi_j\left|\left[\sum_\beta{}'M_\beta\dot{\mathbf{r}}_\beta\right]\right|\phi_{j'}\right\rangle\sum_\alpha{}'\mathbf{p}_\alpha\ ,\end{aligned}\tag{A7}$$

with $\dot{\mathbf{r}}_\beta$ from Eqs. (A2) and (A3). The corresponding nuclear equation of motion reads as follows:

$$\left[\sum_\alpha{}'\frac{1}{2M_\alpha}\mathbf{p}_\alpha^2-\frac{1}{2M_0}\left[\sum_\alpha{}'\mathbf{p}_\alpha\right]^2+\frac{1}{2M}\mathbf{k}^2+\varepsilon_j(\mathbf{k};\{\mathbf{r}_\alpha\})-E\right]\chi_j(\mathbf{k};\{\mathbf{r}_\alpha\})+\sum_{j'}\Lambda_{jj'}^S\chi_{j'}(\mathbf{k};\{\mathbf{r}_\alpha\})=0\ .\tag{A8}$$

The screened Born-Oppenheimer approximation is—as usual—obtained by ignoring the coupling terms $\Lambda_{jj'}^S$.

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