

# Exactly solvable model mimicking the H<sub>2</sub> molecule in the limit of large nuclear masses

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Avoiding the limitations of the Born–Oppenheimer approximation remains an issue of continuing importance in molecular physics. If we take the H<sub>2</sub> molecule as a prototype, then one uses, in some sense, the ratio of electron mass  $m$  to nuclear mass  $M$  as an expansion parameter, sometimes cited to be explicitly  $(m/M)^{1/4}$ . Here, we employ a model of such a two-electron diatomic molecule set up by Makarewicz [Am. J. Phys. 54 (1986) 178] to study the exact ground-state wave function obtained by treating electrons and nuclei on the same footing. Of course, to obtain such a wave function analytically means adopting model force laws, both for confinement and for the interelectronic interaction. From the exact wave function and ground-state energy, contact is finally established with the large nuclear mass limit.

**KEY WORDS:** nuclear motion, Makarewicz’s model, Born–Oppenheimer approximation, adiabatic approximation, harmonic approximation

## 1. Background

Although it will be necessary to adopt model interactions to make analytical progress in treating molecular systems without invoking the Born–Oppenheimer (BO) approximation, it will be useful background to the model

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of a two-electron diatomic molecule such as  $H_2$  to review molecular systems as often treated in current quantum-mechanical literature.

Consider a molecular system described by the Hamiltonian

$$H = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{\nabla_{R_\alpha}^2}{2M_\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{R_{\alpha\beta}}. \quad (1)$$

Take an eigenfunction  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n; \mathbf{R}_1, \dots, \mathbf{R}_N)$  of (1). In the traditional BO or adiabatic approximation the molecular wavefunction is decomposed as

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n; \mathbf{R}_1, \dots, \mathbf{R}_N) = \Phi_{\mathbf{R}_1, \dots, \mathbf{R}_N}(\mathbf{r}_1, \dots, \mathbf{r}_n) X(\mathbf{R}_1, \dots, \mathbf{R}_N) \text{ or} \\ \Psi(\mathbf{r}; \mathbf{R}) = \Phi_{\mathbf{R}}(\mathbf{r}) X(\mathbf{R}) \quad (2)$$

with  $\mathbf{R} \equiv \mathbf{R}_1, \dots, \mathbf{R}_N$  and  $\mathbf{r} = \mathbf{r}_1, \dots, \mathbf{r}_n$ .  $\Phi_{\mathbf{R}_1, \dots, \mathbf{R}_N}(\mathbf{r}_1, \dots, \mathbf{r}_n)$  is an electronic wavefunction, depending parametrically on the nuclear positions, and  $X(\mathbf{R}_1, \dots, \mathbf{R}_N)$  is a nuclear wavefunction. A variational way to formulate the adiabatic approximation and derive the equations that  $\Phi_{\mathbf{R}}(\mathbf{r})$  and  $X(\mathbf{R})$  satisfy is the following (see, e.g., Messiah [1] and Rainer [2]).

Let us require *a priori* that  $\Phi_{\mathbf{R}}(\mathbf{r})$  satisfy the electronic equation

$$\left( -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) \Phi_{\mathbf{R}}(\mathbf{r}) = \mathcal{E}(\mathbf{R}) \Phi_{\mathbf{R}}(\mathbf{r}). \quad (3)$$

We say that  $\Phi_{\mathbf{R}}(\mathbf{r})$  depends parametrically on  $\mathbf{R}$  because the external potential in (3) depends on  $\mathbf{R}$ . As a consequence, we have

$$\int \int d\mathbf{r}^{(n)} |\Phi_{\mathbf{R}}(\mathbf{r}_1, \dots, \mathbf{r}_n)|^2 = 1 \quad (4)$$

for every  $\mathbf{R}$ .

Next, let us form the expectation value of the full Hamiltonian (1)

$$E = \int \int d\mathbf{R}^{(N)} X^*(\mathbf{R}) \left\{ \int \int d\mathbf{r}^{(n)} \Phi_{\mathbf{R}}^*(\mathbf{r}_1, \dots, \mathbf{r}_n) H \Phi_{\mathbf{R}}(\mathbf{r}_1, \dots, \mathbf{r}_n) \right\} X(\mathbf{R}) \quad (5)$$

and minimize  $E$  by varying  $X$ . We cannot vary  $\Phi_{\mathbf{R}}(\mathbf{r})$  as well, since  $\Phi_{\mathbf{R}}(\mathbf{r})$  was determined in the previous step. As a result of the minimization, we obtain the Schrödinger equation for  $X$ :

$$\left\{ -\sum_\alpha \frac{\nabla_{R_\alpha}^2}{2M_\alpha} + \frac{1}{2} \sum_{\alpha,\beta} \frac{1}{R_{\alpha\beta}} + \mathcal{E}(\mathbf{R}) + \sum_\alpha \frac{1}{2M_\alpha} \int \int d\mathbf{r}^{(n)} |\nabla_{R_\alpha} \Phi_{\mathbf{R}}(\mathbf{r})|^2 \right\} X(\mathbf{R}) = EX(\mathbf{R}). \quad (6)$$

In the BO approximation the last small positive potential term on the left-hand side of equation (6) is neglected.

Having given this background to current treatments in molecular physics [3], we shall proceed by moving from the complete non-relativistic Hamiltonian (1) to a simplified model in which, for the analog of the  $H_2$  molecule, one modifies the three Coulombic terms entering equation (1), but retains the treatment of the kinetic energy operators of electrons and nuclei on the same footing. We follow Makarewicz [4] by simplifying both ‘confinement’ and interparticle interactions to allow a solution. It is important to stress that, we limit the discussion below to the lowest energy state, which involves the  $L = 0$  rotational state. Furthermore, as the title indicates, we are mimicking the  $H_2$  molecule, with  $1/2$  spin nuclei coupled to a singlet.

## 2. Hamiltonian of Makarewicz’s model

In early work on a model two-electron atom, Kestner and Sinanoglu [5] replaced attractive Coulomb confinement of ‘electrons’ by ‘nuclei’ using harmonic forces. This is the first change therefore, we make in the realistic non-relativistic Hamiltonian (1) of conventional quantum chemistry. Second, following Makarewicz [4], the repulsive Coulomb potentials  $1/r_{ij}$  are replaced by inverse square terms  $1/r_{ij}^2$ . Then Makarewicz solves by an exact analytical approach a number of problems, from which we single out his example of a four-body system: namely a two-electron diatomic molecule. We use his notation for this system, which is explained in figure 1.

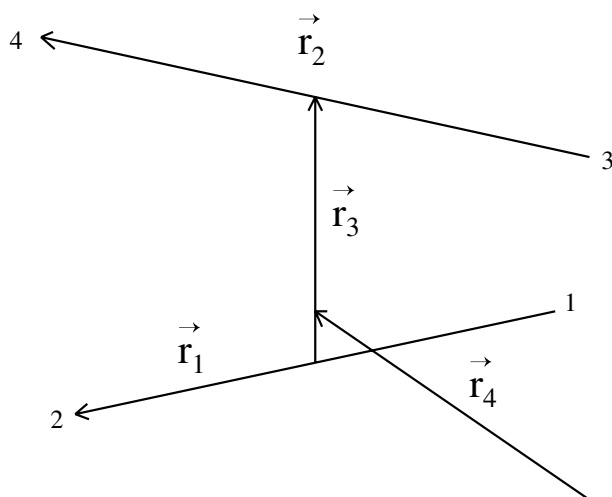


Figure 1. Jacobi coordinates  $\mathbf{r}$  in the model homonuclear diatomic molecule.

We take particles 1 and 2 to be the nuclei, with equal masses  $M$ , and 3 and 4 to be electrons, each of mass  $m$ . The attractive (harmonic) interactions are then characterized in Makarewicz's model by constants  $\kappa_{13} = \kappa_{14} = \kappa_{23} = \kappa_{24} = \kappa_A$ , and the repulsive  $1/r_{ij}^2$  interactions by constants  $\kappa_{12} = \kappa_{34} = \kappa_R$ . The ground-state solution of the Schrödinger equation has the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \Psi_1(\mathbf{r}_1)\Psi_2(\mathbf{r}_2)\Psi_3(\mathbf{r}_3)\exp(i\mathbf{K}\cdot\mathbf{r}_4) \quad (7)$$

the last term merely representing the center-of-mass motion, We emphasize, as in figure 1, that

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \\ \mathbf{r}_4 \end{bmatrix}, \quad (8)$$

whereas the actual positional coordinates  $\mathbf{x}$  given by

$$\mathbf{x} = \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \mathbf{x}_3 \\ \mathbf{x}_4 \end{bmatrix} \quad (9)$$

are related by a matrix  $A$  as set out below.

### 2.1. Form of transformation matrix from original coordinates $x$ to Jacobi coordinates $r$

As set out formally by Makarewicz [4], the transformation  $\mathbf{r} = A\mathbf{x}$  relates original positional coordinates  $\mathbf{x}$  to the Jacobi coordinates  $\mathbf{r}$  entering equation (7), where the matrix  $A$  is found to have the form

$$A = \begin{bmatrix} 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ -1/2 & -1/2 & 1/2 & 1/2 \\ M/[2(M+1)] & M/[2(M+1)] & 1/[2(M+1)] & 1/[2(M+1)] \end{bmatrix} \quad (10)$$

with units, in which the electron mass  $m = 1$ . Having established the coordinate transformation for this model homonuclear diatomic molecule, let us immediately proceed as an example to the so-called BO limit, in which the (equal) nuclear masses  $M$  are allowed to become large. This limit is given by

$$\lim_{M \rightarrow \infty} A = \begin{bmatrix} 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ -1/2 & -1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & 0 & 0 \end{bmatrix}. \quad (11)$$

Using the general matrix  $A$  in equation (10), our first objective is to derive the Hamiltonian  $\widehat{H}$  in the form, corresponding to the separable wave function (7),

$$\widehat{H} = h_1(\mathbf{r}_1) + h_2(\mathbf{r}_2) + h_3(\mathbf{r}_3) + h_4(\mathbf{r}_4). \quad (12)$$

The simplest term is  $h_4(\mathbf{r}_4)$ , which corresponds to a free-particle Hamiltonian (see equation (40) below). The next simplest term is  $h_3(\mathbf{r}_3)$ , which corresponds to a harmonic oscillator Hamiltonian (see equation (39)) as can be confirmed using the matrix (10). This yields, almost immediately, the explicit form of the unnormalized  $\Psi_3(\mathbf{r}_3)$  in equation (7),

$$\Psi_3(\mathbf{r}_3) = \exp\left(-2\sqrt{M\kappa_A/(1+M)}r_3^2\right) \quad (13)$$

with again  $m = 1$ .

As to  $h_1$  and  $h_2$ , it can be shown from equation (10) that they contain 'kinetic' parts of the form  $-\lambda_i \nabla_i^2/2$ , and explicitly the Schrödinger equations for  $\Psi_1(\mathbf{r}_1)$  and  $\Psi_2(\mathbf{r}_2)$  entering equation (7) are then

$$\left(-\frac{\hbar^2}{M}\nabla_1^2 + \kappa_A r_1^2 + \frac{\kappa_R}{r_1^2}\right)\Psi_1 = \epsilon_1 \Psi_1 \quad (14)$$

and

$$\left(-\frac{\hbar^2}{M}\nabla_2^2 + \kappa_A r_2^2 + \frac{\kappa_R}{r_2^2}\right)\Psi_2 = \epsilon_2 \Psi_2. \quad (15)$$

The physical solutions are readily verified to be

$$\Psi_1(\mathbf{r}_1) = \left[\left(M\kappa_A/\hbar^2\right)^{1/4} r_1\right]^{\left(\sqrt{1+4M\kappa_R/\hbar^2}/2-1/2\right)} \exp\left(-\sqrt{M\kappa_A/\hbar^2}r_1^2/2\right) \quad (16)$$

and

$$\Psi_2(\mathbf{r}_2) = \left[\left(m\kappa_A/\hbar^2\right)^{1/4} r_1\right]^{\left(\sqrt{1+4M\kappa_R/\hbar^2}/2-1/2\right)} \exp\left(-\sqrt{m\kappa_A/\hbar^2}r_2^2/2\right). \quad (17)$$

Corresponding to the exact ground-state wave function described above, the ground-state energy for  $\kappa = 0$  in equation (7) is readily written as

$$E_{\text{ground-state}} = \sqrt{\kappa_A} \left(2 + \sqrt{1 + 4\kappa_R}\right) + 3\sqrt{\frac{(1+M)\kappa_A}{M}} + \sqrt{\frac{\kappa_A}{M}} \left(2 + \sqrt{1 + 4\kappa_R M}\right). \quad (18)$$

This is the point to consider physical consequences of the above exact ground-state wave function in which the kinetic energy operators of nuclei and electrons have been treated on the same footing.

### 3. Probability density of nuclear separation in the two-electron ‘artificial’ molecule

In order to make some contact with the large nuclear mass limit, which is a major focus of the present study, it will be useful next to calculate the probability density of nuclear separation from the exact wave function (7). Starting from the general probability density  $\Psi\Psi^*$ , this is immediately known as an explicit function of  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$ . But, we wish to integrate out the electronic positional coordinates  $\mathbf{x}_3$  and  $\mathbf{x}_4$  to obtain the following conditional probability density

$$P_n(\mathbf{x}_1, \mathbf{x}_2) = \Psi_1^2(\mathbf{r}_1) \int \Psi_2^2(\mathbf{r}_2) \Psi_3^2(\mathbf{r}_3) d\mathbf{x}_3 d\mathbf{x}_4. \quad (19)$$

But by changing the integration variables to  $(\mathbf{x}_3 + \mathbf{x}_4)/2$  and  $(\mathbf{x}_3 - \mathbf{x}_4)$ , the integral in equation (19) is unity for normalized  $\Psi_2$  and  $\Psi_3$  and  $P_n$  is evidently equivalent, in this artificial two-electron molecule, to  $\Psi_1^2(\mathbf{r}_1)$ , which is known explicitly from equation (16). The radial density  $4\pi r^2 P_n(r)$  is plotted in figure 2, for different masses  $M$  and for  $\kappa_A = 1$  and  $\kappa_R = 1$ . The resulting internuclear potential energy is shown in figure 3. The choice of  $\kappa_A$  and  $\kappa_R$  determines the position of the maximum of the radial density above for a given mass  $M$ . For fixed  $\kappa_A$  and  $\kappa_R$  and for sufficiently large  $M$  the position of this maximum becomes independent of nuclear mass. Figure 4 shows a plot of the average internuclear separation as a function of  $(1/M)^{1/4}$ . At the limit of infinite mass, the nuclei have the same behavior as in the harmonic approximation, displaying very small oscillations around a well-defined equilibrium position. But the lower their mass, the higher the amplitude of these oscillations, and in this new regime the effects of anharmonicity become more evident. Anharmonicity results in an average internuclear separation which increases with  $1/M^{1/4}$ , as shown in figure 4. The standard deviation of the internuclear separation, which is related to the half-width of the radial distribution  $4\pi r^2 P_n(r)$ , is displayed in figure 5 against the same variable  $1/M^{1/4}$ . This would become exactly linear at sufficiently large nuclear mass. In this context, a further interesting property to analyze is the relative motion nuclear kinetic energy. This quantity is plotted in figure 6. In this case, in the large mass limit, the above contribution to the kinetic energy becomes equal to half the zero point energy of the harmonic approximation as expected.

Turning from this conditional nuclear probability to  $\Psi\Psi^*$  itself again, we can rewrite this, for sufficiently large nuclear mass, as

$$\Psi\Psi^* = f_{M \text{ large}}(\mathbf{r}_1) \Psi_2^2(\mathbf{r}_2) \lim_{M \rightarrow \infty} \Psi_3^2(\mathbf{r}_3). \quad (20)$$

Let us then focus on non-analytic behavior, for sufficiently large  $M$ , in the function  $f_{M \text{ large}}(\mathbf{r}_1)$ . We can write this function as

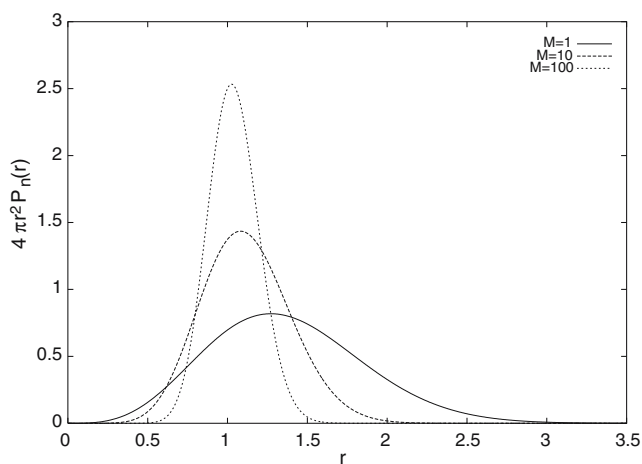


Figure 2. Radial density  $4\pi r^2 P_n(r)$  as defined below equation (19) for three different nuclear masses  $M = 1, 10,$  and  $100,$  and for potential energy parameters  $\kappa_A = 1$  and  $\kappa_R = 1,$  for units in which electron mass is itself unity. Note the modest dependence of peak position on nuclear mass  $M.$

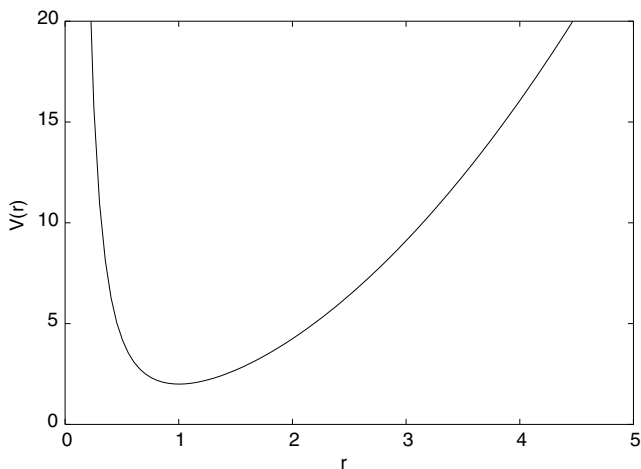


Figure 3. Internuclear potential energy as a function of the internuclear separation for  $\kappa_A = 1$  and  $\kappa_R = 1.$

$$\begin{aligned}
 f_{M \text{ large}}(\mathbf{r}) = & \left[ \sqrt{\frac{\kappa_A}{M}} r^2 \right]^{\sqrt{M\kappa_R}} \exp \left[ -\sqrt{M\kappa_A} r^2 \right] \\
 & \times \left\{ \frac{(\sqrt{M\kappa_R} + \ln(\sqrt{M\kappa_A} r^2))}{2^5 \pi r \sqrt{\kappa_R} (M^3 \kappa_A)^{1/4}} + \mathcal{O}(M^{-5/4}) \right\}. \quad (21)
 \end{aligned}$$

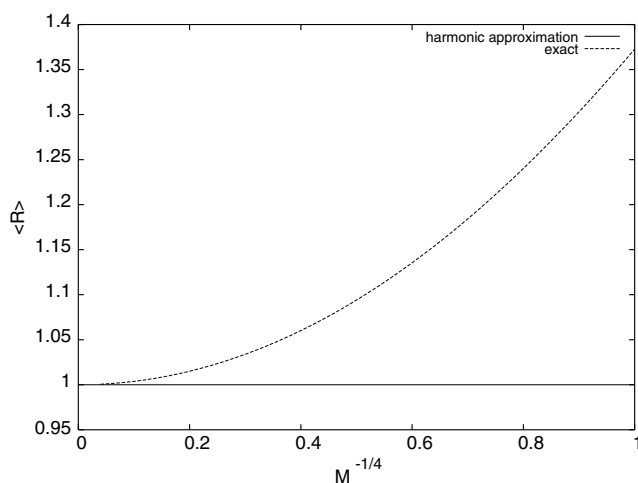


Figure 4. Average internuclear distance (in atomic units) as a function of the BO expansion parameter  $1/M^{1/4}$  for the exact model solution, and comparison with the equilibrium distance in the harmonic approximation.

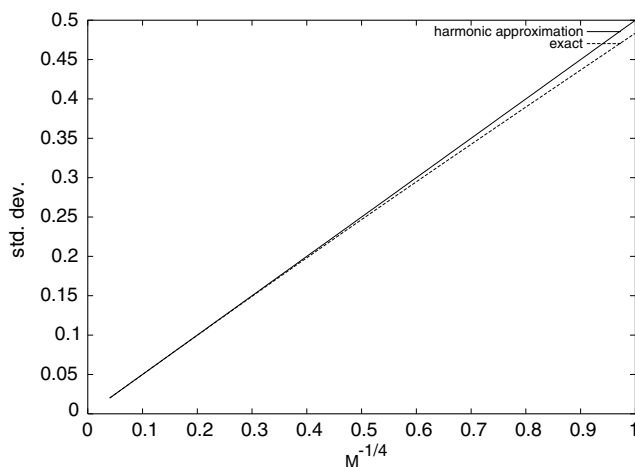


Figure 5. Standard deviation of the internuclear separation radial distribution  $4\pi r^2 P_n(r)$  as a function of  $1/M^{1/4}$  for the exactly solvable model and for the harmonic approximation, in units in which electron mass is taken as unity.

Already, the  $(m/M)^{1/4}$ , identified in figures 2 and 3, is evident as one expansion parameter. But, what seems remarkable about equation (21) is that other non-analytic parameters involving the ratio of electron to nuclear mass also enter, and this must come from the motion of a single particle in a potential well (see figure 4), this being defined by the Schrodinger equation (14). However, the new non-analytic  $M$ -dependent terms entering equation (21), beyond



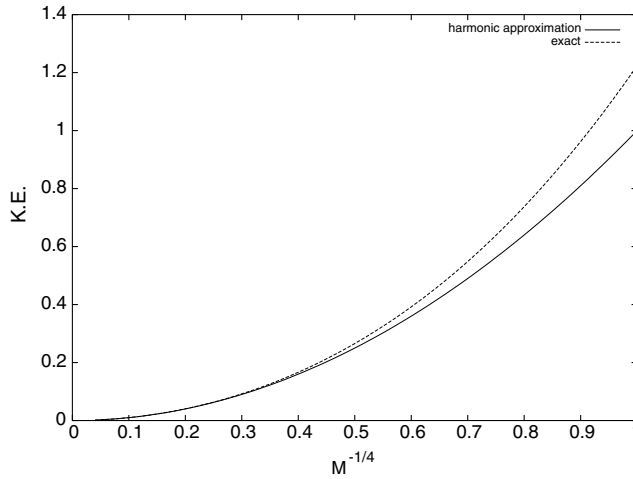


Figure 6. Relative motion nuclear kinetic energy as a function of  $1/M^{1/4}$  for the exactly solvable model, and comparison with half the zero point energy of the harmonic approximation.

the customary expansion parameter  $(m/M)^{1/4}$  already exhibited, come from the normalization of  $\Psi_1^2 \mathbf{r}$ . These terms are worthy of emphasis, and have the forms (a)  $\ln(\sqrt{M})$  (b)  $(1/\sqrt{M})\sqrt{M}$ . Although these precise forms may well be model-dependent, they caution that, say beyond order  $(m/M)^{1/4}$ , there may well be other non-analytic behavior in the large mass limit. We emphasize that this behavior is distinct from the expected delta-function singularity around the nuclear wavefunction in the limit  $m/M \rightarrow 0$ .

#### 4. Connection of exact ground-state energy (18) with Born–Oppenheimer and adiabatic approximations

In this section, we revert to the notation used in setting out the Background section. Let us employ  $\mathbf{r}_1$  and  $\mathbf{r}_2$  for electrons (mass  $m$ ) and  $\mathbf{R}_1$  and  $\mathbf{R}_2$  for nuclei (mass  $M$ ). In the BO approximation, we must solve in the order

$$\hat{H}_e \Phi_e = E_e \Phi_e \tag{22}$$

$$\hat{H}_{\text{BO}} \Phi_n = E_{\text{tot}}^{\text{BO}} \Phi_n, \tag{23}$$

where

$$\hat{H}_e = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \kappa_A(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_1, \mathbf{R}_2) \begin{pmatrix} 2 & 0 & -1 & -1 \\ 0 & 2 & -1 & -1 \\ -1 & -1 & 2 & 0 \\ -1 & -1 & 0 & 2 \end{pmatrix} \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{R}_1 \\ \mathbf{R}_2 \end{pmatrix}$$

$$+\frac{\kappa_R}{r_{12}^2} + \frac{\kappa_R}{R_{12}^2} \quad (24)$$

and

$$\hat{H}_{\text{BO}} = -\frac{\hbar^2}{2M}(\nabla_{\mathbf{R}_1}^2 + \nabla_{\mathbf{R}_2}^2) + E_e(\mathbf{R}_1, \mathbf{R}_2) \quad (25)$$

with  $\kappa_A$  and  $\kappa_R$  the typical constants of the solvable model treated in the body of the text. The electronic Hamiltonian can be rearranged in the following way

$$\hat{H}_e = \hat{h}_1 + \hat{h}_2 + U(\mathbf{R}_1, \mathbf{R}_2), \quad (26)$$

$$\hat{h}_1 = -\frac{\hbar^2}{M}\nabla_{12}^2 + \kappa_A r_{12}^2 + \frac{\kappa_R}{r_{12}^2}, \quad (27)$$

$$\hat{h}_2 = -\frac{\hbar^2}{4m}\nabla_{\mathbf{p}}^2 + 4\kappa_A \left(\mathbf{p} - \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2)\right)^2 \quad (28)$$

$$U(\mathbf{R}_1, \mathbf{R}_2) = \kappa_A R_{12}^2 + \frac{\kappa_R}{R_{12}^2} \quad (29)$$

by putting as usual  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$  and  $\mathbf{p} = (1/2)(\mathbf{r}_1 + \mathbf{r}_2)$ . The electronic energy is then

$$E_e = E_1 + E_2 + U(\mathbf{R}_1, \mathbf{R}_2), \quad (30)$$

$$E_1 = \sqrt{\kappa_A}(2 + \sqrt{1 + 4\kappa_R}), \quad E_2 = 3\sqrt{\kappa_A}. \quad (31)$$

To complete we must solve the BO equation (23). Again by using  $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$  and  $\mathbf{P} = (1/2)(\mathbf{R}_1 + \mathbf{R}_2)$  we have

$$\hat{H}_{\text{BO}} = -\frac{1}{M}\nabla_{\mathbf{R}_{12}}^2 + \kappa_A R_{12}^2 + \frac{\kappa_R}{R_{12}^2} - \frac{1}{4M}\nabla_{\mathbf{P}}^2 + E_1 + E_2, \quad (32)$$

which leads to the following total internal energy (center of mass motion omitted)

$$E_{\text{tot}}^{\text{BO}} = E_1 + E_2 + \sqrt{\frac{\kappa_A}{M}} \left(2 + \sqrt{1 + 4\kappa_R M}\right). \quad (33)$$

This is the BO result that is also the leading term of the exact result in some  $m/M$  expansion. The exact result is given in equation (18) of the main text, and using this one can write

$$E_{\text{tot}} = E_{\text{tot}}^{\text{BO}} + \frac{3}{2}\sqrt{\kappa_A}\frac{m}{M} + O((m/M)^2). \quad (34)$$

So, the unique effect is due to a reduced mass used in the exact treatment involving the pair electron mass and the pair nuclear mass.

As a final comment, we can consider briefly the adiabatic approximation, To the BO Hamiltonian we should then add the following operator

$$-\frac{m}{4M}(\langle \Phi_e | \nabla_{\mathbf{P}}^2 \Phi_e \rangle_e + 2 \langle \Phi_e | \nabla_{\mathbf{P}} \Phi_e \rangle_e \cdot \nabla_{\mathbf{P}}), \quad (35)$$

where integration is done over the electronic coordinates. The second integral is zero for the lowest energy state  $\Phi_e$  while the first is a constant (not depending on nuclear coordinates). More precisely we have

$$-\frac{m}{4M} \langle \Phi_e | \nabla_{\mathbf{P}}^2 \Phi_e \rangle_e = \frac{3m}{2M} \sqrt{\kappa_A}. \quad (36)$$

It becomes clear that the adiabatic approximation, in this solvable model, corrects the BO approximation to first order in  $m/M$ .

## 5. Summary and future directions

To conclude, we wish to make a rather general comment on the status of the adiabatic or Born–Oppenheimer approximation in the electronic structure problem of molecules and condensed phases. The recent book by Martin [6] treats this in a brief Appendix, which begins as follows: ‘The only small parameter in the electronic structure problem is the inverse nuclear mass  $1/M$ , i.e., the nuclear kinetic energy terms. The adiabatic or BO approximation is a systematic expansion in the small parameter that is fundamental to all electronic structure theory’. We reiterate that, while the model used here is for an ‘artificial two-electron molecule’, in this exactly solvable problem such a systematic expansion poses considerable questions. We exhibit the expansion parameter  $(m/M)^{1/4}$  quite clearly, though other non-analytic terms enter our large- $M$  limit. Further work, of course, is needed as to whether parallel non-analyticities occur in ‘real molecules’ with purely Coulomb interactions. Naturally expanding the ground-state energy (see section 4) in  $1/M$  is a relatively straightforward matter, compared with related attempts to expand probability densities, as, for example, in equations (20) and (21).

### Appendix: ground state in united-atom limit of diatomic molecule treated in main text

Our purpose in this Appendix is to report the solution, for essentially the same model, in which the two nuclei, denoted 1 and 2 in the main text, are fused together – the united-atom limit. Then, we have a three-body problem when we retain finite nuclear mass, which, for convenience of terminology, we shall denote

by  $M_a (= 2M)$ . Makarewicz has set up the transformation from positional coordinates  $\mathbf{x}$  to Jacobi coordinates  $\mathbf{r}$ , and after correcting a minor misprint in this paper, we can write the matrix  $A_a$  as

$$A_a = \begin{bmatrix} 1 & -1 & 0 \\ -1/2 & -1/2 & 1 \\ 1/(2 + M_a) & 1/(2 + M_a) & M_a/(2 + M_a) \end{bmatrix}, \quad (37)$$

where the last row of  $A_a$  becomes 0, 0, 1 in the BO approximation, corresponding to the limit of large  $M_a$ . Once again,  $\mathbf{r}$  and  $\mathbf{x}$  denote column vectors:

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \end{bmatrix} : \quad \mathbf{x} = \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \mathbf{x}_3 \end{bmatrix}. \quad (38)$$

Using these results, One obtains fairly readily the kinetic energy operator  $\hat{T}$  in the form

$$\hat{T} = -\frac{1}{2} \left[ 2\nabla_1^2 + \left( \frac{1}{2} + \frac{1}{M_a} \right) \nabla_2^2 + \frac{1}{2 + M_a} \nabla_3^2 \right], \quad (39)$$

while the potential energy  $V$  follows as

$$V = \frac{1}{2} \kappa_A r_1^2 + 2\kappa_A r_2^2 + \frac{\kappa_R}{r_1^2} \quad (40)$$

with the force constants given by

$$\kappa_{13} = \kappa_{23} = \kappa_A, \quad \kappa_{12} = \kappa_R. \quad (41)$$

Again the wave function evidently separates into the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2) \exp(i\mathbf{k} \cdot \mathbf{r}_3), \quad (42)$$

$\Psi_2(\mathbf{r}_2)$  is entirely similar to  $\Psi_3(\mathbf{r}_3)$  above, while  $\Psi_1(\mathbf{r}_1)$  is a scaled form of  $\Psi_2$  given earlier. Hence a complete solution is available for this artificial united atom.

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