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Molecular second quantized Hamiltonian: electron correlation and non-adiabatic coupling treated on an equal footing

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We introduce a new theoretical and computational framework for treating molecular quantum mechanics without the Born-Oppenheimer approximation. The molecular wavefunction is represented in a tensor-product space of electronic and vibrational basis functions, with electronic basis chosen to reproduce the mean-field electronic structure at all geometries. We show how to transform the Hamiltonian to a fully second quantized form with creation/annihilation operators for electronic and vibrational quantum particles; paving the way for polynomial-scaling approximations to the tensor-product space formalism. In addition, we make a proof-of-principle application of the new ansatz to the vibronic spectrum of C_2 .

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I. INTRODUCTION

From the physical viewpoint chemistry is just the motion of electrons and nuclei, instantaneously attracting and repelling each other through Coulomb forces. This can be elegantly summarised in a molecular Hamiltonian,

$$H_{\text{mol}} = T_e + T_n + V_{ee} + V_{en} + V_{nn} \quad (1)$$

where T and V are kinetic energy and Coulomb operators. The subscripts e and n represent electrons and nuclei, and their pairs indicate interaction of respective particles. All that is required from a quantum chemist is to solve the formidable time-dependent or -independent Schrödinger equation (SE) for a molecular wavefunction, Ψ_{mol} , and any desired observable properties can then be obtained.

Quantum chemists have risen to the task and developed an impressive arsenal of methods and approaches for solving the SE. The Born-Oppenheimer (BO) approximation lays the foundation on which most other methods are built.¹⁻³ It uses the disparity between electron and nuclear masses to justify separation of their dynamics. The electrons are said to follow the nuclear motion instantaneously, and the electronic structure is governed only by the clamped nuclei Hamiltonian,

$$H_e = T_e + V_{ee} + V_{en} + V_{nn}. \quad (2)$$

Solution of the corresponding electronic SE leads to adiabatic states Ψ_P and potential energy hyper-surfaces (PES) $E_P^{(e)}$. There are well known hierarchies of methods that allow calculation of ground and excited states with increasing accuracy.

The only thing left is to solve for the nuclear wavefunction, defined on a chosen PES according to a simplified molecular SE

$$(E_P^{(e)} + T_n)\Phi_{P,Q} = E_{\text{mol}}^{P,Q}\Phi_{P,Q}, \quad (3)$$

where the grouped index P, Q indicates that for each electronic state P there is a spectrum of nuclear states Q . The overall molecular wavefunction becomes a simple product $\Psi_{\text{mol}}^{P,Q} = \Psi_P\Phi_{P,Q}$.

This procedure can explain a large part of molecular spectroscopy and chemical reactivity. But, just as the BO approximation is uniformly understood, accepted and taught to all

students of chemistry, so is the fact that it often fails. There are a range of effects, from Jahn-Teller and intensity borrowing, to chemiluminescent reactions and electron transfer processes, that require mixing of different electronic states.

To go beyond the BO approximation, the molecular wavefunction can be expressed using the Born-Huang (BH) ansatz,⁴

$$\Psi_{\text{mol}}^i = \sum_P^{N_a} \Psi_P \Phi_P^i \quad (4)$$

where Ψ_P are the adiabatic solutions to electronic SE. The nuclear wavefunction can now be defined and, in the case of a time-dependent problem, evolve on a manifold of PESs governed by H_{mol} . The fact that Ψ_P depends parametrically on nuclear geometry introduces the nuclear kinetic energy coupling (NKEC) term

$$\Lambda_{PQ} = \langle \Psi_P | T_n | \Psi_Q \rangle, \quad (5)$$

which is responsible for non-adiabatic coupling (NAC). It is well known that the strength of Λ_{PQ} depends on the energy separation of the states P, Q , and diverges when they become degenerate, forming a so-called conical intersections.⁵⁻⁷ To avoid instabilities, as well as to support the fitting of smooth geometry-dependent parameters to carry the electronic energies, it is more common to use a set of pseudo-diabatic states that are defined by finding a unitary transformation of the chosen adiabatic states that gives $\Lambda = 0$. While in general this cannot be done exactly,⁸ there are procedures for defining approximate transformations.⁹⁻¹⁷

The necessity for diabaticization is a consequence of starting with the BO approximation. The usual assumption that the clamped nuclei Hamiltonian constitutes the dominant term becomes invalid when close-lying states give rise to large or divergent Λ , whereas in the pseudo-diabatic representation all of the NKEC is moved into the electronic Hamiltonian, which is no longer diagonal in that basis. While experience has shown that this procedure works well for molecular systems, one has to wonder whether it remains so when system size increases and the band structure begins to appear. In this paper, we explore whether more nuanced theories can be developed to treat nuclear and electron dynamics on the same footing by detaching ourselves from the BO approximation.

Not surprisingly, methods based on a similar line of thought already exist in the literature. We follow Mátyus in calling them pre-BO theories.¹⁸ Often, the terms non-BO or beyond

BO are also used, but we find that those terms would encompass the traditional approaches based on Born-Huang ansatz which break the BO approximation and include NKEC term. One family of pre-BO approaches is based on diagonalising H_{mol} directly in a basis of explicitly correlated Gaussians.^{18–22} The basis functions depend on all inter-particle distances and can achieve extremely accurate results. However, because of the factorial cost for variational solutions, such calculations are limited to few-atom systems.

Another prominent family of methods generalises the orbital picture to the nuclei. We will call them nuclear orbital (NO) based methods in this manuscript. They treat each nucleus as a quantum particle alongside the electrons, and solve generalised Hartree-Fock (HF) equations in a basis of single particle functions.^{23–27} For electrons, these are the standard atomic orbitals (AO) resulting in molecular orbitals (MO); for the nuclei, an analogous basis of Gaussian type functions is used, resulting in nuclear orbitals. The molecular Hilbert space is spanned by symmetrised products of nuclear and molecular orbitals, so that particles follow correct fermionic or bosonic statistics depending on their spin. This rather ingenious treatment allows the full machinery of electronic structure theory to be applied, natively accounting for electron and nuclear dynamics. Some of the methods already reported include HF,^{24,25} many-body perturbation theory,^{28–30} Configuration Interaction (CI),^{31–33} density-matrix renormalization group,³⁴ multi-configuration self-consistent-field,²⁵ coupled cluster,^{28,35,36} time dependent HF³⁷ and some explicitly correlated variants.^{38–40}

This framework cannot, however, be applied to the whole molecular system in a general manner. The centres of the AO basis functions are fixed in space, and although the exact position can be optimised variationally they are no longer clamped to the nuclei. During nuclear dynamics the electron density is polarised away from AO centres, leading to strong electron-nuclear coupling.^{33,41–43} This results in slow convergence with respect to the AO basis, which is trying to describe both electron-electron and electron-nucleus cusps. Explicitly correlated methods can help to reduce basis set dependence at the cost of increased complexity. Overall, this approach is best for small nuclei like H.²⁷

Similar ideas can be found in the world of theoretical attosecond spectroscopy, where the energy bandwidth of a pulse covers multiple electronic states and can lead to photoionisation.⁴⁴ Strong coupling to an external pulse causes significant changes in electronic and nuclear dynamics, necessitating multiconfigurational representation of the wavefunction. But, since the

time scale of a pulse is larger than typical vibrational motion, one can begin by adopting the clamped nuclei approximation. Such a framework is implemented in the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method,⁴⁵⁻⁴⁸ which defines propagation of the electronic wavefunction in a basis of Slater determinants with time-dependent MOs. However, electron dynamics can be strongly effected by the nuclei⁴⁹ and there are at least two related methods for treating the whole system quantum mechanically and expressing Ψ_{mol} as an outer product of electron and nuclear basis functions. Kato and Yamanouchi developed an extended MCTDHF method by using a basis of Slater determinants with time-dependent nuclear orbitals for the protons and keeping heavy nuclei clamped.⁴⁹⁻⁵¹ In another work, Nest developed multiconfiguration electron-nuclear dynamics method, which instead works with vibrational coordinates of the whole molecule and uses Hartree products of time-dependent vibrational single particle functions as a basis.⁵²⁻⁵⁴ Both approaches use geometry independent MOs and share limitations of NO based methods to strong electron-nuclear correlation, which can however be assumed to be less important on short time scale.

In the same spirit, Haxton *et al.* developed an interesting ansatz for including quantum treatment of nuclei into MCTDHF, but specialised to diatomic molecules only.⁵⁵ By adopting prolate spheroidal coordinates for electrons, they could define atom-centred AOs that correctly reproduce electron-nucleus cusps, and derived an efficient procedure for evaluating overlap and Hamiltonian matrix elements. The nuclear wavefunction was defined using the vibrational stretching coordinate, instead of treating each nucleus individually as in NO based methods. This method showed rapid convergence in vibronic states of HD^+ , HD, H_2 and LiH,⁵⁵ but did not perform as well at calculating the dissociative photoionization cross section of H_2^+ .⁵⁶ It was conjectured that prolate spheroidal coordinates do not behave physically in the asymptotic region, and some alternatives were suggested. Nonetheless, one of the important contributions of this work is to show that one can choose geometry-dependent AOs that satisfy key physical conditions to get around the strong electron-nuclear coupling. There are many other approaches to treating non-adiabatic effects, such as path-integral molecular dynamics,⁵⁷⁻⁶³ path-integral Monte-Carlo,⁶⁴⁻⁶⁶ quantum Monte-Carlo^{67,68} and wavepacket methods,⁶⁹⁻⁷³ however, as they are not directly related to current work, we will not discuss them in detail.

Our interest in this topic, and the purpose of this manuscript, is to begin defining a new

ansatz for solving the molecular problem in a manner that is general and extendable to large systems. Like NO based methods, we want to take advantage of the great progress in electronic structure theory by adopting single particle basis functions and working in second quantization. To ensure that AOs have a consistent, if not exact, description of electron-nucleus cusp, we follow the lead of Haxton et al.⁵⁵ and adopt traditional AO basis fixed to the nuclei. We set a physical condition that should be satisfied by a successful choice of MOs that they should have correct HF energy at all geometries. This might appear to take us back to the problem of NKEC term in Eq. (5), which is known to be unstable in the BH ansatz. However, unlike solutions of clamped nuclei Hamiltonian which are usually unique, the HF energy is invariant to MO rotations within occupied-occupied and virtual-virtual blocks. We explore the conjecture that there is always a well defined choice of MOs, which could be based on principles of locality or diabaticity,¹⁰ that has well behaved NKEC term. For the nuclear degrees of freedom, we choose to work with vibrational coordinates, but leave basis functions undefined until applications. Choosing a geometry-dependent set of orbitals means that the molecular Hamiltonian is a many-body operator and its integration over nuclear degrees of freedom has to be obtained numerically. We note however, that this is not a major weakness, since integration can be done through quadrature and there are many highly efficient methods for solving the HF equations.

Introducing a new ansatz necessarily raises a myriad of questions and many technical details have to be worked out and tested. We do not attempt to cover everything in a single manuscript; instead we here concentrate on the basic methodology and a simple showcase application. We envision that on this foundation we can build a hierarchy of methods using many-body theory that can tackle large systems at various levels of accuracy, just as in electronic structure theory.⁷⁴ This framework would be particularly suited to study non-adiabatic effects in spectroscopy of large conjugated systems (e.g. conducting polymers, organic semiconductors). After reviewing some background theory in Section II, we show how to quantize electronic and nuclear degrees of freedom and derive our molecular second quantized Hamiltonian in Section III. In Section IV we discuss how the choice of MOs affects the wavefunction and behaviour of the NKEC terms. It also contains a rather unintuitive conclusion that our ansatz is not invariant to the choice of MOs, except for in the limit of infinite basis. Finally, in Section V we show results for a proof-of-concept application to the

vibronic spectrum of C_2 .

II. BACKGROUND THEORY

A. Molecular Hamiltonian

We start with a Hamiltonian in the molecular frame containing N_n nuclei and N_e electrons with electronic positions denoted as \mathbf{x} . The nuclear degrees of freedom are described by N_v mass weighted rectilinear vibrational coordinates, \mathbf{X} .³

$$H_{\text{mol}} = H_e + T_n \quad (6)$$

$$H_e = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 + V_{nn}(\mathbf{X}) + V_{en}(\mathbf{x}, \mathbf{X}) + V_{ee}(\mathbf{x}) \quad (7)$$

$$T_n = -\frac{1}{2} \nabla_n \cdot \nabla_n \quad (8)$$

where H_e is the clamped nuclei electronic Hamiltonian; T_n is the nuclear kinetic energy (NKE) operator; V_{nn}, V_{ne}, V_{ee} are Coulomb operators for nuclear-nuclear, electron-nuclear and electron-electron interaction; $\nabla_n = \{\nabla_\kappa, \kappa = 1, N_v\}$ and ∇ indicates a partial derivative with respect to an electronic or vibrational coordinate, depending on context.

In the first instance we choose to ignore the rotational-vibrational coupling, mass polarization and Watson terms. The following derivation can be generalised to include these effects and use a different set of nuclear coordinates, but the current choices should suffice for many systems.

We are looking for solutions to the time-independent Schrödinger equation,

$$H_{\text{mol}} \Psi_{\text{mol}} = E_{\text{mol}} \Psi_{\text{mol}} \quad (9)$$

where the molecular wavefunction, $\Psi_{\text{mol}}(\mathbf{x}, \mathbf{X})$, contains all information about nuclear and electronic structure, and E_{mol} is the energy eigenvalue of this state.

Let us introduce many-particle basis functions $\Phi_{\mathbf{P}}(\mathbf{X})$ for vibrations and $\Psi_{\mathbf{P}}(\mathbf{x}; \mathbf{X})$ for electrons, where semicolon implies parametric dependence. We reserve capitalised Latin letters P, Q, R, \dots as indices of many-particle basis functions, with bold-face font when

particles are distinguishable, for example collection of vibrational modes. In the following, we will suppress showing geometry dependence of quantities unless it is not clear from context, or to highlight important relationships. The vibrational basis is assumed orthonormal over \mathbf{X} , $\int \Phi_P^* \Phi_Q d\mathbf{X} = \delta_{PQ}$, and electronic basis is orthonormal over electronic space, $\int \Psi_P^* \Psi_Q d\mathbf{x} = \delta_{PQ}$, for each \mathbf{X} . We make no other assumption about the nature of basis functions at this point, and we should note that the special case of a geometry independent electronic basis (e.g. plane-waves) conforms to our specification, albeit in a trivial manner. Then the molecular Hilbert space, \mathcal{H}_{mol} , is spanned by their direct product, $\Psi_P(\mathbf{x}; \mathbf{X}) \Phi_Q(\mathbf{X})$. In Dirac notation, $|\Psi_P, \Phi_Q\rangle = |\Psi_P\rangle |\Phi_Q\rangle$ without specifying the order of integration.

The matrix elements of H_{mol} in this basis are,

$$\begin{aligned} H_{PQ,RS} &= \langle \Psi_P, \Phi_R | H_{\text{mol}} | \Psi_Q, \Phi_S \rangle \\ &= \langle \Phi_R | H_{PQ}(\mathbf{X}) | \Phi_S \rangle, \end{aligned} \quad (10)$$

where integration over electrons is carried out first, leading to

$$H_{PQ} = H_{PQ}^{(e)} + T_n \delta_{PQ} - \frac{1}{2} \Lambda_{PQ}, \quad (11)$$

with the first term coming from the clamped nuclei Hamiltonian Eq. (7)

$$H_{PQ}^{(e)}(\mathbf{X}) = \langle \Psi_P | H_e(\mathbf{x}, \mathbf{X}) | \Psi_Q \rangle. \quad (12)$$

The second term in Eq. (11) is the NKE operator, now acting only on the vibrational basis, since integration over the electronic coordinates has already occurred. The third term is the nuclear kinetic energy coupling (NKEC), which arises from T_n acting on $|\Psi_Q\rangle$. It can be written as

$$\begin{aligned} \Lambda_{PQ} &= 2\mathbf{F}_{PQ} \cdot \nabla_n + G_{PQ} \\ &= \sum_{\kappa}^{N_v} \left(2F_{PQ}^{(\kappa)} \nabla_{\kappa} + G_{PQ}^{(\kappa)} \right) \end{aligned} \quad (13)$$

where \mathbf{F} and G , commonly known as vector and scalar coupling terms, have the following definition,

$$F_{PQ}^{(\kappa)} = \langle \Psi_P | \nabla_{\kappa} \Psi_Q \rangle \quad (14)$$

$$G_{PQ}^{(\kappa)} = \langle \Psi_P | \nabla_{\kappa}^2 \Psi_Q \rangle. \quad (15)$$

Some of their properties are readily evident. Firstly, due to the orthonormality condition,

$$F_{PQ}^{(\kappa)} = -F_{QP}^{(\kappa)*}, \quad (16)$$

which shows that the matrix $F^{(\kappa)}$ is anti-Hermitian for all \mathbf{X} .

By differentiation of Eq. (14), the scalar coupling term can be decomposed into anti-Hermitian and Hermitian matrices,

$$G_{PQ}^{(\kappa)} = \left[\nabla_{\kappa} F_{PQ}^{(\kappa)} \right] - K_{PQ}^{(\kappa)} \quad (17)$$

where ∇_{κ} does not operate outside of square brackets and the Hermitian matrix $K^{(\kappa)}$ is as follows,

$$K_{PQ}^{(\kappa)} = \langle \nabla_{\kappa} \Psi_P | \nabla_{\kappa} \Psi_Q \rangle. \quad (18)$$

This means that in general $G_{PQ} \neq G_{QP}$ and, after integration over vibrational degrees of freedom,

$$G_{PQ,RS} \neq G_{QP,SR}, \quad (19)$$

thus making it non-Hermitian in the molecular Hilbert space, \mathcal{H}_{mol} .⁹ The notation in Eq. (19) follows from Eq. (10), with implicit complex conjugation of relevant basis functions when indices are swapped.

The overall contribution from Λ is of course Hermitian, revealing that there are cancellations among components of $F^{(\kappa)}\nabla_{\kappa}$ and G . We can carry them out explicitly by substituting Eq. (17) into Eq. (13) and rewriting Λ with individually Hermitian terms

$$\Lambda_{PQ} = \sum_{\kappa}^{N_v} (O_{PQ}^{(\kappa)} - K_{PQ}^{(\kappa)}), \quad (20)$$

with a new intermediate term

$$O_{PQ}^{(\kappa)} = 2F_{PQ}^{(\kappa)}\nabla_{\kappa} + \left[\nabla_{\kappa} F_{PQ}^{(\kappa)} \right]. \quad (21)$$

It is clear that

$$K_{PQ,RS}^{(\kappa)} = K_{QP,RS}^{(\kappa)} = K_{PQ,SR}^{(\kappa)} = K_{QP,SR}^{(\kappa)}, \quad (22)$$

which together with Eq. (16) gives

$$O_{PQ,RS}^{(\kappa)} = -O_{QP,RS}^{(\kappa)} = -O_{PQ,SR}^{(\kappa)} = O_{QP,SR}^{(\kappa)}. \quad (23)$$

These symmetries are conserved for any form of $K^{(\kappa)}$ and $F^{(\kappa)}$ with conditions that $K_{PQ}^{(\kappa)} = K_{QP}^{(\kappa)}$ and Eq. (16) are satisfied. That guarantee makes us prefer Eq. (20) when deriving our Hamiltonian in later sections.

B. Born-Huang ansatz and the Born-Oppenheimer approximation

A good choice of electronic basis is essential for compact representation of Ψ_{mol} . Born and Huang proposed to use solutions of clamped nuclei Hamiltonian,⁴

$$H_e \tilde{\Psi}_P(\mathbf{x}; \mathbf{X}) = E_P^{(e)}(\mathbf{X}) \tilde{\Psi}_P(\mathbf{x}; \mathbf{X}) \quad (24)$$

where the eigenvalue $E_P^{(e)}$ is the potential energy hypersurface for state P . The electronic basis $\tilde{\Psi}_P(\mathbf{x}; \mathbf{X})$ is often referred to as adiabatic and it depends on \mathbf{X} parametrically.

For each adiabatic state there is a corresponding nuclear state, $\tilde{\Phi}_P$,

$$\begin{aligned} \Psi_{\text{mol}} &= \sum_P \tilde{\Psi}_P \tilde{\Phi}_P \\ &= \sum_P \sum_Q C_{P,Q} \tilde{\Psi}_P \tilde{\Phi}_Q \end{aligned} \quad (25)$$

where second equality arises from expanding nuclear states in a basis. By construction, the first term in Eq. (10) no longer couples different electronic states, $H_{PQ}^{(e)} = E_P^{(e)} \delta_{PQ}$, and non-adiabatic effects are solely due to NKEC term, Λ .

Using an extension of the Hellman-Feynman theory, the off-diagonal elements of the vector coupling term can be shown to be,⁷⁵

$$\mathbf{F}_{PQ} = \frac{\langle \tilde{\Psi}_P | \nabla_n H_e | \tilde{\Psi}_Q \rangle}{E_Q^{(e)} - E_P^{(e)}} \quad (26)$$

which is generally non-zero. Through resolution of identity and assuming a complete basis,

$$K_{PQ} = - \sum_R \mathbf{F}_{PR} \cdot \mathbf{F}_{RQ} \quad (27)$$

which makes it clear that the behaviour of Λ is dominated by \mathbf{F} .

Because of the disparity between electron and nuclear masses, Λ should make a relatively small contribution compared to $H_{PQ}^{(E)}$. In fact, Born and Oppenheimer used PT to show that energy contribution from Λ is of the order $\mathcal{O}(m_e/m_n)$, where m_e is electron mass and m_n is nucleus mass.¹ However, it is clear from Eq. (26) that it becomes larger for close lying electronic states. In particular, special treatment is necessary when two or more states become degenerate with non-zero numerator in Eq. (26) and form conical intersections.⁵⁻⁷

For many chemical systems, it becomes sensible to make the Born-Oppenheimer approximation and ignore Λ in its entirety.¹ Then, the molecular Hamiltonian does not couple different electronic states and Ψ_{mol} can be written exactly as,

$$\Psi_{\text{mol}}^i = \tilde{\Phi}_i \tilde{\Psi}_i \quad (28)$$

where i is a collective index.

The electronic and nuclear problems decouple and after solving Eq. (24) for all relevant conformations, the nuclear problem becomes,

$$(W(\mathbf{X}) + T_n)\tilde{\Phi}_i = E_{\text{mol}}^i \tilde{\Phi}_i \quad (29)$$

where $W = E_i^{(e)}$. The electrons can be said to follow the nuclei adiabatically, adjusting instantaneously to changes in nuclear positions.

An improvement to BO approximation can be made while retaining exact form of Eqs. (28) and (29), by including the diagonal component of Λ . This can be achieved by letting,

$$W = E_i^{(e)} + \frac{1}{2} \sum_{\kappa}^{N_v} K_{ii}^{(\kappa)} \quad (30)$$

where the last term is often called adiabatic or diagonal BO correction (DBOC).¹⁹

The off-diagonal elements of Λ , often called non-adiabatic elements, can play an essential role in physical effects such as radiationless decay. However, instead of working with them directly it is more common to move into a diabatic basis.

The pseudo-diabatic basis, $\tilde{\Psi}^d$, can be defined as a unitary transformation of the chosen finite set of adiabatic states,

$$\tilde{\Psi}_P^d = \sum_Q U_{QP} \tilde{\Psi}_Q \quad (31)$$

such that the vector coupling becomes zero by satisfying the following condition,⁷

$$\sum_{\kappa} (F^{(\kappa)}U + \nabla_{\kappa}U) = 0 \quad (32)$$

All of the non-adiabatic coupling is moved into $H_{PQ}^{(e)}$ which now contains off-diagonal elements.

In general this transformation cannot be defined exactly without a complete basis.⁸ There are a variety of methods that can satisfy Eq. (32) approximately, without the strict equality, to define quasi-diabatic states.^{9–17}

Approaches reviewed in this section form the traditional set of tools. The BO approximation is always made as the first step, with post-BO corrections introduced for more difficult cases. This is very effective when only a few states need to be coupled for capturing the underlying physics or when non-adiabatic coupling is small.

III. FULLY SECOND QUANTIZED MOLECULAR HAMILTONIAN

We start with the molecular Hamiltonian of Eq. (6) and normal mode coordinates, \mathbf{X} . Each vibrational mode, κ , has a basis of M^κ modals, $\{\phi_p^\kappa(X_\kappa), p = 1, M^\kappa\}$. The functional form of modals is not important for the derivation, but some common choices include harmonic oscillator functions, or solutions of the vibrational self-consistent-field problem.⁷⁶ In the following, we will use small Latin letters p, q, r, \dots to denote indices of single-particle basis, and adopt an implicit summation convention for the indices of second quantized orbitals.

The many-particle vibrational basis functions are a direct product of modals,

$$\Phi_{\mathbf{P}}(\mathbf{X}) = \phi_{\mathbf{P}_1}^1(X_1) \phi_{\mathbf{P}_2}^2(X_2) \dots \phi_{\mathbf{P}_{N_v}}^{N_v}(X_{N_v}) \quad (33)$$

The electronic basis functions are the traditional Slater determinants,

$$\Psi_{\mathbf{P}}(\mathbf{x}; \mathbf{X}) = \mathcal{A} [\psi_{P_1}(\mathbf{x}_1; \mathbf{X}) \psi_{P_2}(\mathbf{x}_2; \mathbf{X}) \dots \psi_{P_{N_e}}(\mathbf{x}_{N_e}; \mathbf{X})] \quad (34)$$

where \mathcal{A} is an antisymmetrizing operator and $\psi_p(\mathbf{x}; \mathbf{X})$ are fully geometry dependent orthonormal MOs. The choice of MOs should provide a good static description of electronic structure at all \mathbf{X} . Using orbitals satisfying the HF equations and AOs fixed to the nuclei is one such choice, although their exact definition is not important for the rest of the derivation.

At this point, we can start deriving a second quantized molecular Hamiltonian, \hat{H}_{mol} , by requiring that it generates the same Hamiltonian matrix. This can be carried out in steps,

first quantizing the electrons and then vibrations,

$$\begin{aligned} \langle \Psi_P, \Phi_{\mathbf{R}} | H_{\text{mol}}(\mathbf{x}, \mathbf{X}) | \Psi_Q, \Phi_{\mathbf{S}} \rangle &= \langle \Psi_P, \Phi_{\mathbf{R}} | \hat{H}_{\text{mol}}(\mathbf{X}) | \Psi_Q, \Phi_{\mathbf{S}} \rangle \\ &= \langle \Psi_P, \Phi_{\mathbf{R}} | \hat{H}_{\text{mol}} | \Psi_Q, \Phi_{\mathbf{S}} \rangle \end{aligned} \quad (35)$$

A. Quantizing the electronic degrees of freedom

Quantizing electronic degrees of freedom in the clamped nuclei Hamiltonian, leads to the familiar expression

$$\hat{H}_e = h_0(\mathbf{X}) + h_{pq}(\mathbf{X}) a_p^\dagger a_q + \frac{1}{2} g_{pqrs}(\mathbf{X}) a_p^\dagger a_r^\dagger a_s a_q \quad (36)$$

where $h_0 = V_{nn}(\mathbf{X})$ is the nuclear-nuclear repulsion energy, h_{pq} and g_{pqrs} are core and electron-repulsion integrals (ERI), respectively, a^\dagger and a are the usual fermionic creation and annihilation operators.

$$h_{pq} = \int \psi_p^*(\mathbf{x}_1) \left(-\frac{1}{2} \nabla_{\mathbf{x}_1}^2 - \sum_{\kappa} \frac{Z_{\kappa}}{R_{1,\kappa}} \right) \psi_q(\mathbf{x}_1) d\mathbf{x}_1 \quad (37)$$

where Z_{κ} is the nuclear charge and $R_{1,\kappa}$ is the electron-nucleus distance, and parametric dependence on \mathbf{X} is not shown.

$$g_{pqrs} = \int \int \psi_p^*(\mathbf{x}_1) \psi_q(\mathbf{x}_1) \frac{1}{r_{12}} \psi_r^*(\mathbf{x}_2) \psi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (38)$$

where r_{12} is the inter-electron distance and ERIs are geometry dependent because the AOs, and therefore the MOs, move with the nuclei.

Quantization of NKEC terms, Eq. (20), was done by firstly deriving Slater-Condon rules for matrix elements in Eqs. (14) and (18), and formulating second quantized operators that reproduce them. Similar procedures have previously been applied to derive diagonal Born-Oppenheimer corrections.^{77,78}

$$\hat{F}^{(\kappa)} = f_{pq}^{(\kappa)}(\mathbf{X}) a_p^\dagger a_q \quad (39)$$

$$\hat{K}^{(\kappa)} = k_{pq}^{(\kappa)}(\mathbf{X}) a_p^\dagger a_q - d_{pqrs}^{(\kappa)}(\mathbf{X}) a_p^\dagger a_r^\dagger a_s a_q \quad (40)$$

where new one-electron integrals are introduced,

$$f_{pq}^{(\kappa)} = \int \psi_p^*(\nabla_{\kappa} \psi_q) d\mathbf{x}_1 \quad (41)$$

$$k_{pq}^{(\kappa)} = \int (\nabla_{\kappa} \psi_p^*) (\nabla_{\kappa} \psi_q) d\mathbf{x}_1 \quad (42)$$

$$d_{pqrs}^{(\kappa)} = f_{pq}^{(\kappa)} f_{rs}^{(\kappa)} \quad (43)$$

From MO the orthonormality condition we know that $f^{(\kappa)}$ is anti-hermitian, $f_{pq}^{(\kappa)} = -f_{qp}^{(\kappa)*}$, and $k^{(\kappa)}$ is hermitian by definition, $k_{pq}^{(\kappa)} = k_{qp}^{(\kappa)*}$.

To simplify notation, let us sum all $\hat{K}^{(\kappa)}$ from Eq. (40) into a single term,

$$\hat{K} = k_{pq}(\mathbf{X}) a_p^\dagger a_q - d_{pqrs}(\mathbf{X}) a_p^\dagger a_r^\dagger a_s a_q \quad (44)$$

$$k_{pq} = \sum_{\kappa}^{N_v} k_{pq}^{(\kappa)} \quad (45)$$

$$d_{pqrs} = \sum_{\kappa}^{N_v} d_{pqrs}^{(\kappa)} \quad (46)$$

At this point, it is important to realise that a^\dagger and a are applied only to products of electronic basis functions, and have the effect of converting one such orbital product into another one. They themselves do not explicitly reference nuclear geometry, but the resulting orbital product will have a changed geometry dependence as a consequence of the dependence of the basis functions on geometry. This dependence will appear in second-quantized formulations via the integrals of relevant operators in the basis set, with the integrals carrying all functional dependence on \mathbf{X} , such that

$$[\nabla_{\kappa} \hat{F}^{(\kappa)}] = [\nabla_{\kappa} f_{pq}^{(\kappa)}] a_p^\dagger a_q \quad (47)$$

We can construct the NKEC term in Eq. (20),

$$\hat{O}^{(\kappa)} = 2F^{(\kappa)} \nabla_{\kappa} + [\nabla_{\kappa} F^{(\kappa)}] \quad (48)$$

$$\hat{\Lambda} = \sum_{\kappa}^{N_v} \hat{O}^{(\kappa)} - \hat{K} \quad (49)$$

Now we have a partially quantized molecular Hamiltonian,

$$\hat{H}_{\text{mol}}(\mathbf{X}) = \hat{H}_e(\mathbf{X}) - \frac{1}{2} \hat{\Lambda}(\mathbf{X}) + T_n \quad (50)$$

We can write it in full form,

$$\begin{aligned}
\hat{H}_{\text{mol}}(\mathbf{X}) = & T_n + h_0(\mathbf{X}) + \left(h_{pq}(\mathbf{X}) + \frac{1}{2} k_{pq}(\mathbf{X}) \right) a_p^\dagger a_q \\
& - \sum_{\kappa}^{N_v} \left(f_{pq}^{(\kappa)}(\mathbf{X}) \nabla_{\kappa} + \frac{1}{2} [\nabla_{\kappa} f_{pq}^{(\kappa)}(\mathbf{X})] \right) a_p^\dagger a_q \\
& + \frac{1}{2} g_{pqrs}(\mathbf{X}) a_p^\dagger a_r^\dagger a_s a_q - \frac{1}{2} d_{pqrs}(\mathbf{X}) a_p^\dagger a_r^\dagger a_s a_q
\end{aligned} \tag{51}$$

where we grouped together terms of the same symmetry. This is an appropriate point to apply the frozen-core (FC) approximation, which is described in Appendix A. Since the Hamiltonian remains of the same form we continue without changing notation.

B. Quantizing the vibrational degrees of freedom

For the sake of quantizing over vibrational modes Eq. (50) is just a many-body vibrational operator. There are at least two ways to perform this transformation. One could follow the approach described by Hirata and treat vibrations as phonons, using harmonic oscillator modal basis and corresponding raising and lowering “ladder” operators.⁷⁹ It would require approximating \hat{H}_{mol} in Eq. (50) with a Taylor series expansion around the reference geometry \mathbf{X}^0 up to finite order, but theoretically allows use of an infinite vibrational basis. However, truncation of the Hamiltonian could lead to instabilities and make it quasi-bound, as is often the case in vibrational problems.⁸⁰ It could still be an interesting approach with some model systems or with generalisations of this Hamiltonian to solids where its truncation is more likely to be bound.

The second approach, which we follow in this article, is to apply quantisation over arbitrary modals, following the approach of Christiansen.⁷⁶ The key idea is to avoid the introduction of phonons, but instead to deal directly with the truncated Hilbert space defined by the chosen basis set in each vibrational coordinate. Second quantization can then be introduced via excitation operators that act in the usual way on wavefunctions that are linear combinations of these basis functions^{76,81}. A feature of this approach is that the entire single-mode space can be reached through a single excitation operator, rather than having to apply multiple ladder operators, which can be an advantage in formulating compact approximate many-body theories such as coupled-cluster. In contrast to normal identical-particle second

quantization, the Hilbert space is not part of an arbitrary-particle-number Fock space, since all whole-system wavefunctions of interest lie in the tensor-product space where the basis functions for any given vibrational mode appear exactly once. However, in developing any many-body theory it is usually convenient to be able to manipulate annihilation and creation operators separately. This can be achieved by defining a fictitious Fock space generated by annihilators and creators that are defined such that normal-ordered annihilator-creator pairs are identical to the excitation operator. This definition is sufficient but not unique, since the Hamiltonian contains only normal-ordered single excitations; in particular the field operators can be defined to be either bosonic (as in Ref. 76) or fermionic, with generalised commutation relationships

$$\left[b_i^\kappa, b_j^{\lambda\dagger} \right]_{\pm} = \delta_{\kappa,\lambda} \delta_{i,j}, \quad \left[b_i^\kappa, b_j^\lambda \right]_{\pm} = \left[b_i^{\kappa\dagger}, b_j^{\lambda\dagger} \right]_{\pm} = 0, \quad (52)$$

where $[x, y]_{\pm} = xy \pm yx$ is the commutator (bosons) or anticommutator (fermions). Bosonic and fermionic creation/annihilation operators also commute,

$$\left[b_i^{\kappa\dagger}, a_p^\dagger \right]_{\pm} = \left[b_i^{\kappa\dagger}, a_p \right]_{\pm} = \left[b_i^\kappa, a_p^\dagger \right]_{\pm} = \left[b_i^\kappa, a_p \right]_{\pm} = 0, \quad (53)$$

and once again we can instead choose anticommutation, provided this is done consistently throughout, in particular with a defined order of modes and electrons in the tensor-product space. Finally, although the intention of the above is to support manipulations of the Hilbert space, vibrational modes can formally be introduced by acting with the creators on a vacuum.

Using the many body expansion (MBE),⁸² we introduce a decomposition of any operator $\Omega(\mathbf{X})$ into a sum of n -body operators, $\Omega^{\kappa,\lambda,\dots}(X_\kappa, X_\lambda, \dots)$, where n is the number of modes referenced:

$$\Omega(\mathbf{X}) = \Omega^0 + \Omega^{[1]}(\mathbf{X}) + \Omega^{[2]}(\mathbf{X}) + \dots \quad (54)$$

$$\Omega^0 = \Omega(\mathbf{X}^0) \quad (55)$$

$$\Omega^{[1]}(\mathbf{X}) = \sum_{\kappa}^{N_v} \Omega^\kappa(X_\kappa) \quad (56)$$

$$\Omega^{[2]}(\mathbf{X}) = \sum_{\kappa < \lambda}^{N_v} \Omega^{\kappa,\lambda}(X_\kappa, X_\lambda) \quad (57)$$

$$\Omega^\kappa(X_\kappa) = \Omega(X_\kappa) - \Omega^0 \quad (58)$$

$$\Omega^{\kappa,\lambda}(X_\kappa, X_\lambda) = \Omega(X_\kappa, X_\lambda) - \Omega^\kappa - \Omega^\lambda - \Omega^0 \quad (59)$$

where $\Omega(X_\kappa)$ is a 1-D slice through mode κ , i.e. setting all $X_\lambda = 0, \lambda \neq \kappa$. Similarly, $\Omega(X_\kappa, X_\lambda)$ is a 2-D plane through modes κ, λ . The superscript $[n]$ indicates that only n -body operators are involved. If carried to completion MBE is exact by definition. However, unlike Taylor expansion it can be truncated without introducing artificial instabilities.

We can require that the SQ operator, $\hat{\Omega}$, has the same matrix elements,

$$\langle \Phi_P | \Omega(\mathbf{X}) | \Phi_Q \rangle = \langle \Phi_P | \hat{\Omega} | \Phi_Q \rangle \quad (60)$$

leading to the following form,

$$\hat{\Omega} = \Omega^0 + \sum_{\kappa}^{N_v} \sum_{p,q}^{M^\kappa} \Omega_{pq}^\kappa b_p^{\kappa\dagger} b_q^\kappa + \sum_{\kappa < \lambda}^{N_v} \sum_{p,q}^{M^\kappa} \sum_{r,s}^{M^\lambda} \Omega_{pq,rs}^{\kappa,\lambda} b_p^{\kappa\dagger} b_q^\kappa b_r^{\lambda\dagger} b_s^\lambda + \dots \quad (61)$$

with multidimensional integrals

$$\Omega_{pq}^\kappa = \langle \phi_p^\kappa | \Omega^\kappa | \phi_q^\kappa \rangle \quad (62)$$

$$\Omega_{pq,rs}^{\kappa,\lambda} = \langle \phi_p^\kappa \phi_r^\lambda | \Omega^{\kappa,\lambda} | \phi_q^\kappa \phi_s^\lambda \rangle. \quad (63)$$

The subscript indices for distinguishable particles are separated by commas, with superscripts identifying individual modes.

The kinetic energy operator in Eq. (8) can be quantized without MBE,

$$\hat{T}_n = \sum_{\kappa}^{N_v} \sum_{p,q}^{M^\kappa} t_{pq}^\kappa b_p^{\kappa\dagger} b_q^\kappa \quad (64)$$

with NKE integrals,

$$t_{pq}^\kappa = -\frac{1}{2} \langle \phi_p^\kappa | \nabla_\kappa^2 | \phi_q^\kappa \rangle. \quad (65)$$

In the following, we quantize different components of $\hat{H}_{\text{mol}}(\mathbf{X})$, carrying the MBE up to first order only.

The clamped nuclei Hamiltonian in Eq. (36) and $\hat{K}(\mathbf{X})$ in Eq. (44) become, in second-quantized first-order MBE form,

$$\hat{H}_e^0 = h_0^0 + h_{pq}^0 a_p^\dagger a_q + \frac{1}{2} g_{pqrs}^0 a_p^\dagger a_r^\dagger a_s a_q \quad (66)$$

$$\hat{H}_e^\kappa = h_{0,pq}^\kappa b_p^{\kappa\dagger} b_q^\kappa + h_{pq,rs}^\kappa a_p^\dagger a_q b_r^{\kappa\dagger} b_s^\kappa + \frac{1}{2} g_{pqrs,tu}^\kappa a_p^\dagger a_r^\dagger a_s a_q b_t^{\kappa\dagger} b_u^\kappa \quad (67)$$

$$\hat{K}^0 = k_{pq}^0 a_p^\dagger a_q - d_{pqrs}^0 a_p^\dagger a_r^\dagger a_s a_q \quad (68)$$

$$\hat{K}^\kappa = k_{pq,rs}^\kappa a_p^\dagger a_q b_r^{\kappa\dagger} b_s^\kappa - d_{pqrs,tu}^\kappa a_p^\dagger a_r^\dagger a_s a_q b_t^{\kappa\dagger} b_u^\kappa \quad (69)$$

For the operator $\hat{O}^{(\kappa)}$ in Eq. (48), noting the discussion after Eq. (21), we apply MBE to $f_{pq}^{(\kappa)}$,

$$f_{pq}^{(\kappa)} \approx f_{pq}^{(\kappa),0} + \sum_{\lambda}^{N_v} f_{pq}^{(\kappa),\lambda}. \quad (70)$$

Substituting Eq. (70) into Eq. (48), using Eq. (39) and Eq. (47), and organising the result by level of mode coupling, we get

$$\hat{O}_{\text{MBE1}}^{(\kappa)} = \hat{O}_{\text{MBE1}}^{(\kappa),[1]} + \hat{O}_{\text{MBE1}}^{(\kappa),[2]}, \quad (71)$$

$$\hat{O}_{\text{MBE1}}^{(\kappa),[1]} = 2a_p^\dagger a_q f_{pq}^{(\kappa),0} \nabla_\kappa + 2a_p^\dagger a_q f_{pq}^{(\kappa),\kappa} \nabla_\kappa + a_p^\dagger a_q [\nabla_\kappa f_{pq}^{(\kappa),\kappa}], \quad (72)$$

$$\hat{O}_{\text{MBE1}}^{(\kappa),[2]} = 2a_p^\dagger a_q \sum_{\lambda \neq \kappa}^{N_v} (f_{pq}^{(\kappa),\lambda}) \nabla_\kappa, \quad (73)$$

where the subscript MBE1 indicates that Eq. (70) was used. Since we are not currently interested in two-mode coupling terms $\hat{O}_{\text{MBE1}}^{(\kappa),[2]}$ can be ignored, without loss of overall Hermiticity.

After defining the following integrals,

$$\lambda_{pq,rs}^{(\kappa),0} = f_{pq}^{(\kappa),0} \langle \phi_r^\kappa | \nabla_\kappa | \phi_s^\kappa \rangle, \quad (74)$$

$$\lambda_{pq,rs}^{(\kappa),\kappa} = \langle \phi_r^\kappa | f_{pq}^{(\kappa),\kappa} \nabla_\kappa + \frac{1}{2} [\nabla_\kappa f_{pq}^{(\kappa),\kappa}] | \phi_s^\kappa \rangle \quad (75)$$

we can write Eq. (72) in fully second quantized form,

$$\hat{O}_{\text{MBE1}}^{(\kappa),[1]} = 2 (\lambda_{pq,rs}^{(\kappa),0} + \lambda_{pq,rs}^{(\kappa),\kappa}) a_p^\dagger a_q b_r^{\kappa\dagger} b_s^\kappa \quad (76)$$

Now we can write the complete \hat{H}_{mol} operator with up to one-mode coupling,

$$\hat{H}_{\text{mol}} = \hat{T}_n + \hat{H}_{\text{mol}}^0 + \sum_{\kappa}^{N_v} \hat{H}_{\text{mol}}^\kappa, \quad (77)$$

$$\hat{H}_{\text{mol}}^0 = h_0^0 + \left(h_{pq}^0 + \frac{1}{2} k_{pq}^0 \right) a_p^\dagger a_q + \frac{1}{2} g_{pqrs}^0 a_p^\dagger a_r^\dagger a_s a_q - \frac{1}{2} d_{pqrs}^0 a_p^\dagger a_r^\dagger a_s a_q, \quad (78)$$

$$\begin{aligned} \hat{H}_{\text{mol}}^\kappa = & h_{0,pq}^\kappa b_p^{\kappa\dagger} b_q^\kappa + \left(h_{pq,rs}^\kappa + \frac{1}{2} k_{pq,rs}^\kappa \right) a_p^\dagger a_q b_r^{\kappa\dagger} b_s^\kappa - (\lambda_{pq,rs}^{(\kappa),0} + \lambda_{pq,rs}^{(\kappa),\kappa}) a_p^\dagger a_q b_r^{\kappa\dagger} b_s^\kappa \\ & + \frac{1}{2} g_{pqrs,tu}^\kappa a_p^\dagger a_r^\dagger a_s a_q b_t^{\kappa\dagger} b_u^\kappa - \frac{1}{2} d_{pqrs,tu}^\kappa a_p^\dagger a_r^\dagger a_s a_q b_t^{\kappa\dagger} b_u^\kappa. \end{aligned} \quad (79)$$

IV. CHOICE OF MOLECULAR ORBITALS

A. Relation to BH ansatz

Consider a molecular system with some choice of AO basis. We can construct a set of MOs $\psi_p(\mathbf{x}; \mathbf{X})$ and SD basis $\Psi_P(\mathbf{x}; \mathbf{X})$ in Eq. (34), which defines the electronic Hilbert space at each \mathbf{X} . While there are many schemes for generating MOs, the BH ansatz is completely defined by the AO basis alone. Any variation in MOs is just a linear rotation leading to the same solution of Eq. (24),

$$\tilde{\Psi}_P = \sum_Q C_{PQ}(\mathbf{X}) \Psi_Q(\mathbf{x}; \mathbf{X}). \quad (80)$$

This invariance to the choice of MOs is a very desirable feature, which is preserved in many approximate methods for solving the electronic SE. By definition, this extends to the molecular Hilbert space.

Solution to the molecular SE with BH ansatz can be expressed in SD basis using Eq. (80),

$$\begin{aligned} \tilde{\Psi}_{\text{mol}} &= \sum_P \sum_Q \tilde{C}_{Q,P} \Phi_Q(\mathbf{X}) \tilde{\Psi}_P(\mathbf{x}; \mathbf{X}) \\ &= \sum_P \sum_Q C'_{Q,P}(\mathbf{X}) \Phi_Q(\mathbf{X}) \Psi_P(\mathbf{x}; \mathbf{X}), \end{aligned} \quad (81)$$

where the new expansion coefficients, $C'_{Q,P}(\mathbf{X}) = \sum_R \tilde{C}_{Q,R} C_{RP}(\mathbf{X})$, are geometry dependent.

To understand the relation between BH and our ansatz, we can consider projection of $\tilde{\Psi}_{\text{mol}}$ onto our Hilbert space,

$$\begin{aligned} \Psi_{\text{mol}} &= \sum_P \sum_Q |\Psi_P, \Phi_Q\rangle \langle \Psi_P, \Phi_Q | \tilde{\Psi}_{\text{mol}} \rangle \\ &= \sum_P \sum_Q K_{Q,P} \Phi_Q(\mathbf{X}) \Psi_P(\mathbf{x}; \mathbf{X}), \end{aligned} \quad (82)$$

with

$$K_{Q,P} = \sum_R \langle \Phi_Q | C'_{R,P}(\mathbf{X}) | \Phi_R \rangle.$$

Due to geometric dependence of CI coefficients C' , the projection in Eq. (82) is exact only in the limit of a complete vibrational basis. As a consequence, our ansatz is not invariant to the choice of MOs.

The vibrational basis functions are playing a dual role, simultaneously describing the vibrational structure and any changes in CI coefficients due to choice of MOs and electron correlation. If there is an artificial strong geometry dependence of MOs, it would need a large vibrational basis to counteract it. This could be a big weakness in our approach if the wavefunction converges slowly with increasing vibrational basis. However, even in a finite basis the variational principle still holds when the full Hamiltonian is used.

At this point it is important to note that simply ignoring NKEC terms in our ansatz does not lead to the BO solutions, even in a complete basis. This is because truncation of the Hamiltonian breaks the variation principle, and different choices of MOs would lead to different Hamiltonians.

B. Canonical HF MOs

If we use real canonical HF MOs as our basis, we can express vector coupling terms in Eq. (41) analytically by applying generalised Hellman-Feynman theory⁷⁵

$$f_{pq}^{(\kappa)} = \frac{\langle \psi_p | \nabla_{\kappa} \mathcal{F} | \psi_q \rangle}{\epsilon_q - \epsilon_p}, \quad (83)$$

where \mathcal{F} is the Fock operator and ϵ are orbital energies. Clearly, the vector coupling terms once again diverge at degeneracies. However, the points of degeneracy for MOs are not necessarily the same as conical intersections with BO states.

We could of course choose a different set of MOs, for example by rotating the occupied and virtual orbitals among themselves. This could be done based on principles of locality or diabaticity.¹⁰ As we noted in previous section our ansatz is not invariant to the choice of MOs even with a fixed AO basis, and different MOs could have a varying rate of convergence with respect to vibrational basis. This requires a careful analysis which we defer to a later publication. In the current manuscript we use canonical MOs to investigate dependence on the size of vibrational basis.

V. APPLICATION TO C₂

The derivation of the second quantized Hamiltonian in Eqs. (77), (78) and (79) is formally exact. We have carried out the MBE only to the first level, but the same procedure can be applied to derive higher-level coupling terms. The main point which requires clarity is what effect the MOs have on the final solution. In Section IV A we have shown that our ansatz is not invariant to the choice of MOs unless the vibrational basis is complete. And, in Section IV B we discussed some potential instabilities in the Hamiltonian with canonical MOs. In this section, we address both points with a proof of concept application of our ansatz, testing how quickly the vibrational basis converges and whether there are any instabilities arising from NKEC terms.

The vibronic spectrum of C₂ presents an ideal test case. Ignoring coupling to rotations and translations, it is a 1-mode system, making the Hamiltonian in Eq. (77) exact within the basis set limit. Furthermore, the spectrum is complicated by an avoided crossing between the ground state $X^1\Sigma_g^+$ that couples non-adiabatically through the C–C stretch to excited state $B'^1\Sigma_g^+$.⁸³ The next excited state that can couple, $D^1\Sigma_g^+$, is high in energy and one expects that it can be ignored.⁸⁴ Thus we can use two-state BH ansatz as a reference to study the vibronic spectrum in the region of avoided crossing.

To measure the extent of NAC, we define a vibrational density matrix

$$\rho_{pq}^\kappa = \langle \Psi_{\text{mol}} | b_p^{\kappa\dagger} b_q^\kappa | \Psi_{\text{mol}} \rangle, \quad (84)$$

and since there is only one mode we will drop the superscript κ .

By analogy with natural orbitals in electronic structure theory, the eigenfunctions of ρ_{pq} provide the most compact vibrational basis for representation of Ψ_{mol} . The eigenvalues, σ , play a similar role to electronic natural orbital occupation numbers. If Ψ_{mol} can be represented as a simple product as in Eq. (28) then $\sigma = \{1, 0, 0, \dots\}$. Otherwise, there is more than one non-zero value and, since there is only one mode, this must be a result of NAC. Thus σ provides a direct measure of NAC that does not depend on electronic basis.

A. Reference calculations with Born-Huang ansatz

We used the cc-pVDZ AO basis⁸⁵ with only s and p functions. MOs were defined by solving the spin-restricted Hartree-Fock equations. The two lowest energy MOs were kept frozen, leaving 16 active MOs. The stationary states of the clamped nuclei Hamiltonian Eq. (24) were found by obtaining the eigensolutions of the Full CI problem, and the elements of the molecular Hamiltonian $H_{PQ}^{(e)}$ and Λ_{PQ} were constructed on a grid as a function of C–C distance, R_{CC} , with step size $\Delta R_{CC} = 0.01 \text{ \AA}$. The vector and scalar coupling terms, Eqs. (14) and (18), were calculated by finite difference with a 5-point stencil and a step size of 0.005 \AA . All electronic structure calculations were performed using PySCF⁸⁶ with modifications to include core orbitals in the overlap of FCI wavefunctions. The resultant surfaces are shown in Fig. 1.

We used C mass, $m_C = 12.011 \text{ u}$, equilibrium C–C bond length $R_{eq} = 1.2755 \text{ \AA}$, and normal mode coordinate

$$Q = (R_{CC} - R_{eq})/\sqrt{\mu} \quad (85)$$

where $\mu = m_C/2$ is the reduced mass.

The vibrational basis consisted of 101 distributed Gaussians,⁸⁷

$$\chi_\nu(Q) = \left(\frac{2\gamma}{\pi}\right)^{\frac{1}{4}} \exp[\gamma(Q - Q_\nu)^2], \quad (86)$$

using an equidistant grid from $\Delta R_{CC} = -0.3 \text{ \AA}$ to 1.0 \AA inclusive, and $\gamma = 1/\Delta Q^2 = 0.151358$, where ΔQ is the step size along the normal mode coordinate. This grid covers the region of the avoided crossing at around $\Delta R_{CC} = 0.5 \text{ \AA}$. The number of distributed Gaussians was chosen to converge the first 30 vibronic states to within 1 cm^{-1} .

An orthonormal set of vibrational basis functions, $\phi_p = \sum_\nu C_{\nu p} \chi_\nu$, was defined by solving the BO vibrational problem for the electronic ground state, Eq. (29). This basis was used with both Born-Huang and our ansätze.

The molecular Hamiltonian matrix was constructed by interpolating surfaces in Fig. 1 and numerically integrating matrix elements in Eq. (10). It was then diagonalised for the reference vibronic states. This procedure was done with *Mathematica*.⁸⁸

The vibronic states were assigned based on the population of electronic states. The ener-

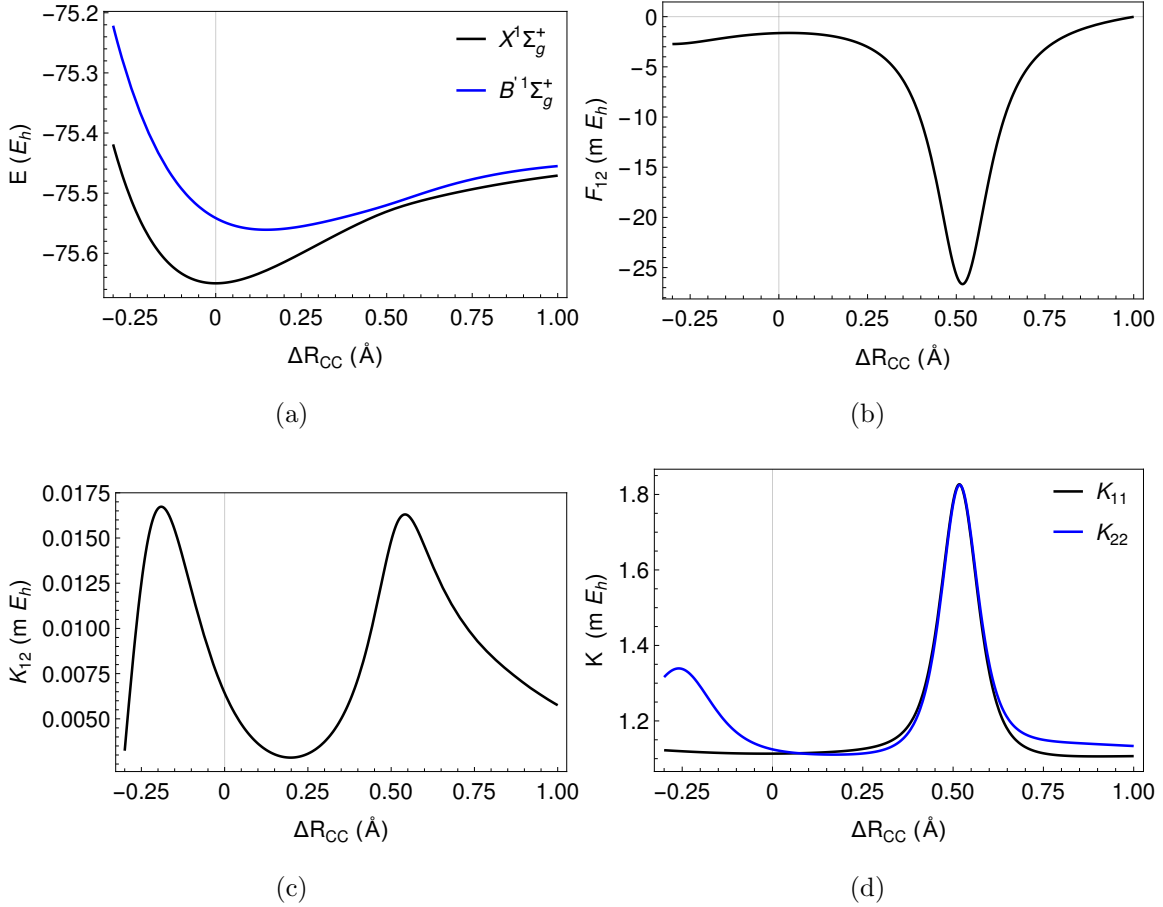


FIG. 1: Components of H_{mol} in Eq. (10) for C_2 with $\Delta R_{\text{CC}} = R_{\text{CC}} - R_{\text{eq}}$. (a) Potential energy surfaces, (b) F_{12} term in Eq. (14), (c) off-diagonal elements of K in Eq. (18), (d) diagonal elements of K in Eq. (18). Derivatives in F and K are with respect to Q in Eq. (85).

getic contributions from Λ were decomposed into DBOC, Eq. (30), O term, Eq. (21), and off-diagonal elements of K , Eq. (18). The first is just the adiabatic correction and the last two lead to non-adiabatic coupling. The level of non-adiabaticity was measured using eigenvalues, σ , of the vibrational density matrix, ρ_{pq} . Since there are only two electronic states there can be at most two non-zero eigenvalues. The results are summarised in Table I.

The first 19 states have relatively small non-adiabatic coupling, judging by values of σ . The DBOC is almost a constant offset in this region, within a few cm^{-1} . The last 10 states have strong non-adiabatic coupling which does not always map to a large contribution from the O term. The off-diagonal elements of K make a negligible contribution for all states. It is

TABLE I: Vibronic states of C_2 using Born-Huang ansatz, $M = 101$. The first column indicates state number, ν , with assignment in the footnote either to ground $X^1\Sigma_g^+$ or excited $B'^1\Sigma_g^+$ electronic states. The second column shows energy of each state relative to ground state energy at equilibrium, $E = -75.649896E_h$. Columns 3 and 5 show the energetic contributions (cm^{-1}) from diagonal and off-diagonal elements of K , respectively, and column 4 shows contributions from O term in Eq. (20). Columns 6 and 7 are the two largest eigenvalues of vibrational density matrix Eq. (84), ordered by magnitude.

ν	E/cm^{-1}	K_{PP}	O_{PQ}	K_{PQ}	σ_1	σ_2	ν	E/cm^{-1}	K_{PP}	O_{PQ}	K_{PQ}	σ_1	σ_2
1 ^a	920	122.2	0.0	0.0	1.00	0.00	16 ^a	21944	126.8	-10.5	0.0	1.00	0.00
2 ^a	2701	122.2	-0.1	0.0	1.00	0.00	17 ^b	22646	122.7	1.2	0.0	1.00	0.00
3 ^a	4457	122.3	-0.2	0.0	1.00	0.00	18 ^a	23345	129.3	-18.5	0.0	1.00	0.00
4 ^a	6186	122.4	-0.4	0.0	1.00	0.00	19 ^b	23831	123.4	3.4	0.0	1.00	0.00
5 ^a	7889	122.5	-0.5	0.0	1.00	0.00	20 ^a	24703	133.2	-35.9	0.0	0.98	0.02
6 ^a	9565	122.5	-0.7	0.0	1.00	0.00	21 ^b	24996	125.0	10.9	-0.0	0.99	0.01
7 ^a	11214	122.7	-0.9	0.0	1.00	0.00	22 ^a	25999	137.6	-77.2	0.1	0.86	0.14
8 ^a	12835	122.8	-1.1	0.0	1.00	0.00	23 ^b	26159	128.8	36.8	-0.1	0.87	0.13
9 ^a	14428	123.0	-1.5	0.0	1.00	0.00	24 ^b	27191	138.6	-107.2	0.1	0.54	0.46
10 ^a	15992	123.3	-2.0	0.0	1.00	0.00	25 ^a	27358	138.1	46.1	-0.1	0.53	0.47
11 ^a	17528	123.7	-2.9	0.0	1.00	0.00	26 ^b	28315	141.9	-112.0	0.1	0.67	0.33
12 ^a	19034	124.3	-4.2	0.0	1.00	0.00	27 ^a	28552	144.1	29.8	-0.1	0.65	0.35
13 ^b	20199	122.0	0.1	0.0	1.00	0.00	28 ^b	29425	145.8	-118.4	0.1	0.65	0.35
14 ^a	20507	125.2	-6.5	0.0	1.00	0.00	29 ^a	29691	144.5	23.2	0.0	0.62	0.38
15 ^b	21436	122.2	0.4	0.0	1.00	0.00	30 ^b	30534	147.0	-118.8	0.0	0.56	0.44

^a Dominant electronic state $X^1\Sigma_g^+$

^b Dominant electronic state $B'^1\Sigma_g^+$

important to note that the energies have almost no dependence on number of vibrational basis functions, M . For example, using the minimal basis, $M = \nu$, to calculate state ν leads to maximum error of 0.5 cm^{-1} with most deviations within 0.1 cm^{-1} . This is the benefit of using solutions of vibrational problem for the ground state as our basis.

B. Convergence of our ansatz with vibrational basis

We used the same MOs and vibrational basis in our ansatz as with BH calculations. The integrals f_{pq} and k_{pq} , in Eqs. (41) and (45), were calculated with finite difference of analytical MO overlaps. We used a 5-point stencil with a step size of $0.005 a_0$ along the normalised normal mode coordinate. They were evaluated on a grid and interpolated with a cubic spline using SciPy.⁸⁹ Integrals between distributed Gaussians were evaluated with 6 point Gauss-Hermite quadrature and an overlap threshold of 10^{-7} . During integration, elements of the electronic Hamiltonian Eq. (36) were calculated on the fly.

We implemented a general full CI procedure in our general configuration interaction (gci) code. The full CI vector is represented as contiguous blocks of electronic CI vectors with each block corresponding to a different vibrational basis function. This allows Hamiltonian operation on CI vector to be implemented as a nested loop over pairs of vibrational basis functions in the input and result vectors, followed by extraction of relevant electronic Hamiltonian, $\langle \Phi_{\mathbf{P}} | \hat{H}_{\text{mol}} | \Phi_{\mathbf{Q}} \rangle$, and using a standard routine for operation of electronic Hamiltonian on an electronic CI vector. The overall procedure can be easily parallelised over vibrational basis functions.

Using energies from the BH ansatz as a reference, we calculated differences from our ansatz with M vibrational basis functions. Results for the first and last 15 states are shown in Table II and Table III, respectively. Blank spaces indicate that M is too small to form a vibrational state ν on the electronic ground state $X^1\Sigma_g^+$, that is $\nu > M$. Note that this also applies to vibronic states which are assigned to an excited electronic state $B'^1\Sigma_g^+$, because the vibrational basis is ill-suited for those states and that fact overshadows any lack of invariance to the rotation of MOs that is the current focus.

Looking along each column, it is evident that the convergence is fairly rapid. Only a few extra basis functions are required to ensure convergence within 1 cm^{-1} . The errors due to vibrational basis incompleteness also reduce for higher energy states. This is presumably because the basis is already flexible enough. More localised vibronic states require smaller bases, as can be seen from rows $\nu = 13, 15$ in Table II. They are the vibrational ground and first excited states of $B'^1\Sigma_g^+$, which are both much more localised than for example state $\nu = 14$ in the same table.

TABLE II: Energy difference between vibronic states calculated with the Born-Huang ansatz and with our ansatz, $E^{\text{our}}(\nu, M) - E^{\text{BH}}(\nu)$, in cm^{-1} , for increasing vibrational basis set size, M .

ν	M							
	1	2	3	4	5	10	15	20
1	206.3	2.5	0.1	0.0	0.0	0.0	0.0	0.0
2		406.5	7.2	0.3	-0.1	-0.1	-0.1	-0.1
3			603.7	14.1	0.7	-0.2	-0.2	-0.2
4				799.8	23.0	-0.3	-0.3	-0.3
5					995.7	-0.3	-0.3	-0.3
6						-0.3	-0.4	-0.4
7						0.7	-0.5	-0.5
8						7.8	-0.6	-0.6
9						91.0	-0.6	-0.6
10						1965.0	-0.6	-0.7
11							0.3	-0.8
12							4.1	-0.8
13							0.0	0.0
14							29.9	-0.9
15							-0.1	-0.1

Table IV summarises converged results with our ansatz. It includes three eigenvalues of vibrational density matrix, because this ansatz is not limited to just two electronic states. It is evident that a third state becomes significant at higher energies. There is a close energetic agreement with maximum difference of 1.1 cm^{-1} . The small difference is not surprising, since the BH ansatz only contains two electronic states and our ansatz is in the full space. We used a minimal AO basis to explore how the agreement improves when more electronic states are included in the BH ansatz (see Supplementary Material). With two states, the energy differences are very similar with maximum deviation of 1.1 cm^{-1} and root-mean-squared-deviation (RMSD) of 0.7 cm^{-1} . The RMSD reduces down to 0.3 cm^{-1} with four states,

TABLE III: Energy difference between vibronic states calculated with the Born-Huang ansatz and with our ansatz, $E^{\text{our}}(\nu, M) - E^{\text{BH}}(\nu)$, in cm^{-1} , for increasing vibrational basis set size, M .

ν	M			
	20	25	30	35
16	-0.7	-1.0	-1.0	-1.0
17	-0.2	-0.2	-0.2	-0.2
18	0.3	-1.0	-1.1	-1.1
19	-0.3	-0.3	-0.3	-0.3
20	5.0	-1.1	-1.1	-1.1
21		-0.3	-0.3	-0.3
22		-1.0	-1.2	-1.2
23		-0.4	-0.4	-0.4
24		-0.6	-1.1	-1.1
25		0.0	-0.6	-0.6
26			-1.0	-1.1
27			-0.7	-0.8
28			-1.0	-1.1
29			-0.7	-0.9
30			32.4	-1.1

which shows that the deviation is due to different electronic spaces.

It is interesting to note that all NKEC terms lead to an almost constant offset and, except for k^0 , are generally quite small. In this respect, canonical MOs form a more stable basis than the BH ansatz, which shows a more chaotic energy decomposition in Table I due to the avoided crossing.

We repeated the calculations without any NKEC terms in the Hamiltonian. Table V shows how the energies relative to ground state with this approximation compare to those with BH ansatz. There is an excellent energetic agreement and the σ values are consistent with results

TABLE IV: Vibronic states of C_2 using our ansatz, $M = 35$. The first column indicates state number, ν ; the second column shows the energy difference relative to the Born-Huang ansatz, $\Delta E(\nu) = E^{\text{our}}(\nu) - E^{\text{BH}}(\nu)$. Later columns show energetic contributions from different terms in Eqs. (78) and (79). The last three columns show the largest eigenvalues of vibrational density matrix Eq. (84), ordered by magnitude.

ν	$\Delta E/\text{cm}^{-1}$	k^0	k^1	λ	d^0	d^1	σ_1	σ_2	σ_3
1	0.0	122.3	0.0	-1.9	-0.2	0.0	1.00	0.00	0.00
2	-0.1	122.3	0.0	-2.0	-0.2	0.0	1.00	0.00	0.00
3	-0.2	122.3	0.1	-2.1	-0.2	0.0	0.99	0.01	0.00
4	-0.3	122.2	0.1	-2.2	-0.2	0.0	0.99	0.01	0.00
5	-0.3	122.2	0.2	-2.3	-0.2	0.0	0.99	0.01	0.00
6	-0.4	122.2	0.2	-2.3	-0.2	0.0	0.99	0.01	0.00
7	-0.5	122.2	0.2	-2.4	-0.2	0.0	0.99	0.01	0.00
8	-0.6	122.2	0.3	-2.4	-0.2	-0.1	0.98	0.02	0.00
9	-0.6	122.2	0.3	-2.5	-0.2	-0.1	0.98	0.02	0.00
10	-0.7	122.2	0.3	-2.5	-0.2	-0.1	0.98	0.02	0.00
11	-0.8	122.2	0.3	-2.5	-0.2	-0.1	0.97	0.03	0.00
12	-0.9	122.2	0.3	-2.5	-0.2	-0.1	0.97	0.03	0.00
13	0.0	122.8	1.4	-1.6	-2.5	-0.7	1.00	0.00	0.00
14	-0.9	122.2	0.3	-2.5	-0.2	-0.1	0.97	0.03	0.00
15	-0.1	122.8	1.4	-1.6	-2.5	-0.7	0.99	0.01	0.00
16	-1.0	122.2	0.2	-2.4	-0.3	-0.1	0.96	0.04	0.00
17	-0.2	122.8	1.3	-1.6	-2.5	-0.7	0.99	0.01	0.00
18	-1.1	122.2	0.2	-2.4	-0.3	-0.1	0.95	0.05	0.00
19	-0.3	122.7	1.2	-1.6	-2.5	-0.7	0.98	0.02	0.00
20	-1.1	122.2	0.3	-2.3	-0.4	-0.1	0.92	0.07	0.01
21	-0.3	122.7	1.1	-1.6	-2.4	-0.6	0.96	0.03	0.01
22	-1.2	122.3	0.3	-2.0	-0.7	-0.2	0.78	0.19	0.02
23	-0.4	122.6	0.9	-1.8	-2.1	-0.5	0.83	0.15	0.01
24	-1.1	122.5	0.6	-1.7	-1.5	-0.4	0.58	0.40	0.01
25	-0.6	122.4	0.6	-2.1	-1.3	-0.3	0.54	0.43	0.02
26	-1.1	122.5	0.6	-1.7	-1.8	-0.4	0.69	0.28	0.02
27	-0.8	122.4	0.5	-2.0	-1.2	-0.3	0.63	0.34	0.02
28	-1.1	122.5	0.5	-1.8	-1.6	-0.4	0.66	0.31	0.02
29	-0.9	122.4	0.5	-1.8	-1.4	-0.3	0.64	0.33	0.02
30	-1.1	122.4	0.4	-1.9	-1.3	-0.3	0.61	0.36	0.02

from the full Hamiltonian in Table IV, indicating that the wavefunction did not deteriorate.

TABLE V: Difference in vibronic spectrum with $M = 35$ and NKEC terms ignored in our ansatz, $\Delta E(\nu) = (E^{\text{our}}(\nu) - E^{\text{our}}(\nu = 1)) - (E^{\text{BH}}(\nu) - E^{\text{BH}}(\nu = 1))$. The last three columns show largest eigenvalues of vibrational density matrix Eq. (84), ordered by magnitude.

ν	$\Delta E/\text{cm}^{-1}$	σ_1	σ_2	σ_3
1	0.0	1.00	0.00	0.00
2	0.0	1.00	0.00	0.00
3	0.0	0.99	0.01	0.00
4	0.0	0.99	0.01	0.00
5	0.0	0.99	0.01	0.00
6	0.0	0.99	0.01	0.00
7	0.0	0.99	0.01	0.00
8	0.0	0.98	0.02	0.00
9	0.0	0.98	0.02	0.00
10	0.0	0.98	0.02	0.00
11	-0.0	0.97	0.03	0.00
12	-0.1	0.97	0.03	0.00
13	0.8	1.00	0.00	0.00
14	-0.1	0.97	0.03	0.00
15	0.9	0.99	0.01	0.00
16	-0.1	0.96	0.04	0.00
17	0.9	0.99	0.01	0.00
18	-0.2	0.95	0.05	0.00
19	0.9	0.98	0.02	0.00
20	-0.2	0.92	0.07	0.01
21	1.0	0.96	0.03	0.01
22	-0.2	0.78	0.19	0.02
23	0.9	0.83	0.15	0.01
24	0.3	0.58	0.40	0.01
25	0.5	0.54	0.43	0.02
26	0.5	0.69	0.28	0.02
27	0.3	0.63	0.34	0.02
28	0.5	0.66	0.31	0.02
29	0.3	0.64	0.33	0.02
30	0.4	0.61	0.36	0.02

VI. CONCLUSIONS

In this paper, we have introduced a new computational framework for treating molecular quantum mechanics without the Born-Oppenheimer approximation. The assumption of the

conventional Born-Huang approach, that an accurate non-adiabatic treatment can be obtained with just a few clamped-nucleus states, is removed by construction. Additionally, the method avoids instabilities in the Hamiltonian matrix elements and need for diabatisation, by adopting a more flexible choice of electronic basis. Instead of requiring that adiabatic states exactly reproduce the static electronic structure at all geometries, as in the Born-Huang ansatz, we only require that the mean-field structure is captured, by using a basis of Slater determinants. These advantages come at the cost of introducing a very large combined electron-nuclear tensor-product space in which the wavefunction is expanded, and the cost of solving the full configuration interaction problem in this space is even greater than the similarly-factorial-scaling electronic full CI. The scaling with vibrational degrees of freedom can be reduced somewhat by using a truncated many-body expansion. We derived a fully second quantized molecular Hamiltonian in Eqs. (77), (78), (79) with single particle creation/annihilation operators for electrons and different vibrational modes. It lays the foundation for polynomial-scaling approximations to the tensor-product space formalism, similar to conventional approaches to electronic structure such as coupled-cluster and many-body perturbation theories. We have presented a proof-of-principle example where there is only one vibrational mode but significant non-adiabatic effects, and have shown that the tensor-product framework yields additional characterisation of the vibronic interaction via the vibrational reduced density matrix. Future efforts will focus on realising practical approximations that can be deployed on larger molecules.

SUPPLEMENTARY MATERIAL

See Supplementary Material for vibronic spectrum calculations using a minimal AO basis with up to 4 states in the BH ansatz.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

Appendix A: Frozen Core Approximation

After quantizing electronic degrees of freedom, we can adopt a frozen core Hamiltonian by including the effect of fixed doubly occupied core orbitals.^{90–92} In the following we assume there are n_c core orbitals and use letters i, j for their indices. Spin summation over core orbitals is also carried out.

Freezing core orbitals leaves the Hamiltonian of the same form as in Eq. (51), but core orbitals are excluded from the summation; the modified energy h_0^c is used instead of h_0 ,

$$h_0^c = 2 \sum_i^{n_c} (h_{ii} + k_{ii}) + \sum_{ij}^{n_c} (2g_{iijj} - g_{ijji} - d_{ijji}), \quad (\text{A1})$$

and modified core integrals h_{pq}^c are used instead of h_{pq} ,

$$h_{pq}^c = h_{pq} + k_{pq} + \sum_i^{n_c} (2g_{iipq} - g_{iqpi} - d_{iqpi}). \quad (\text{A2})$$

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