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Comparison of approximate methods for computation of the concerted adiabatic electronic and nuclear fluxes in aligned $H_2^+(^{2}\Sigma_g^+)$

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ABSTRACT

Approximate methods of computing the concerted electronic and nuclear fluxes associated with electronically adiabatic processes are developed and applied to the prototypal system, namely aligned H_2^+ vibrating in its electronic ground state $(2\Sigma_g^+)$, the only realistic system for which highly accurate (exact) electronic (EPD) and nuclear (NPD) probability densities, electronic (EFD) and nuclear (NFD) *flux* densities, as well as corresponding fluxes, are available. Alternative formulas for the electronic flux, $F_{e,EPD}$ and $F_{e,EFD}$, based on either the EPD or the EFD, are derived from the continuity equation. The results of Born-Oppenheimer approximation (BOA) and of an ordered sequence of Born-Huang expansions (BHE) are presented. The BOA and first-order BHE are in excellent agreement with the exact for both the NPD and NFD, as well as for the EPD and $F_{e,EPD}$ up to about 1ps. Higher-order BHE are necessary to achieve similar accuracy at longer times. In contrast, the BOA and first-order BHE yield zero EFD and therefore also zero $F_{e,EFD}$. Although the higher-order BHE give non-zero values for these properties, they disagree flagrantly with their exact correlates. The error is traceable to numerical ill-conditioning of the working expression for the EFD. In summary, the BOA is adequate to compute accurate NPD, NFD, EPD and $F_{e,EPD}$ for times corresponding to several dozens of vibrational periods; the higher-order BHE is required for longer times. But neither the BOA nor the BHE can provide reliable estimates of the EFD and $F_{e,EFD}$.

1. Introduction

This article concerns the quantum-mechanical description of such fundamental processes as vibration and dissociation of isolated molecules. Traditionally, a molecular process is characterized only by a time sequence of maps of the *population density* (PD) of the fundamental particles (electrons and nuclei) that constitute the system together with their time derivatives and the corresponding (reaction) rates [1,2]. The map, which comprises the number densities $\rho(\mathbf{x}, t)$ at points of observation \mathbf{x} , tells us where the particles are likely to be at time *t*, but gives us no information on how they get there (i.e., on the mechanism of the process).

The mechanism of a molecular process is minutely revealed by a time sequence of maps of the population *flux density* (FD) $\mathbf{j}(\mathbf{x}, t)$ of particles (i.e., the number of particles per unit area passing per unit time in a specific direction at point of observation **x** at time *t*). The maps of $\mathbf{j}(\mathbf{x}, t)$ indicate the expected pathways followed by the particles. Less

detailed information on the mechanism is afforded by the *flux* F(t) of particles between two regions (I and II) of the system separated by a prescribed surface of observation *S* (i.e., the flux is the number of particles crossing *S* per unit time at time *t*). The flux of particles *from* region I to region II is equal to the *negative* of the rate of change of the number of particles in region I, which can be expressed in terms of the PD as

$$F_{\rm PD}(t) = -\int_{V} d\mathbf{x} \partial \rho(\mathbf{x}, t) / \partial t$$
(1.1)

where *V* denotes the volume of region I. From the continuity equation $[\partial \rho(\mathbf{x}, t)/\partial t - \nabla_{\mathbf{x}} \cdot \mathbf{j}(\mathbf{x}, t) = 0]$ we derive the alternative expression in terms of the FD

$$F_{\rm FD}(t) = \int_{S} d\mathbf{S} \cdot \mathbf{j}(\mathbf{x}, t) \tag{1.2}$$

where $d\mathbf{S} = \mathbf{n}dS$ and \mathbf{n} is the outwardly directed normal to the element of area dS at point \mathbf{x} on S. Judicious choices of S can yield insight into

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the mechanisms of flow of the particles.

The principal goal of this work is to develop reliable approximate methods of computing the concerted electronic and nuclear fluxes associated with electronically adiabatic processes. We focus below on the ideal prototypal system, namely aligned H₂⁺ vibrating in its electronic ground state $(^{2}\Sigma_{g}^{+})$, because it is the only realistic system that allows highly accurate (exact) calculations of all the relevant quantities, including the electronic and nuclear PDs, electronic and nuclear FDs, as well as corresponding fluxes [3–7]. The exact results are benchmarks for assessing the reliability of the approximate methods. An ancillary goal of this investigation is to provide guidance on the approximate methods that counterbalance the level accuracy desired with the computational cost. Before turning to the specific application to the prototype, we continue the development for the generic system.

A special challenge is to calculate the flow of electrons that accompany the process. Invoking the equivalence of the $N_{\rm e}$ electrons in the system, we derive formulas for the electron population density (EPD)

$$\rho_{\rm e}(\mathbf{x},t) = N_{\rm e} \int d\mathbf{R} \int d\mathbf{r}'_1 |\Psi(\mathbf{r},\mathbf{R},t)|^2_{\mathbf{r}_1=\mathbf{x}}$$
(1.3a)

and the electronic flux density (EFD)

$$\mathbf{j}_{e}(\mathbf{x},t) = \frac{N_{e}\hbar}{2m_{e}i}\int d\mathbf{R}\int d\mathbf{r}_{1}' \left[\Psi^{*}(\mathbf{r},\mathbf{R},t)\nabla_{\mathbf{r}_{1}}\Psi(\mathbf{r},\mathbf{R},t) - \Psi(\mathbf{r},\mathbf{R},t)\nabla_{\mathbf{r}_{1}}\Psi^{*}(\mathbf{r},\mathbf{R},t)\right]_{\mathbf{r}_{1}=\mathbf{x}}$$
(1.3b)

where the wave function Ψ obeys the Schrödinger equation $i\hbar \partial \Psi / \partial t = H\Psi$, **r** and **R** stand for configurations of electrons and nuclei, respectively, and $\int d\mathbf{r}'_1$ signifies integrations over the coordinates of all electrons except the "first."

Henceforward in this article we constrain our attention to electronically adiabatic processes (i.e., processes during which transitions among electronic states do not occur). We emphasize that the notion of adiabaticity depends implicitly upon separation of the electronic and nuclear motions, as postulated by the Born-Oppenheimer approximation (BOA) [6]. (In the application to the prototype, adiabaticity is ensured by specification of an initial state having mean energy well below the threshold for dissociation.) The total Hamiltonian can be cast as $H = H_e + T_n$, where H_e refers to the electrons in the field of the nuclei and T_n is the kinetic energy of relative (internal) nuclear motions. In the BOA an adiabatic wave function is expressed as a simple product

$$\Psi_{n\nu}^{\text{BOA}}(\mathbf{r}, \mathbf{R}) = \phi_n(\mathbf{r}; \mathbf{R}) \chi_{n\nu}^{\text{BOA}}(\mathbf{R})$$
(1.4)

where $\phi_n(\mathbf{r};\mathbf{R})$ is a *real* eigenfunction of H_e with the nuclei *fixed* in the configuration \mathbf{R} , and $\chi_{nv}^{\text{BOA}}(\mathbf{R})$ is a vibrational-rotational eigenfunction of the nuclear Hamiltonian (i.e., $[T_n + V_n(\mathbf{R})]\chi_{nv}^{\text{BOA}}(\mathbf{R}) = E_{nv}^{\text{BOA}}\chi_{nv}^{\text{BOA}}(\mathbf{R})$, where $V_n(\mathbf{R})$, the eigenvalue of H_e , serves as the potential energy). Thus, within the framework of the BOA, $\phi_n(\mathbf{r};\mathbf{R})\chi_{nv}^{\text{BOA}}(\mathbf{R})$ is the approximate adiabatic eigenfunction of H and E_{nv}^{BOA} is the approximate eigenvalue.

The time-dependent BOA wave function governing a particular electronically adiabatic process is given by

$$\Phi^{\text{BOA}}(\mathbf{r}, \mathbf{R}, t) = \phi_n(\mathbf{r}; \mathbf{R}) \chi_n^{\text{BOA}}(\mathbf{R}, t) = \sum_{\nu} c_{n\nu}^{\text{BOA}} \exp(-iE_{n\nu}^{\text{BOA}} t /\hbar) \phi_n(\mathbf{r}; \mathbf{R}) \chi_{n\nu}^{\text{BOA}}(\mathbf{R})$$
(1.5)

where the constants $c_{n\nu}^{\text{BOA}}$ depend on the initial wave function $\Phi(\mathbf{r}, \mathbf{R}, 0)$. Plugging the BOA wave function into the general formula for $\mathbf{j}_{e}(\mathbf{x}, t)$ (Eq. (1.3b)), we get

$$\mathbf{j}_{e}^{\text{BOA}}(\mathbf{x},t) = \frac{N_{e}\hbar}{m_{e}} \text{Im}\left\{\int d\mathbf{R} |\boldsymbol{\chi}_{n}^{\text{BOA}}(\mathbf{R},t)|^{2} \int d\mathbf{r}_{1}' \left[\phi_{n}(\mathbf{r};\mathbf{R}) \nabla_{\mathbf{r}_{1}} \phi_{n}(\mathbf{r};\mathbf{R})\right]_{\mathbf{r}_{1}=\mathbf{x}}\right\} = \mathbf{0}$$
(1.6)

The mathematical reason that $\mathbf{j}_{e}^{\text{BOA}}$ vanishes is that $\phi_{n}(\mathbf{r};\mathbf{R})$ is real [8]. We conclude that the BOA wave function *always* yields a vanishing EFD. The rationale for this anti-intuitive result goes as follows. In the BOA the electrons adjust *instantaneously* to the movement of the nuclei.

They are not dynamically coupled to the nuclei and therefore remain permanently in a *stationary* state described by a *real* wave function $\phi_n(\mathbf{r};\mathbf{R})$. But a stationary state has no associated flux [8]. In contrast, the nuclei respond dynamically to the changing spatial distribution of the electrons. They are in a non-stationary state in which their relative motion is governed by a complex wave packet $\chi_n^{BOA}(\mathbf{R}, t)$. A calculation of the nuclear flux density, by means of a formula analogous to Eq. (1.3b), indeed yields a non-zero result.

The correction of this failure of the BOA (i.e., zero EFD) necessitates accounting somehow for the dynamical coupling between electrons and nuclei. A number of approaches have been proffered [3-7,9-16]. Here we present the results of a computational study utilizing the so-called Born-Huang expansion (BHE) [17,18], which appears to provide a systematic way of increasing the degree of electronic-nuclear coupling. Thus, we replace the simple product (Eq. (1.4)) with

$$\Psi_{\nu}^{\mathrm{BH}(N_{\mathrm{s}})}(\mathbf{r},\,\mathbf{R}) = \sum_{n=0}^{N_{\mathrm{s}}-1} \,\phi_{n}(\mathbf{r};\mathbf{R})\chi_{n\nu}^{N_{\mathrm{s}}}(\mathbf{R})$$
(1.7)

where we refer to the total number of states N_s included in the BHE as the order. In the limit of infinite order Ψ_{ν}^{BH} satisfy the eigenvalue equation $H\Psi_{\nu}^{\text{BH}} = E_{\nu}^{\text{BH}}\Psi_{\nu}^{\text{BH}}$ exactly. The BHE (Eq. (1.7)) leads to a set of coupled differential equations for the N_s expansion coefficients $\chi_{n\nu}^{N_c}(\mathbf{R})$, which depend upon the order and manifest the coupling among electronic states induced by the nuclear motion. Fixing the order yields a set of approximate eigenfunctions $\Psi_{\nu}^{\text{BH}(N_s)}$ and corresponding eigenvalues $E_{\nu}^{\text{BH}(N_s)}$. One of course expects these to converge to their exact counterparts as N_s increases. Throughout the article we refer to highly accurate quantities (e.g., the wave function that obeys the Schrödinger equation with arbitrarily high precision, or at least the highest precision attainable in practice by the available numerical method) as "exact."

Instead of the BOA wave function (Eq. (1.5)) we have the analogue

$$\Phi^{\mathrm{BH}(N_{\mathrm{b}})}(\mathbf{r},\,\mathbf{R},\,t) = \sum_{\nu} b_{\nu}^{N_{\mathrm{s}}} \exp(-iE_{\nu}^{N_{\mathrm{s}}}t/\hbar) \Psi_{\nu}^{\mathrm{BH}(N_{\mathrm{b}})}(\mathbf{r},\,\mathbf{R})$$
(1.8)

represented in terms of the approximate $BH(N_s)$ eigenstates of *H*. Substituting the $BHE(N_s)$ wave function into Eq. (1.3a), we obtain the following expression for the EPD

$$\rho_{\rm e}^{\rm BH(N_S)}(\mathbf{x}, t) = \sum_{\nu} \sum_{\nu'} b_{\nu}^{N_S} b_{\nu'}^{N_S} \cos[(E_{\nu}^{N_S} - E_{\nu'}^{N_S})t/\hbar] \rho_{\rm e,BH(N_S)}^{\nu\nu'}(\mathbf{x})$$
(1.9)

where

$$\rho_{\mathrm{e,BH}(N_{\mathrm{S}})}^{\nu\nu'}(\mathbf{x}) \equiv \int d\mathbf{r}_{1}' \int_{0}^{\infty} d\mathbf{R} \left[\Psi_{\nu}^{\mathrm{BH}(N_{\mathrm{S}})}(\mathbf{r}, \mathbf{R}) \Psi_{\nu'}^{\mathrm{BH}(N_{\mathrm{S}})}(\mathbf{r}, \mathbf{R}) \right]_{\mathbf{r}_{1}=\mathbf{x}}$$
(1.10)

In like manner, we get

$$\mathbf{j}_{e}^{BH(N_{s})}(\mathbf{x}, t) = \sum_{\nu} \sum_{\nu'} b_{\nu}^{N_{s}} b_{\nu}^{N_{s}} \sin[(E_{\nu}^{N_{s}} - E_{\nu'}^{N_{s}})t/\hbar] \mathbf{J}_{e,BH(N_{s})}^{\nu\nu'}(\mathbf{x})$$
(1.11)

where

$$\sum_{e, BH(N_{s})}^{e}(\mathbf{x})$$

$$\equiv \frac{\hbar}{2\mu_{e}} \int d\mathbf{r}_{1}' \int_{0}^{\infty} d\mathbf{R}$$

$$\left[\Psi_{\nu}^{BH(N_{s})}(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{r}_{1}} \Psi_{\nu'}^{BH(N_{s})}(\mathbf{r}, \mathbf{R}) - \Psi_{\nu'}^{BH(N_{s})}(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{r}_{1}} \Psi_{\nu}^{BH(N_{s})}(\mathbf{r}, \mathbf{R}) \right]_{\mathbf{r}_{1}=\mathbf{x}}$$

$$(1.12)$$

and μ_{e} is the reduced mass of the electron with respect to the nuclei. It is interesting that the auxiliary quantity $\mathbf{J}_{e,BH(N_{S})}^{\nu\nu'}(\mathbf{x})$ has dimensions of flux density, as well as a form reminiscent of that of the EFD (see Eq. (1.3b)), except that it involves two (approximate) stationary eigenstates of *H*. Hence, we refer to $\mathbf{J}_{e,BH(N_{S})}^{\nu\nu'}(\mathbf{x})$ loosely as the *stationary electronic transition flux density*. We note that it is the analogue of the "transition current density" defined by Nafie [19]. We emphasize that, although the process under consideration is electronically adiabatic, its description nevertheless *in principle* requires the participation of all electronic states. Otherwise, the quantity of principal interest, the EFD, may vanish. If, for example, only a single electronic state is involved, as in the case of either the BOA or first-order BHE, then the EFD is zero. Only for orders $N_s \ge 2$ does the BHE yield non-zero EFD (see Fig. 3 below). The working hypothesis is, of course, that as N_s increases, $\mathbf{j}_e^{\text{BH}(N_s)}(\mathbf{x}, t)$ should converge to the exact EFD, in parallel with the expected convergence of the eigenfunctions $\Psi_{\nu}^{\text{BH}(N_s)}$ and corresponding eigenvalues $E_{\nu}^{\text{BH}(N_s)}$.

Plugging Eqs. (1.9) and (1.11) into Eqs. (1.1) and (1.2) respectively, we get the following specific BHE expressions for the *electronic flux*:

$$F_{e,EPD}^{BH(N_s)}(t) = -\int_V d\mathbf{x} \partial \rho_e^{BH(N_s)}(\mathbf{x}, t) / \partial t$$
(1.13a)

$$F_{e,EFD}^{BH(N_s)}(t) = \int_S d\mathbf{S} \cdot \mathbf{j}_e^{BH(N_s)}(\mathbf{x}, t)$$
(1.13b)

Either formula can be employed to compute the flux. The precision to which the two accord depends on the accuracy of the wave function used to compute the EPD and EFD. We expect the exact wave function to lead to the best agreement. The alternative formulas are likely to be discrepant for less accurate EPDs and EFDs generated by the BOA and BHE approximations. The discrepancy serves as a rough measure of the accuracy of the wave function.

2. Theory and computational methods

2.1. Description of the model system

We take the H_2^+ to be so placed and oriented that the nuclear center of mass (NCM) is located at the origin of the laboratory coordinate frame, one proton (a) is at $\mathbf{R}_a = R\mathbf{e}_z/2$ and the other proton (b) at $\mathbf{R}_b = -R\mathbf{e}_z/2$ (see Fig. 1). The position of the electron is denoted by \mathbf{r} and the distance between the nuclei by $R = |\mathbf{R}_a - \mathbf{R}_b|$. The total internal Hamiltonian (exclusive of the total center of mass contribution) is

$$H = -\frac{\hbar^2}{2\mu_{\rm n}} \frac{\partial^2}{\partial R^2} + \frac{e^2}{4\pi \in_0 R} - \frac{\hbar^2}{2\mu_{\rm e}} \nabla_{\mathbf{r}}^2 - \frac{e^2}{4\pi \in_0 r_a} - \frac{e^2}{4\pi \in_0 r_b}$$
$$= -\frac{\hbar^2}{2\mu_{\rm n}} \frac{\partial^2}{\partial R^2} + H_{\rm e}(R)$$
(2.1)



where the second line implicitly defines the electronic Hamiltonian $H_e(R)$, which depends parametrically on R. The symbols appearing in Eq. (2.1) are defined as follows: $\mu_e = m_e M_{ab}/(m_e + M_{ab})$, $\mu_n = M_a M_b/M_{ab}$, $M_{ab} = M_a + M_b$, $M_a = M_b = M_p$, and $M_p/m_e = 1836.15267245$; \in_0 is the permittivity of vacuum; \hbar is the reduced Planck constant. The distance of the electron from proton α is $r_{\alpha} = |\mathbf{r} - \mathbf{R}_{\alpha}|$, where $\alpha = a, b$.

Since the potential energy is cylindrically symmetric, we can write the *complete* (internal) eigenfunction of H in the form

$$\Psi_{\rm C}(\mathbf{r}, R) = \Psi(r, \theta, R) \exp(i\Lambda\phi) / \sqrt{2\pi}$$
(2.2)

where (r, θ, ϕ) are spherical coordinates of the electron and $\Lambda\hbar$ is the *z*component of the electronic angular momentum (i.e., $\exp(i\Lambda\phi)/\sqrt{2\pi}$ is the normalized eigenfunction of $L_z = -i\hbar\partial/\partial\phi$). Here we are concerned only with states of H₂⁺ having ${}^{2}\Sigma_{g}^{+}$ symmetry, for which $\Lambda = 0$. Therefore, to describe these eigenfunctions we require only the coordinates *r*, θ , and *R*. Using the multipole expansion [20]

$$\frac{1}{|\mathbf{r} - \mathbf{R}_{\alpha}|} = \sum_{l=0}^{\infty} \frac{r_{\alpha, l}^{l}}{r_{\alpha, l}^{l+1}} P_{l}(\cos\theta_{\alpha})$$
(2.3)

we can cast the (constrained) Hamiltonian in terms of these coordinates as

$$H = -\frac{\hbar^2}{2\mu_n}\frac{\partial^2}{\partial R^2} + \frac{e^2}{4\pi\epsilon_0}R - \frac{\hbar^2}{2\mu_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] - \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha=a,b}\sum_{l=0}^{\infty}\frac{r_{\alpha<}^l}{r_{\alpha>}^{l+1}}P_l(\cos\theta_{\alpha})$$
(2.4)

Here $P_l(\cos\theta_{\alpha})$ is the Legendre polynomial; $\cos\theta_a = \cos\theta$ and $\cos\theta_b = -\cos\theta$; $r_{\alpha <} = \min(r, R_{\alpha})$ and $r_{\alpha >} = \max(r, R_{\alpha})$.

2.2. Eigenstates of the complete Hamiltonian

2.2.1. "Exact" eigenstates

In Appendix A of the Supplementary Information (SI) we outline our method of determination of highly accurate (henceforth for convenience referred to as "exact") eigenstates of the complete Hamiltonian *H*. The properties computed from wave functions based on these serve as benchmarks for judging the quality of results obtained through alternative approximations (see Sections 2.2.2 and 2.2.3). The exact eigenfunctions are expressed as [4]

$$\Psi_{\lambda}(r,\,\theta,\,R) = \sum_{i=1}^{N_{\rm e}} \sum_{l=0}^{l_{\rm max}} \sum_{j=1}^{N_{\rm n}} c_{ilj}^{\,\lambda} r^{-1} B_i(r) \chi_l(\cos\theta) B_j(R)$$
(2.5)

where the constant coefficients c_{ili}^{λ} and eigenvalues E_{λ} are found as described in Appendix A. Here χ_l , the normalized eigenfunction of the electronic angular momentum L^2 , is given by $\chi_l(\cos\theta) = \sqrt{(2l+1)/2} P_l(\cos\theta)$ in terms of $P_l(\cos\theta)$, the Legendre polynomial of degree *l*; $B_i(r)$ and $B_i(R)$ are B-spline functions [21,22]; $N_{\rm e}$ and $N_{\rm n}$ are the numbers of B-splines describing the electronic and nuclear motion, respectively. Note that the electronic and nuclear Bspline functions depend on $N_{\rm e}$ and $N_{\rm n}$, respectively, but to simplify the notation, we do not explicitly indicate this dependence henceforth. The Σ_{σ}^{+} symmetry of the system implies that the summation on *l* is restricted to even numbers $l = 0, 2, ... l_{max}$. This restriction is indicated by the asterisk (henceforth, for the sake of notational simplicity, the asterisk is suppressed). The upper limit l_{\max} (equivalent to the maximum electronic angular momentum, according to the relation $L^2\chi_l = l(l+1)\hbar^2\chi_l$ is related to the number N_l of eigenfunctions χ_l by $N_l = l_{max}/2 + 1$. We take the eigenfunctions Ψ_{λ} to be real and orthonormal, i.e.

$$\int_{0}^{\infty} dR \int_{0}^{\infty} dr \, r^{2} \int_{-1}^{1} d(\cos\theta) \Psi_{\lambda}(r,\,\theta,\,R) \Psi_{\lambda'}(r,\,\theta,\,R) = \delta_{\lambda\lambda'}$$
(2.6)

2.2.2. The Born-Huang expansion (BHE)

The alternative method of determining eigenstates of H proceeds via

Fig. 1. Schematic diagram of aligned H₂⁺ showing coordinates.

$$\Psi_{\nu}^{\rm BH}(r,\,\theta,\,R) = \sum_{n} \phi_{n}(r,\,\theta;R)\chi_{n\nu}(R)$$
(2.7)

where, in principle, the summation on *n* runs over the complete (infinite) set of electronic energy eigenfunctions ϕ_n , which satisfy the eigenvalue equation

$$H_{\rm e}(R)\phi_n(r,\,\theta;R) = V_n(R)\phi_n(r,\,\theta;R) \tag{2.8}$$

(The numerical solution of Eq. (2.8) is detailed in Appendix B (see Eq. (B.6))). In practice, we truncate the summation on n in Eq. (2.7) to $N_{\rm s} - 1$ terms, where $N_{\rm s}$ denotes the total number of electronic states (the ground state is designated as 0). Retaining the terminology introduced in Section 1, we refer henceforward to $N_{\rm s}$ as the "order" of the BHE. Thus, the $N_{\rm s}$ -order wave function corresponding to the *exact* (i.e., infinite-order) one in Eq. (2.7), is written

$$\Psi_{\nu}^{\text{BH}(N_{\text{S}})}(r,\,\theta,\,R) = \sum_{n=0}^{N_{\text{S}}-1} \phi_{n}(r,\,\theta;R)\chi_{n\nu}^{N_{\text{S}}}(R)$$
(2.9)

where the superscript $N_{\rm s}$ on $\chi_{n\nu}^{N_{\rm s}}$ emphasizes the dependence of $\chi_{n\nu}^{N_{\rm s}}$ on the order.

We determine the N_s -order BHE eigenstates of H by a procedure analogous to that employed to find the "exact" eigenstates. Thus, we suppose that the nuclear wave functions $\chi_{n\nu}^{N_s}$ can be expanded in terms of B-splines

$$\chi_{n\nu}^{N_{s}}(R) = \sum_{j=1}^{N_{n}} c_{nj}^{\nu,N_{s}} B_{j}(R)$$
(2.10)

so that the BHE eigenfunctions can be represented as

$$\Psi_{\nu}^{\text{BH}(N_{\text{s}})}(r,\,\theta,\,R) = \sum_{n=0}^{N_{\text{s}}-1} \sum_{j=1}^{N_{\text{n}}} c_{nj}^{\nu,N_{\text{s}}} \phi_{n}(r,\,\theta;R) B_{j}(R)$$
(2.11)

The constant coefficients $c_{nj}^{\nu,N_{\rm S}}$ and eigenvalues $E_{\nu}^{\rm BH(N_{\rm S})}$ are then found in the manner detailed in Appendix B of the SI. We take the $\Psi_{\nu}^{\rm BH(N_{\rm S})}$ to be real and orthonormal.

2.2.3. The Born-Oppenheimer Approximation (BOA)

The standard BOA wave function for the electronic ground state is expressed as a simple product

$$\Psi_{\nu}^{\text{BOA}}(r,\,\theta,\,R) = \phi_0(r,\,\theta;R)\chi_{0\nu}^{\text{BOA}}(R) \tag{2.12}$$

where the nuclear wave functions $\chi_{0\nu}^{\text{BOA}}(R)$ are real and orthonormal. By analogy with Eq. (2.10) we expand the latter in B-splines as

$$\chi_{0\nu}^{\text{BOA}}(R) = \sum_{j=1}^{N_{\text{n}}} c_{0j}^{\nu,\text{BOA}} B_j(R)$$
(2.13)

thereby obtaining from Eq. (2.12)

$$\Psi_{\nu}^{\text{BOA}}(r, \,\theta, \,R) = \sum_{j=1}^{N_{\text{n}}} c_{0j}^{\nu,\text{BOA}} \phi_0(r, \,\theta; R) B_j(R)$$
(2.14)

where the constant coefficients $c_{0j}^{\nu,\text{BOA}}$ and energy eigenvalues $E_{0\nu}^{\text{BOA}}$ are determined as outlined in Appendix C of the SI. That the $\chi_{0\nu}^{\text{BOA}}(R)$ are real and orthonormal implies that the Ψ_{ν}^{BOA} are likewise.

For the sake of consistency in comparing $N_{\rm s}$ -order BHE (Section 2.2.2) and BOA (Section 2.2.3) results with the exact results, we employ the same parameters for which the latter converge: $N_{\rm e} = 80$, $N_l = 13$, $N_{\rm n} = 100$, $r_{\rm max} = 10a_0$ and $R_{\rm max} = 20a_0$. (See Appendix A of the SI.)

2.3. Time evolution of the system and its dynamical properties

2.3.1. Wave functions

Since the exact eigenfunctions $\{\Psi_{\lambda}\}$ constitute a complete orthonormal set of basis functions on the full electronic-nuclear space, we can express any wave function that satisfies the Schrödinger equation

by

$$\Phi(r,\,\theta,\,R,\,t) = \sum_{\lambda} a_{\lambda} \exp(-iE_{\lambda}t/\hbar) \Psi_{\lambda}(r,\,\theta,\,R)$$
(2.15a)

where the constant coefficients (amplitudes) are given by

$$a_{\lambda} = \int_0^{\infty} dR \int_0^{\infty} dr \, r^2 \int_{-1}^1 d(\cos\theta) \Psi_{\lambda}(r,\,\theta,\,R) \Phi(r,\,\theta,\,R,\,0)$$
(2.15b)

in terms of the initial (t = 0) wave function. For the approximate N_s -order BHE and the BOA we have the analogues of the exact expressions (Eq. (2.15)):

$$\Phi^{\mathrm{BH}(N_{\mathrm{S}})}(r,\,\theta,\,R,\,t) = \sum_{\nu} b_{\nu}^{N_{\mathrm{S}}} \exp(-iE_{\nu}^{N_{\mathrm{S}}}t/\hbar)\Psi_{\nu}^{\mathrm{BH}(N_{\mathrm{S}})}(r,\,\theta,\,R)$$
(2.16a)

$$b_{\nu}^{N_{\rm s}} = \int_0^\infty dR \int_0^\infty dr \, r^2 \int_{-1}^1 d(\cos\theta) \Psi_{\nu}^{\rm BH(N_{\rm s})}(r,\,\theta,\,R) \Phi(r,\,\theta,\,R,\,0)$$
(2.16b)

and

$$\Phi^{\text{BOA}}(r,\,\theta,\,R,\,t) = \sum_{\nu} c_{\nu}^{\text{BOA}} \exp(-iE_{\nu}^{\text{BOA}}t/\hbar)\Psi_{\nu}^{\text{BOA}}(r,\,\theta,\,R)$$
(2.17a)

$$c_{\nu}^{\text{BOA}} = \int_{0}^{\infty} dR \int_{0}^{\infty} dr \, r^2 \int_{-1}^{1} d(\cos\theta) \Psi_{\nu}^{\text{BOA}}(r,\,\theta,\,R) \Phi(r,\,\theta,\,R,\,0)$$
(2.17b)

We note that the exact expansion (2.15a) solves the Schrödinger equation exactly, whereas the N_s -order BHE (Eq. (2.16a)) and BOA (Eq. (2.17a)) expansions solve it only approximately.

2.3.2. Initial state

We envision the initial state of the H₂⁺ to be prepared by photoionization of the aligned H₂ molecule in the vibrational ground state $\nu = 0 (\chi_{00}^{H_2})$ of the electronic ground state $[\phi_0^{H_2}(\mathbf{r}_1, \mathbf{r}_2; R)]$, as depicted in Fig. 2. We take $\chi_{00}^{H_2}$ from Ref. [23]. We approximate the probability amplitudes of the initial vibrational states of the H₂⁺ in the BOA by the Franck-Condon factors

$$f_{\nu} \equiv \int_{0}^{\infty} dR \chi_{0\nu}^{\text{BOA}}(R) \chi_{00}^{\text{H}_{2}}(R)$$
(2.18)

where $\chi_{0\nu}^{BOA}(R)$ denotes the ν th vibrational excited-state eigenfunction of the electronic ground state of H₂⁺ (see Eq. (C.2) of Appendix C of the SI). The initial wave function of the H₂⁺ is taken to be



Fig. 2. Five lowest potential curves for $H_2^+(^{2}\Sigma_g^+)$ with (BOA) vibrational levels embedded in ground-state potential curve. Solid lines correspond to present method with $N_e = 80$ electronic B-splines and $N_l = 13$ Legendre polynomials (see Eq. (B.6) of Appendix B of the SI); dots correspond to results obtained by exact method of Ref. [25]. Also shown is a schematic depiction of preparation of initial state by photo-ionization of $H_2(^{1}\Sigma_g^+)$ in Franck-Condon approximation.

$$\Phi(r,\,\theta,\,R,\,0) = \phi_0(r,\,\theta;R) \sum_{\nu=0}^{N_0} f_\nu \chi_{0\nu}^{\rm BOA}(R) = \phi_0(r,\,\theta;R) \chi_0^{\rm BOA}(R,\,0)$$
(2.19)

In Eq. (2.19) $N_0 + 1 = 18$ is the number of vibrational states of H_2^+ in the electronic ground state in the BOA; $\chi_0^{BOA}(R, 0)$ denotes the initial nuclear wave packet of H_2^+ . We note that $\sum_{\nu=0}^{N_0} f_{\nu}^2 = 0.98$ We therefore renormalize the nuclear wave packet by the factor $1/\sqrt{\sum_{\nu=0}^{N_0} f_{\nu}^2}$. From a physical point of view, this adjustment is equivalent to neglecting the small probability (=0.02) of dissociation of H_2^+ during photo-ionization of H_2 . From a mathematical point of view, it is necessary because the vibrational bound states $\chi_{0\nu}^{BOA}$ are not complete (i.e., the continuum states are neglected). The amplitudes, given formally by expressions in Eqs. (2.15b), (2.16b) and (2.17b), are worked out in terms of the expansion coefficients in Appendix D of the SI.

2.3.3. Dynamical observables

We characterize the dynamics of the H₂⁺ by the following observables: nuclear probability density (NPD), $\rho_n(R', t) = \langle \Phi(t) | \delta(R' - R) | \Phi(t) \rangle$; nuclear flux density (NFD), $j_n(R', t) = \langle \Phi(t) | \delta(R' - R)\dot{R} | \Phi(t) \rangle$; electronic probability density (EPD), $\rho_e(\mathbf{r}', t) = \langle \Phi(t) | \delta(\mathbf{r}' - \mathbf{r}) | \Phi(t) \rangle$; and electronic flux density (EFD), $\mathbf{j}_e(\mathbf{r}', t) = \langle \Phi(t) | \delta(\mathbf{r}' - \mathbf{r}) | \Phi(t) \rangle$; not electronic flux density (EFD), $\mathbf{j}_e(\mathbf{r}', t) = \langle \Phi(t) | \delta(\mathbf{r}' - \mathbf{r}) | \Phi(t) \rangle$. In these formulas R' and \mathbf{r}' stand for points of observation in the NCM frame. Using the specific expressions for the exact wave function (Eq. (2.15a)), we have [6]

$$\rho_{n}(R', t) = \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \cos(\omega_{\lambda\lambda'} t) \int_{0}^{\infty} dr \, r^{2} \int_{-1}^{1} d(\cos\theta) \Psi_{\lambda}(r, \theta, R')
\Psi_{\lambda'}(r, \theta, R') = \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \cos(\omega_{\lambda\lambda'} t) \rho_{n}^{\lambda\lambda'}(R')$$
(2.20a)

$$j_{n}(R', t) = \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \sin(\omega_{\lambda\lambda'} t) \int_{0}^{\infty} dr \, r^{2} \int_{-1}^{1} d(\cos\theta) \Psi_{\lambda}(r, \theta, R')$$
$$\frac{\hbar}{\mu_{n}} \frac{\partial}{\partial R} \Psi_{\lambda'}(r, \theta, R') = \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \sin(\omega_{\lambda\lambda'} t) j_{n}^{\lambda\lambda'}(R')$$
(2.20b)

$$\rho_{\rm e}(r',\,\theta',\,t) = \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \cos(\omega_{\lambda\lambda'}t) \int_{0}^{\infty} dR \,\Psi_{\lambda}(r',\,\theta',\,R) \Psi_{\lambda'}(r',\,\theta',\,R)$$
$$= \sum_{\lambda,\lambda'} a_{\lambda} a_{\lambda'} \cos(\omega_{\lambda\lambda'}t) \rho_{\rm e}^{\lambda\lambda'}(r',\,\theta')$$
(2.20c)

 $\mathbf{j}_{\mathrm{e}}(r',\,\theta',\,t)$

$$= \sum_{\lambda} \sum_{\lambda'} a_{\lambda} a_{\lambda'} \sin(\omega_{\lambda\lambda'} t) \int_{0}^{\infty} dR \left[\Psi_{\lambda}(r, \theta, R) \frac{\hbar}{\mu_{e}} \nabla_{\mathbf{r}} \Psi_{\lambda'}(r, \theta, R) \right]_{r=r', \theta=\theta'}$$

$$= \sum_{\lambda} \sum_{\lambda'} a_{\lambda} a_{\lambda'} \sin(\omega_{\lambda\lambda'} t) \int_{0}^{\infty} dR$$

$$\left[\Psi_{\lambda}(r, \theta, R) \frac{\hbar}{\mu_{e}} \left[\frac{\partial}{\partial r} \mathbf{e}_{r} + \frac{1}{r} \frac{\partial}{\partial \theta} \mathbf{e}_{\theta} \right] \Psi_{\lambda'}(r, \theta, R) \right]_{r=r', \theta=\theta'}$$

$$= \sum_{\lambda} \sum_{\lambda'} a_{\lambda} a_{\lambda'} \sin(\omega_{\lambda\lambda'} t) \mathbf{j}_{e}^{\lambda\lambda'}(r', \theta') = \sum_{\lambda} \sum_{\lambda'>\lambda} \mathbf{j}_{e,\lambda\lambda'}(r', \theta', t)$$
(2.20d)

where $\omega_{\lambda\lambda'} = (E_{\lambda} - E_{\lambda'})/\hbar$ and, for the purpose of simplifying the notation, the *stationary* quantities $\rho^{\lambda\lambda'}$ and $j^{\lambda\lambda'}$ are implicitly defined (e.g., $\mathbf{j}_{e}^{\lambda\lambda'}(r', \theta') \equiv \int_{0}^{\infty} dR \left[\Psi_{\lambda}(r, \theta, R)\frac{\hbar}{\mu_{e}}\left[\frac{\partial}{\partial r}\mathbf{e}_{r} + \frac{1}{r}\frac{\partial}{\partial \theta}\mathbf{e}_{\theta}\right]\Psi_{\lambda'}(r, \theta, R)\right]_{r=r',\theta=\theta'}$. Likewise, for later convenience we introduce the auxiliary quantity

Likewise, for later convenience we introduce the auxiliary quantity $\mathbf{j}_{e,\lambda l'}(r', \theta', t) \equiv a_{\lambda}a_{\lambda'}\sin(\omega_{\lambda l'}t)[\mathbf{j}_{e}^{\lambda l'}(r', \theta') - \mathbf{j}_{e}^{\lambda l'}(r', \theta')]$. The same expressions hold for the *N*_s-order BHE wave function (see Eq. (2.16a)), except *a* is replaced by $b^{N_{s}}$, λ by ν , and $\omega_{\lambda l'}$ by $\omega_{\nu l'}^{\text{BH}(N_{s})} = (E_{\nu}^{\text{BH}(N_{s})} - E_{\nu'}^{\text{BH}(N_{s})})/\hbar$; likewise for the BOA wave function (see Eq. (2.17a)) with *a* replaced by c^{BOA} , λ by ν , and $\omega_{\lambda l'}$ by $\omega_{\nu l'}^{\text{BOA}} = (E_{\nu}^{\text{BOA}} - E_{\nu'}^{\text{BOA}})/\hbar$. Appendix E of the SI derives detailed expressions for the stationary quantities in terms of the expansion coefficients.

2.3.4. The electronic flux

We also compute the *electronic flux* from a *ball* of radius *r* centred on the NCM, $F_e(r, t)$. From the continuity equation for the electrons we have

$$F_{\rm e}(r,t) = \int_{V} dV \,\nabla \cdot \mathbf{j}_{\rm e}(\mathbf{r},t) = -\frac{\partial}{\partial t} \int_{V} dV \rho_{\rm e}(\mathbf{r},t)$$
(2.21)

where V is the volume of the ball. Using the divergence theorem, we recast Eq. (2.21) as

$$-\frac{\partial}{\partial t}\int_{V}dV\rho_{\rm e}(\mathbf{r},t) = \int_{S}d\mathbf{S}\cdot\mathbf{j}_{\rm e}(\mathbf{r},t)$$
(2.22)

where *S* is the surface of the ball and *d***S** is the directed element of surface area. In terms of spherical coordinates $d\mathbf{S} = r^2 \sin\theta d\theta d\phi \mathbf{e}_r$ and $dV = r^2 dr \sin\theta d\theta d\phi$. We therefore have the explicit relation

$$-\int_{0}^{r} dr' r'^{2} \int_{-1}^{1} d(\cos\theta) \partial \rho_{\rm e}(r',\,\theta,\,t) / \partial t = r^{2} \int_{-1}^{1} d(\cos\theta) j_{\rm er}(r,\,\theta,\,t)$$
(2.23)

where j_{er} is the radial component of the EFD. We may use either member of Eq. (2.23) to compute the desired flux. For future reference, we call the expression on the LHS $F_{e,EPD}(r, t)$ and the one on the RHS $F_{e,EFD}(r, t)$. That is, the formula on the LHS utilizes the EPD, while the one on the RHS uses the EFD. The degree to which the two members of Eq. (2.23) agree numerically depends on the accuracy of the wave function. Being the most accurate, the exact wave function (Eq. (2.15a)) should satisfy the relation $F_{e,EPD}(r, t) = F_{e,EFD}(r, t)$ with the greatest precision. Indeed we find that it does so (see Section 3.4). However, the less accurate wave functions generated by the BHE and BOA techniques are not expected to obey Eq. (2.23) as precisely. We assume the discrepancy between the two members of Eq. (2.23) can be taken as a measure of the accuracy of the wave function.

Explicit expressions $F_{e,EPD}(r, t)$ and $F_{e,EFD}(r, t)$ in terms of amplitudes and expansion coefficients are worked out in Appendix F of the SI.

2.3.5. Complementary observables

Three additional observables that enter the discussion in Section 3 are the autocorrelation of the wave function, the mean total energy of the system, and the mean internuclear separation. According to Eq. (2.15a), the exact autocorrelation function is given by

$$\langle \Phi(0) | \Phi(t) \rangle = \sum_{\lambda} a_{\lambda}^{2} \exp(-iE_{\lambda}t/h)$$
(2.24)

The exact mean total energy is

$$\langle \Phi(t) | H | \Phi(t) \rangle = \sum_{\lambda} a_{\lambda}^{2} E_{\lambda}$$
(2.25a)

From Eqs. (2.16a) and (2.17a) we get the $N_{\rm s}$ -order BHE and BOA expressions

$$\langle H(t) \rangle_{\rm BH(N_{\rm S})} \equiv \langle \Phi^{\rm BH(N_{\rm S})}(t) | H | \Phi^{\rm BH(N_{\rm S})}(t) \rangle = \sum_{\nu} (b_{\nu}^{N_{\rm S}})^2 E_{\nu}^{N_{\rm S}}$$
(2.25b)

$$\langle H(t) \rangle_{\text{BOA}} \equiv \langle \Phi^{\text{BOA}}(t) | H | \Phi^{\text{BOA}}(t) \rangle = \sum_{\nu} (c_{\nu}^{\text{BOA}})^2 E_{\nu}^{\text{BOA}}$$
(2.25c)

where we assume that $\Psi_{\nu}^{\text{BH}(N_s)}$ and Ψ_{ν}^{BOA} are (approximate) eigenvectors of *H*.

The exact expected value of the internuclear separation is given by

$$\langle R(t) \rangle = \langle \Phi(t) | R | \Phi(t) \rangle = \sum_{\lambda} \sum_{\lambda'} a_{\lambda} a_{\lambda'} \cos(\omega_{\lambda\lambda'} t) R_{\lambda\lambda'}$$
(2.26)

where

$$R_{\lambda\lambda'} = \int_0^\infty dR \int_0^\infty dr \, r^2 \int_{-1}^1 d(\cos\theta) \Psi_{\lambda}(r,\,\theta,\,R) R \Psi_{\lambda'}(r,\,\theta,\,R)$$
(2.27)

The explicit expression for $R_{\lambda\lambda'}$ in terms of the expansion coefficients is given in Appendix G of the SI.

Table 1

Lowest 18 eigenenergies of aligned $H_2^+(2\Sigma_g^+)$ calculated by BOA, BHE($N_s = 1, 2, ...5$) and highly accurate (exact) methods. All procedures employ $N_e = 80$ electronic B-splines, $N_l = 13$ Legendre polynomials and $N_n = 100$ nuclear B-splines.

ν	во	Ns = 1	Ns = 2	Ns = 3	Ns = 4	Ns = 5	Accurate
0	-0.59694012	- 0.59688449	-0.59688468	-0.59688471	-0.59688475	-0.59688476	-0.59688495
1	-0.58695337	-0.58689833	-0.58689886	-0.58689889	-0.58689908	-0.58689912	-0.58689971
2	-0.57758198	-0.57752749	-0.57752832	-0.57752855	-0.57752870	-0.57752877	-0.57752971
3	-0.56871710	-0.56866308	-0.56866416	-0.56866452	-0.56866471	-0.56866482	-0.56866604
4	-0.56042953	-0.56037584	-0.56037714	-0.56037764	-0.56037788	-0.56037802	-0.56037949
5	-0.55264538	-0.55259195	-0.55259343	-0.55259409	-0.55259436	-0.55259453	-0.55259619
6	-0.54541767	- 0.54536445	-0.54536610	-0.54536691	-0.54536721	-0.54536741	-0.54536923
7	-0.53866639	-0.53861332	-0.53861510	-0.53861607	-0.53861639	-0.53861662	-0.53861852
8	-0.53245691	-0.53240398	-0.53240585	-0.53240697	-0.53240731	-0.53240755	-0.53240954
9	-0.52672019	-0.52666736	-0.52666944	-0.52667055	-0.52667089	-0.52667113	-0.52667318
10	-0.52151827	-0.52146557	-0.52146774	-0.52146896	-0.52146930	-0.52146956	-0.52147153
11	-0.51679932	-0.51674679	-0.51674909	-0.51675024	-0.51675057	-0.51675082	-0.51675278
12	-0.51262439	-0.51257211	-0.51257440	-0.51257556	-0.51257587	-0.51257612	-0.51257799
13	-0.50895459	-0.50890266	-0.50890493	-0.50890604	-0.50890633	-0.50890656	-0.50890824
14	-0.50584304	-0.50579163	-0.50579380	-0.50579479	-0.50579504	-0.50579525	-0.50579679
15	-0.50328729	-0.50323662	-0.50323853	-0.50323936	-0.50323957	-0.50323975	-0.50324109
16	-0.50128780	-0.50123807	-0.50123964	-0.50124033	-0.50124049	-0.50124064	-0.50124171
17	-0.49977479	-0.49972585	-0.49972724	-0.49972784	-0.49972798	-0.49972811	-0.49972904

3. Results and discussion

We restrict our attention to aligned $H_2^+(^{2}\Sigma_g^+)$ vibrating in the electronic ground state, because it is the only realistic system for which highly accurate numerical (referred to as "exact") results for the relevant dynamic properties (i.e., concerted nuclear and electronically adiabatic fluxes) are available. It serves as a touchstone by which we judge the viability of the approximate methods described in Section 2 (i.e., the BOA and the sequence of BHE(N_s) of increasing order N_s). Our hope is to develop criteria that yield sufficient accuracy at affordable computational cost.

We remind the reader that such common terms as "adiabatic" and "ground electronic state" implicitly assume a separation of nuclear and electronic degrees of freedom characteristic of the BOA. This separation is also valid for the lowest order BHE, namely $N_s = 1$, but not so for the higher orders $N_s > 1$ on account of the coupling of electronic states through the nuclear kinetic energy operator. Of course, the notion of separation of nuclear and electronic motion is totally meaningless in the "exact" case, where all particles are treated on the same footing. Nevertheless, it is convenient for purposes of analysis to retain the BOAbased terminology. We emphasize that we consistently use the term "exact" to refer to the highly numerically accurate treatment summarized in Section 2.2.1, which of course is in fact approximate. The "exact" description approaches the *true* one in the limit of infinite bases. Below we have occasion to distinguish "exact" from "true."

We note a peculiarity due to the alignment of the nuclei of the $H_2^+(^{2}\Sigma_g^+)$. Since the nuclei are constrained to vibrate in one physical dimension, the NFD is equal to the nuclear flux. Both have dimensions of 1/time. In contrast, the EFD, a vector field in three-dimensional space, has dimensions of 1/time × (length)². However, the electronic flux, which results from the integration of the EFD over the surface of a ball (see Eq. (2.22)), has dimensions of 1/time.

We find that the convergence of the approximate results to the exact ones varies from rapid to poor, depending on the particular quantity. Some insight into the variable rate of convergence is afforded by examining the working expressions in Eqs (2.20) and (E.1) of Appendix E of the SI for the NPD, NFD, EPD, and EFD and in eqs (2.21)–(2.23) (plus Eqs. (F.1) and (F.2) of Appendix F of the SI) for the electronic flux. We observe that all of these expressions consist of summations of products of expansion coefficients of the initial wave function (Eqs. (2.15)–(2.17)) times temporal and spatial factors. The (sinusoidal) temporal factors depend on transition frequencies, which in turn depend on differences between eigenenergies. The spatial factors depend on the coefficients of the basis functions in terms of which the corresponding eigenfunctions are expanded (see Eqs. (2.5), (2.11), and (2.14)). The noted factorizations suggest that we begin our presentation with a systematic examination of the convergence of the approximate eigenenergies to the exact values.

3.1. Eigenenergies, mean energies, and potential energy curves

Table 1 compares the approximate eigenenergies with the exact eigenenergies for the lowest 18 bound states. The BOA energies are also shown in Fig. 2 embedded in the potential-energy curve of the electronic ground state. It is interesting that the BOA yields energies that would appear to be "better" than the exact ones because they are lower than the latter. The difference between the BOA and exact energy decreases uniformly from 0.000 055 $E_{\rm h}$ to 0.000 046 $E_{\rm h}$ as the vibrational energy eigenvalue v increases from v = 0 to v = 17. In fact, it can be shown that the BOA eigenvalue, which results from use of an approximate Hamiltonian, is actually a *lower* bound on the *true* energy [24]. The one-term BHE $(N_s = 1)$, which includes electron-nuclear coupling through the non-adiabatic coupling term (NACT) $T_{00}^{(2)}(R)$ (see Eq. (B.10) of Appendix B of the SI), yields eigenenergies that lie above their exact counterparts. As indicated in Table 1 quantitatively, and in Fig. 3 schematically, as the order of the $BHE(N_s)$ increases, the approximate eigenenergies decrease monotonically toward the exact correlates. In fact, the eigenenergies $E_{\nu}^{\text{BH}(N_{\text{S}}=5)}$ agree with the exact ones already to a



Fig. 3. Schematic depicting dependence of the convergence of lowest eigenenergy of $H_2^+(^2\Sigma_g^+)$ to the exact energy on the order N_s of the BHE. Vertical dashed line separates methods that yield zero (left of line) and non-zero electronic flux density.



Fig. 4. Time evolution of mean internuclear distance $\langle R(t) \rangle$ and squared modulus of autocorrelation of the wave function $|\langle \Phi(0)| | \Phi(t) \rangle|^2$. Corresponding vibrational periods are approximately 18.4fs and 17.3fs, respectively.

precision of less than $10^{-6}E_{\rm h}$. Nevertheless, close inspection of Table 1 shows that the convergence of the BHE($N_{\rm s}$) is actually extremely slow. A rough estimate is that to increase the accuracy of the BHE($N_{\rm s}$) energies by one order of magnitude, one must increase the order $N_{\rm s}$ of the BHE by at least 10.

The deviation of the approximate (BOA and BHE(N_s)) eigenenergies from the exact ones engenders a corresponding deviation in the difference between pairs of eigenvalues and therefore in the transition frequencies ω that enter the expressions for the dynamical quantities (see, e.g., Eq. (2.20)). To assess the impact of the deviation, we consider, for example, the transition between states 2 and 3, for which the exact energy gap $\Delta E = E_3 - E_2$ corresponds to a frequency $\omega = \Delta E/\hbar = 0.365 \text{fs}^{-1}$ and, in the harmonic approximation, a corresponding period of 17.2fs. Our choice of this particular pair of states is motivated by our observation that the approximate period of oscillation of the nuclear wave packet, as indicated by the plots of the absolute square of the autocorrelation of the wave function (see Eq. (2.24)) and the expected value of the internuclear separation (see Eq. (2.26)), is about 17.8fs (see Fig. 4).

Examination of Table 1 reveals that the approximate gaps between these eigenenergies are slightly larger than the exact gap. Hence, the vibrational periods (in the harmonic approximation) are slightly shorter than the exact periods, namely by 2.34as, 1.44as, 0.70as and 0.62as for the BOA and BHE(1), BHE(3) and BHE(5), respectively. These small deviations, all less than 3as, may appear to be negligible, but their influence on the dynamical quantities becomes significant at long time. The longer the time the greater the number of vibrational periods and the greater the impact. For example, by t = 5000 fs the vibration has undergone about 5000/17.2 = 291 periods. Hence, in the case of the BOA, the small deviations of 2.34as per period accumulate to a total of 291×2.34 as = 0.68fs, which corresponds to a fraction 0.68/17.2 = .04(or 0.25 rad) of the vibrational period. For the several lowest orders of the BHE(N_s), namely $N_s = 1, 3, 5$ the deviations that accumulate over 5ps are, respectively, 0.42fs, 0.20fs, and 0.18fs, which respectively correspond to 2.4%, 1.2% and 1%. We conclude that though the temporal factors in the expressions for the concerted flux densities and fluxes are accurate for all approximations at short times, the accumulation of deviations leads to phase shifts in the temporal factors that render the associated dynamical quantities increasingly unreliable at sufficiently long times, first for the BOA and then also for the $BHE(N_s)$ with increasing N_s .

The exact mean energy is, according to Eq. (2.25), $\langle H(t) \rangle = -0.5588757 E_{\rm h}$, whereas the approximate mean energies are, respectively, $-0.5589378 E_{\rm h}$, $-0.5588752 E_{\rm h}$, $-0.5588751 E_{\rm h}$, and $-0.5588751 E_{\rm h}$ for the BOA and BHE orders 1, 3 and 5. We note that the

BOA mean energy lies below the exact mean energy by $0.000062 E_h$. The suppression results from two effects. First, all the BOA eigenenergies lie below the corresponding exact ones by $0.000056 E_h$ to $0.000 045 E_h$ for the reason discussed above. Hence, the mean BOA energy is less than the exact mean energy by a similar shift of, say $0.000050 E_h$, which accounts for about 80% of the lowering. Second, even though the exact wave function is represented by a huge basis set, that basis set is nevertheless incomplete. This accounts for the additional 20%.

It is perhaps surprising that the BHE(N_s) mean energies do not converge monotonically to the exact mean energy. In fact, the best agreement is obtained for $N_s = 1$, closely followed by $N_s = 5$, whereas the agreement is worse for $N_s = 3$ than for $N_s = 1$ or 5. The nonmonotonous convergence means that the few low-order mean energies cannot be used to extrapolate reliably to higher-order ones. In light of the above observation of monotonic convergence of the eigenenergies, this result seems contradictory. Some insight into the apparent contradiction is afforded by examination of the expression in Eq. (2.25), which indicates that $\langle H(t) \rangle$ involves not only the eigenenergies, but also the expansion coefficients $b_v^{N_s}$. We then recall that whereas the quality of the eigenenergies is effectively constrained by a variation principle (i.e., they must lie above the true eigenenergies), the corresponding eigenfunctions (or expansion coefficients) do not profit from analogous constraints.

The non-monotonous convergence of the expansion coefficients of the eigenfunctions, and of the properties that depend on them, may be rationalized by an examination of the representation of the $BHE(N_s)$ eigenfunction given by Eq. (2.9). We emphasize that all BHE (N_s) eigenfunctions, and the BOA eigenfunction as well (see Eq. (2.12)), use the same electronic energy eigenfunctions ϕ_n , but different nuclear wave packets $(\chi_{n\nu}^{N_{s}} \text{ or } \chi_{0\nu}^{BOA})$. The ϕ_{n} are solutions of the electronic eigenvalue equation (Eq. (2.8)) (see Appendix B of the SI). The corresponding electronic eigenergies $V_n(R)$, n = 1, 2, ...5 are shown in Fig. 2, where they are compared with the results of the "exact" solutions of Hadinger et al. [25]. The essentially perfect agreement suggests that the present representation of the electronic wavefunctions in terms of $N_{\rm e} = 80$ electronic B-splines and $N_l = 13$ Legendre polynomials is reliable. Thus, the non-monotonous convergence of the $BHE(N_s)$ must be due to a similar non-monotonous character of the representation of the $\chi_{nv}^{N_s}$. We note that with increasing order N_s of the BHE(N_s), not only the number of ϕ_n (which do not depend on N_s) but also the number of $\chi_{nn}^{N_s}$ (which depend on N_s) increases. Since we aim for a fair comparison of all approximate techniques, we use the same basis sets for all, in particular the same set of nuclear B-splines. The price of this "fair comparison" is that as the order $N_{\rm s}$ increases, the *fixed* number ($N_{\rm n}=100$) of nuclear B-splines must be shared by an ever increasing number of $\chi_{n\nu}^{N_{\rm s}}$. This sharing leads to antagonistic effects. On one hand, the quality of the representation of the total wave eigenfunction improves with increasing $N_{\rm s}$. On the other hand, the quality of the numerical representation of the individual components of the $\chi_{nv}^{N_s}$ may decrease. Hence it is quite possible that low-order results may be closer to the exact result than higher-order results.

3.2. Nuclear probability and flux densities

Fig. 5 compares $\rho_n(R, t)$ (NPD) and $j_n(R, t)$ (NFD) for the BOA and BHE(N_s) with their exact correlates at three widely separated times. At t = 10fs all approximations are in essentially perfect agreement with the exact (i.e., the discrepancies are less than the width of the line on the scale of the plots). The second panel of Fig. 5 (t = 1ps) indicates that after more than (1000/18=) 55 periods, deviations of the approximate curves from the exact are still scarcely perceptible. Only at the longest time examined (t = 5ps or ~ 277 periods) do we see significant discrepancies. The quality of the agreement with the exact plot appears to increase in the order BOA, $N_s = 1$, $N_s = 2$, $N_s = 3$. It is remarkable, however, that the BOA does very well over durations (t = 1ps) much longer than those typically required to describe



Fig. 5. Nuclear probability density $(\rho_n(R))$ and nuclear flux density $(j_n(R))$ versus *R* for aligned $H_2^+(^{2}\Sigma_g^+)$ at times t = 10fs, 1ps, and 5ps. BOA (red dashed lines), BHE $(N_s = 1)$ (blue dashed lines), BHE $(N_s = 3)$ (orange dashed lines), BHE $(N_s = 5)$ (green dashed lines) and exact (solid black lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electronic dynamics. Nevertheless, the plots show that eventually the BOA breaks down. Hence, one should take care in the treatment of the NPD and NFD for slower processes (e.g., chemical reactions) by the BOA. Reliable quantum simulations of the NPD and NFD for long times call for the BHE(N_s) approach, albeit at significantly higher computational expense compared with the BOA.

3.3. Electronic probability and flux density

Exploiting the cylindrical symmetry of aligned $H_2^+(^{2}\Sigma_g^+)$, Fig. 6 shows colour-coded contours of the exact EPD in the *x*-*z* plane at 8fs, 10fs, 1ps, and 5ps. These plots are indistinguishable from the BOA or BHE ($N_s = 1,3,5$) plots. A quantitative comparison is provided by Fig. 7, which shows the 1D EPD ($\rho_e(r, t)$) derived by integration of the 3D EPD over the surface of a sphere of radius *r* centred on the NCM. The BOA, BHE($N_s = 1,3,5$) and exact results nearly coincide on the given scale. We conclude that the BOA is good enough for calculations of the EPD, even for times up to 5ps. The robustness of the EPD compared with the NPD, as computed by the BOA, is due to the smoother shape of the EPD compared with the NPD, which is quite wavy (Fig. 5). This is traceable to the huge disparity in mass between electron and proton.

Both the BOA and BHE($N_s = 1$) wave functions consist of the simple product of the real ground-state electronic eigenfunction ϕ_0 and a complex nuclear wave packet ($\chi_0^{N_s=1}$ or χ_0^{BOA}) (see Eqs. (2.12) and (2.9)). Both wave functions describe processes in which the electron remains in a stationary state. It has been known since the advent of quantum mechanics that the flux density associated with a stationary state vanishes [8]. Hence, both the BOA (see Eq. (1.6)) and first-order BHE($N_s = 1$) yield zero EFD. In the present work we circumvent the

problem by going to higher-order BHE. For example, Fig. 6 compares the BHE ($N_s = 5$) EFD with the exact EFD, displaying "arrow" plots in the *x*-*z* plane at t = 8fs and for the same three times (t = 10fs, 1ps, and 5ps) at which the NFD is examined in Section 3.2. On first glance, $\mathbf{j}_e^{N_s=1}(r, \theta, t = 8$ ps) appears to agree reasonably well with the exact $\mathbf{j}_e(r, \theta, t = 8$ ps), but we are saddened to draw the reader's attention to the fact that the BHE($N_s = 5$) plot is multiplied by a factor of 5 in order to render it visible on the scale of the exact plot. Aside from this obvious strong discrepancy revealed in the scaling, scrutiny of the plots at later times indicates that BHE($N_s = 5$) and exact EFDs differ in both direction and magnitude. Moreover, the discrepancy is not uniform over any quadrant (by symmetry $j_{ex}(-x, z, t) = -j_{ex}(x, z, t)$; $j_{ex}(x, -z, t) = j_{ex}(x, z, t)$; $j_{ex}(-x, z, t) = j_{ex}(x, z, t)$; $j_{ex}(x, -z, t) = -j_{ex}(x, z, t)$; $j_{ex}(x, z, t)$; $j_{ex}(x, z, t)$.

Some understanding of the catastrophic failure of the BHE($N_s = 5$) may be acquired by analysing in depth the expression for the EFD given by Eq. (2.20d). For the sake of convenience we focus on the EFD on the internuclear (positive *z*) axis, where $\theta = 0$ and the polar component vanishes by symmetry. We focus further on the lowest radial cross-term of Eq. (2.20d) that contributes to the EFD:

$$\begin{aligned} &= a_0 a_1 \sin(\omega_{01} t) \int_0^\infty dR \frac{\hbar}{\mu_e} \\ &= u_0 a_1 \sin(\omega_{01} t) \int_0^\infty dR \frac{\hbar}{\mu_e} \\ &\quad [\Psi_0(r,\,\theta,\,R) \frac{\partial}{\partial r} \Psi_1(r,\,\theta,\,R) - \Psi_1(r,\,\theta,\,R) \frac{\partial}{\partial r} \Psi_0(r,\,\theta,\,R)]_{\theta=0} \\ &= a_0 a_1 \sin(\omega_{01} t) [j_{er}^{01}(r,\,0) - j_{er}^{10}(r,\,0)] \end{aligned}$$
(3.1)

Plots of $a_0 a_1 j_{er}^{01}(r, 0)$ and $-a_0 a_1 j_{er}^{10}(r, 0)$ versus *r* in Fig. 8 show that $j_{er}^{10}(r, 0)$ and $j_{er}^{10}(r, 0)$ are nearly identical. The difference



Fig. 6. Electronic probability density (EPD) (grey contours) (a_0^{-3}) and electronic flux density (EFD) $(a_0^{-2}fs^{-1})$ in *x*-*z* plane for aligned $H_2^+(2\Sigma_g^+)$ at times t = 8fs, 10fs, 1ps and 5ps. BHE($N_s = 5$), blue arrows; exact, red arrows. Magnitude of EFD indicated at upper left of each panel. Length of blue arrows multiplied by 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 $j_{er}^{01}(r, 0) - j_{er}^{10}(r, 0)$ is therefore very small, as indicated in the lower panel of Fig. 8 (Note that the scales in the two panels differ by a factor of 4). Analogous results hold for the other cross-terms in Eq. (2.20d). We conclude that the EFD is the result of a summation of pairs of terms which are of opposite sign but of approximately the same magnitude. As a consequence, the expression (Eq. (2.20d)) is numerically ill-conditioned. This same sort of ill-conditioned behavior is exhibited by BHE ($N_s = 5$), indicated by Fig. 8. The agreement of the BHE($N_s = 5$)

auxiliary functions $j_{er,01}^{N_8=5}(r, 0)$ and $j_{er,10}^{N_8=5}(r, 0)$ with their exact counterparts appears to be perfect. But the plot of the BHE($N_s = 5$) difference disagrees markedly with that of the exact difference (Fig. 8). Though the shape of the BHE($N_s = 5$) difference plot is similar to that of exact difference plot, the absolute values of the former are about an order of magnitude smaller than those of the latter. Hence, in order to compare the BHE($N_s = 5$) arrow plot with the exact plot in Fig. 6, we scale the former by a factor of 5.



Fig. 7. Radial electronic probability density (left panels) and radial electronic flux (right panels) for aligned $H_2^+(^{2}\Sigma_{g}^+)$ at t = 10fs, 1ps, and 5ps. Exact results (solid black lines) are compared with BOA (red dashed lines) and BHE($N_s = 1$) (blue dashed lines), BHE($N_s = 3$) (orange dashed lines), BHE($N_s = 5$) (green dashed lines). Horizontal dotted lines in right panels indicate zero-valued $F_{e,EFD}$ for BOA and BHE($N_s = 1$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Auxiliary functions $a_0a_j_{er}^{01}(r, 0)$ (component a) and $-a_0a_j_{er}^{10}(r, 0)$ (component b) (upper panel) and their difference (contribution to flux density) (lower panel) as a function of *r* for exact (solid black lines) and BHE($N_s = 5$) (dots) (see Eq. (2.20d)). Note: $\theta = 0$; *r* correspond to positive *z* (i.e., distance along the internuclear axis from the NCM).

We anticipate analogous failures of the BHE(N_s) at higher order and reluctantly conclude that the BHE(N_s) approach to the EFD is ill-conditioned and that we must therefore seek alternative methods for computing the electronic flux *density*.

3.4. Electronic flux

Plots of the radial electronic flux in aligned $H_2^+(2\Sigma_{\alpha}^+)$ based on the alternative formulas given by Eq. (2.23) are displayed in Fig. 7 for the BOA and BHE($N_s = 1,3,5$) approximations, as well as for the exact, at the three widely separated times. In principle, the numerically computed value of $F_{e,EPD}(r, t)$ should agree with that of $F_{e,EFD}(r, t)$. As anticipated by the discussion in Section 2.3.4, this agreement in evident in the exact plots. Close examination reveals that the $F_{e,EPD}$ based on the approximate methods agrees reasonably well with the exact $F_{e,EPD}$, at least for times up to 1ps. Only at 5ps do we see significant deviations that indicate non-monotonic convergence. $F_{e,EPD}$ for BHE($N_s = 5$) is in best agreement with the exact, followed closely by $BHE(N_s = 1)$. In slightly worse agreement than $BHE(N_s = 1)$ is the BOA. The worst approximation is the $BHE(N_s = 3)$. The order of the agreement of the various approximations is remarkably similar to that found for the mean energy (see Section 3.1), which suggests that the non-monotonous convergence of the approximate $F_{e,EPD}$ is due to the same effects discussed in Section 3.1.

In sharp contrast to the behavior of the approximate $F_{e,EPD}$, the approximate $F_{e,EPD}$ disagrees grossly with the exact $F_{e,EPD}$ at all times. Since the EFD vanishes identically for both the BOA and the first-order BHE, it is not surprising that the corresponding electronic fluxes vanish, as indicated by the horizontal dotted lines in Fig. 7. The poor results for the BHE($N_s = 3,5$) reflect the ill-conditioned character of the EFD itself, as detailed in Section 3.3.

We conclude that the $F_{e,EPD}$ yields very good approximations to the exact electronic flux, whereas the $F_{e,EFD}$ is totally useless. Further, the BOA approximation is already adequate for times ($t \leq 1ps$) over which most electronic processes take place. The minor improvement brought

by the BHE does not justify that additional computational cost.

4. Conclusion

Our main purpose in this work is to develop and test approximate methods for computing concerted electronic and nuclear fluxes associated with the aligned H₂⁺ ion vibrating in the electronic ground state ${}^{2}\Sigma_{g}^{+}$. This system is the only one for which highly accurate numerical (exact) results for the relevant dynamic properties are available. The present exact results function as benchmarks by which the viability of the approximation, namely the BOA or N_s-order BHE, is evaluated. We find that the convergence of an approximate property to its exact correlate depends strongly on the particular property.

The BHE eigenenergies decrease monotonously to their exact counterparts as the order increases. Indeed, by fifth order $E_{\nu}^{\rm BH(N_S=5)}$ already agrees with the exact eigenenergies to a precision of $10^{-6}E_h$. We note, however, that the rate of convergence is extremely slow. A crude estimate is that an increase of the order by 10 leads to an increase in the accuracy of $E_{\nu}^{\text{BH}(N_{\text{S}}=5)}$ by only an order of magnitude. Differences between pairs of energies, or corresponding transition frequencies, have a critical impact on dynamical properties, which are expressed as summations of products of sinusoidal temporal factors involving the transition frequencies multiplied by spatial factors. Hence, deviations of approximate energies from the exact ones gives rise to corresponding deviations in the transition frequencies, which in turn lead to deviations in the phase shifts of the sinusoidal temporal factors and consequently to errors in the dynamical properties. We find that the BOA and firstorder BHE yield excellent results for both NPD and NFD, as well as for EPD and $F_{e,EPD}$ up to about 1ps. At longer times the higher-order BHE is substantially more reliable, but their computation is more expensive. Even for tiny differences between approximate and exact energies, the errors in the phase accumulate over many periods of the vibration so that as time increases all approximations eventually break down.

The BOA and also the first-order BHE yield zero EFD and therefore also zero $F_{e,EFD}$. We find that although the BHE($N_s = 3,5$) yield non-zero values for these properties, they are unfortunately in gross disagreement with their exact correlates. We assume that in principle the BHE must converge to the exact in the limit of infinite order, but our analysis shows that the BHE expression for the EFD is numerically ill-conditioned. The convergence is consequently non-monotonic, so that one cannot extrapolate low-order BHE results. We recommend use of the alternative formula $F_{e,EFD}$ for the calculation of the electronic flux.

We emphasize that the development of reliable approximate numerical techniques for calculating the EFD remains a major challenge. Various approaches have been proposed [7,9–16], but to the best of our knowledge, only two of them [7,11] have been tested against benchmarks for realistic model systems.

We close by drawing attention to a mathematical (philosophical?) conundrum. We repeatedly point out above that $F_{e,EFD}$ vanishes in the BOA, and that the $F_{e,EFD}^{BH(N_S)}$ should approach the true value of the electronic flux in infinite order. Then how is it possible that the BOA $F_{e,EPD}$ agrees so well with the exact flux, at least for short times? It would appear that the BOA $F_{e,EPD}$ somehow "magically" brings in the character of the very high-order BHE that we assume would yield a high-order $F_{e,EFD}^{BH(N_S)}$ in good agreement with the exact flux. Are we then justified in making the apparently self-contradictory claim that the BOA in $F_{e,EPD}$?

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2018.05.026.

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