I. INTRODUCTION

Density functional approximations (DFAs) based on many-body perturbation techniques may offer solutions to some of the challenges high density functional approximations continue to face. Commonly used local, semi-local, and hybrid density functionals still face challenges when it comes to describing long-range interactions, static correlation, and electron delocalization. Density functionals of both the occupied and virtual orbitals are able to address these problems. The particle-hole (ph-) Random Phase Approximation (RPA), a functional of occupied and virtual orbitals, has recently known a revival within the density functional theory community. Following up on an idea introduced in our recent communication [H. van Aggelen, Y. Yang, and W. Yang, Phys. Rev. A 88, 030501 (2013)], we formulate more general adiabatic connections for the correlation energy in terms of pairing matrix fluctuations described by the particle-particle (pp-) propagator. With numerical examples of the pp-RPA, the lowest-order approximation to the pp-propagator, we illustrate the potential of density functional approximations based on pairing matrix fluctuations. The pp-RPA is size-extensive, self-interaction free, fully anti-symmetric, describes the strong static correlation limit in H2, and eliminates delocalization errors in H2 and other single-bond systems. It gives surprisingly good non-bonded interaction energies — competitive with the ph-RPA — with the correct R−6 asymptotic decay as a function of the separation R, which we argue is mainly attributable to its correct second-order energy term. While the pp-RPA tends to underestimate absolute correlation energies, it gives good relative energies: much better atomicization energies than the ph-RPA, as it has no tendency to underbind, and reaction energies of similar quality. The adiabatic connection in terms of pairing matrix fluctuation paves the way for promising new density functional approximations. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4865816]
we formulate is similar in form to the well-known ACFD theorem. It is in principle exact. It thus provides a basis for developing density functional approximations based on pairing matrix fluctuations. The most straightforward approximation is the pp-RPA,17,29 the lowest-order approximation to the pp-propagator. As Sec. II illustrates, it is similar in form to the ph-RPA. The pp-RPA is a well-known technique to describe nuclear many-body effects,29 but in contrast to the ph-RPA it has not received much attention within the DFT community. Like the ph-RPA, the pp-RPA can be viewed as an alternative formulation of a coupled-cluster method: the pp-RPA correlation energy amounts to the sum of all ladder diagrams.17 As such, it is equivalent to coupled-cluster doubles (CCD) restricted to ladder diagrams.30–32 Although the adiabatic connection we formulate lays the foundations for a wealth of approximations based on pairing matrix fluctuations, we will take the pp-RPA to be a representative of density functional approximations based on pairing matrix fluctuations and the ph-RPA as a representative of functionals based on density fluctuations. Section IV illustrates some of the main differences between the two types of RPA with numerical examples.

II. PAIRING MATRIX FLUCTUATIONS AND THE ADIABATIC CONNECTION

A. Pairing matrix fluctuations

The particle-particle propagator describes instantaneous pairing matrix fluctuations. For a system with a fixed number of electrons $N$, for which $\langle \hat{N}^2 \rangle = \langle \hat{N} \rangle^2$, the pairing matrix $\kappa$ is identically zero, because it involves components of the wavefunction with different electron numbers,

$$\kappa_{ij} = \langle \Psi_0 | a_i a_j | \Psi_0 \rangle.$$  

Although most quantum chemical methods restrict themselves to eigenstates of the electron number operator $\hat{N}$, it may be beneficial to break particle number symmetry while preserving the electron number expectation value, $\langle \hat{N} \rangle = N$.16 In its time-dependent form, the retarded particle-particle (pp-) propagator,

$$\tilde{K}_{ijkl}(t - t') = \frac{-i}{\hbar} \theta(t - t') \langle \Psi_0 \bigl[ (a_{H_i}(t) a_{H_j}(t), a_{H_k}^\dagger(t') a_{H_l}^\dagger(t')) \bigl] \Psi_0 \rangle,$$  

(1)

describes the response of the pairing matrix to a perturbation in the form of a pairing field, $\bar{F}(t) = \sum_{kl} f_{kl}(t) a_{H_k}^\dagger(t) a_{H_l}^\dagger(t)$. The operators $a_{H_i}^\dagger(t)$ are the creation operators in the Heisenberg picture, $a_{H_i}^\dagger(t) = e^{i[H - \nu \hat{N}] t} a_{H_i}^\dagger e^{-i[H - \nu \hat{N}] t}$ and the term $-\nu \hat{N}$, with $\nu$ the chemical potential, is added to the Hamiltonian such that the N-electron state is the minimum under the total Hamiltonian $\bar{H} - \nu \hat{N}$ when the particle number is allowed to change. Under the influence of such a pairing perturbation, the pairing matrix no longer vanishes, and its change is described by the pp-propagator in the linear response regime,

$$\kappa_{ij}(t) = \frac{-i}{\hbar} \int_{-\infty}^{+\infty} \langle \Psi_0^N \bigl[ \langle a_{H_i}(t) a_{H_j}(t), \bar{F}_H(t') \rangle \bigl] \Psi_0^N \rangle dt'$$

$$= \int_{-\infty}^{+\infty} \sum_{kl} \tilde{K}(t - t') \kappa_{kl}(t') dt',$$

where $\bar{F}_H(t) = \sum_{kl} f_{kl}(t) a_{H_k}^\dagger(t) a_{H_l}^\dagger(t) \theta(t)$ is the Heisenberg form of the pairing field. Since the pairing matrix vanishes for the N-electron ground state, the particle-particle propagator completely describes the dynamic fluctuation of the pairing matrix, i.e.,

$$\tilde{K}_{ijkl}(t - t') = \frac{-i}{\hbar} \theta(t - t') \langle \Psi_0^N \bigl[ (a_{H_i}(t) a_{H_j}(t) - \langle a_i a_j \rangle),$$

$$a_{H_k}^\dagger(t') a_{H_l}^\dagger(t') - \langle a_i a_j \rangle) \bigl] \Psi_0^N \rangle.$$  

From its Fourier transform to the energy domain it is apparent that the retarded particle-particle propagator characterizes double electron addition and ionization processes,

$$\tilde{K}(E)_{ijkl} = \int_{-\infty}^{+\infty} e^{\frac{iE}{\hbar}(t - t')} \tilde{K}_{ijkl}(t - t') dt$$

$$= \sum_n \frac{\langle \Psi_0^N | a_i a_j | \Psi_n^N + 2 \rangle \langle \Psi_n^N + 2 | a_k a_l^\dagger | \Psi_0^N \rangle}{E - \omega_n^{N+2} + i\eta}$$

$$- \sum_n \frac{\langle \Psi_0^N | a_i a_k^\dagger | \Psi_n^N - 2 \rangle \langle \Psi_n^N - 2 | a_j a_l^\dagger | \Psi_0^N \rangle}{E - \omega_n^{N-2} + i\eta},$$  

(2)

since its poles determine the double electron addition and ionization energies, $\omega_n^{N+2} = E_n^{N+2} - E_0^N - 2\nu$ and $\omega_n^{N-2} = E_n^{N-2} - E_0^N - 2\nu$, and the residues determine the corresponding transition amplitudes. These properties of the pp-propagator have been used to compute Auger spectra, which involve double ionization processes, with the pp-RPA.35,34 The time-ordered pp-propagator $\tilde{K}$,

$$K_{ijkl}(t - t') = \frac{-i}{\hbar} \langle \Psi_0^N \bigl[ T[a_{H_i}(t) a_{H_j}(t) a_{H_k}^\dagger(t') a_{H_l}^\dagger(t')] \bigl] \Psi_0^N \rangle$$

with $T$ the time-ordering operator, differs only from the retarded propagator $\tilde{K}$ in the position of its poles in the negative real plane,

$$K_{ijkl}(E) = \int_{-\infty}^{+\infty} e^{\frac{iE}{\hbar}(t - t')} K_{ijkl}(t - t') dt$$

$$= \sum_n \frac{\langle \Psi_0^N | a_i a_j | \Psi_n^{N+2} \rangle \langle \Psi_n^{N+2} | a_k a_l^\dagger | \Psi_0^N \rangle}{E - \omega_n^{N+2} + i\eta}$$

$$- \sum_n \frac{\langle \Psi_0^N | a_i a_k^\dagger | \Psi_n^{N-2} \rangle \langle \Psi_n^{N-2} | a_j a_l^\dagger | \Psi_0^N \rangle}{E - \omega_n^{N-2} - i\eta}.$$  

(3)

The retarded and time-ordered propagator therefore carry much of the same physical information. However, as is the case with the linear response, it is often more convenient to adopt the time-ordered propagator to which the methodology of many-body perturbation theory applies.35
For a non-interacting reference wavefunction, the particle-particle propagator $K^0$ becomes

$$K^0_{ijkl}(E) = \delta_{ik}\delta_{jl} \frac{\theta(i - F)\theta(j - F) - \delta_{ij}\theta(F - j)}{E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \delta_{ij}\delta_{jl} \frac{\theta(F - i)\theta(F - j)}{E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta},$$

where $F$ denotes the Fermi level and $\theta$ the Heaviside function, so the left term generates particle-particle terms and the right term generates hole-hole terms. As the pp-propagator is antisymmetric under the exchange of two electrons, $K^0_{ijkl}(E) = -K^0_{jikl}(E)$, we have used here (and in the following) an antisymmetric basis in which the two-particle indices $ij$ are restricted, $i < j$. The non-interacting propagator is the particle-particle propagator in the uncorrelated limit, and provides a basis in which the exact propagator is approximated in many-body perturbation theory. The adiabatic connection is particularly valuable in this context, as it forms an energetic link between the exact, fully interacting, system described by $K$ and the non-interacting reference system described by $K^0$.

### B. Adiabatic connections in terms of pairing matrix fluctuations

The pp-propagator describes pairing matrix fluctuations and, similar to the well-known ACFD theorem, pairing matrix fluctuations determine the correlation energy via the adiabatic connection. We formulate such an adiabatic connection in this section. It relates the linear response of a system under an external pairing perturbation to its correlation energy in equilibrium and is therefore also a type of fluctuation-dissipation theorem.

The energy of a system involving at most two-particle interactions is determined by its second order density matrix $\Gamma$,

$$\Gamma_{ijkl} = \langle \Psi_0^N | a_i^\dagger a_j^\dagger a_k a_l | \Psi_0^N \rangle = \sum_n \langle \Psi_0^N | a_i^\dagger a_j^\dagger | \Psi_n^{N-2} \rangle \langle \Psi_n^{N-2} | a_k a_l | \Psi_0^N \rangle,$$

but it can also be formulated in terms of other second-order metric matrices, like the G-matrix $G$,

$$G_{ijkl} = \langle \Psi_0^N | a_i^\dagger a_j^\dagger a_k a_l | \Psi_0^N \rangle = \sum_n \langle \Psi_0^N | a_i^\dagger a_j^\dagger | \Psi_n^N \rangle \langle \Psi_n^N | a_k a_l | \Psi_0^N \rangle,$$

In the second line in Eqs. (5) and (6) we have used the completeness of the basis to make the relationship between these second-order metric matrices and the residues of the propagators (such as Eq. (3)) more apparent. All such second-order metric matrices are linearly interrelated via the anticommutation relationships of the creation and annihilation operators; for instance $\Gamma_{ijkl} = -G_{iklj} + \delta_{ij}\gamma_{lk} = G_{iklj} - \delta_{ij}\gamma_{lk}$, where $\gamma_{lk}$ is the first-order density matrix, $\gamma_{ij} = \langle \Psi_0^N | a_i^\dagger a_j^\dagger | \Psi_0^N \rangle$. As a consequence, the adiabatic connection can be formulated equivalently in terms of $G$ and $\Gamma$. The adiabatic connection path is defined by the Hamiltonian $\tilde{H}_\lambda$,

$$\tilde{H}_\lambda = \tilde{h} + \tilde{u}_\lambda + \lambda \tilde{V},$$

where $\tilde{h} = i + \vec{v}_{ext}$ and $\tilde{u}_\lambda$ is so far only specified in the limits $\lambda = 0$ and $\lambda = 1$: $\tilde{u}_0$ is the effective potential that defines the non-interacting reference system and $\tilde{u}_1 = 0$. This ensures that $\tilde{H}_0$ corresponds to the non-interacting Hamiltonian $\hat{H}_0$ when $\lambda = 0$ and to the physical Hamiltonian $\hat{H}$ when $\lambda = 1$. The adiabatic connection is then

$$E - E^0 = \int_0^1 \langle \psi^\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \psi^\lambda \rangle d\lambda = \int_0^1 \vec{V} \gamma^\lambda d\lambda + \int_0^1 \frac{\partial u^\lambda}{\partial \lambda} \gamma^\lambda d\lambda,$$

where

$$E^0 = \langle \psi^0 | \hat{H}_0 | \psi^0 \rangle = \text{tr} (\hat{h} + u_0) \gamma^0.$$

Using the exact exchange functional,

$$E^{HF}[\gamma^0] = \langle \psi^0 | \hat{H} | \psi^0 \rangle = \int_0^1 \vec{V} \gamma^0 d\lambda + \text{tr} \hat{h} \gamma^0,$$

as a reference, the correlation energy $E^c \equiv E - E^{HF}[\gamma^0]$ becomes

$$E^c = \int_0^1 \vec{V} (\Gamma^\lambda - \Gamma^0) d\lambda + \text{tr} u_0 \gamma^0 + \int_0^1 \frac{\partial u^\lambda}{\partial \lambda} \gamma^\lambda d\lambda.$$

Given the linear relation between the second order density matrix and the G-matrix, this gives rise to two equivalent formulae for the correlation energy:

$$E^c = \text{tr} \int_0^1 \vec{V} (\Gamma^\lambda - \Gamma^0) d\lambda + \text{tr} u_0 \gamma^0 + \int_0^1 \frac{\partial u^\lambda}{\partial \lambda} \gamma^\lambda d\lambda,$$

and

$$E^c = \text{tr} \int_0^1 \vec{V} (G^\lambda - G^0) d\lambda - \sum_{ijkl} \int_0^1 (ij|kl) (\gamma^\lambda_{ik} - \gamma^0_{ik}) d\lambda + \text{tr} u_0 \gamma^0 + \int_0^1 \frac{\partial u^\lambda}{\partial \lambda} \gamma^\lambda d\lambda,$$

where

$$\langle ij|kl \rangle = \int \frac{\phi_i^*(x_1)\phi_j^*(x_2)\phi_k(x_1)\phi_l(x_2)}{|r_1 - r_2|} d x_1 d x_2.$$
1. **Constant-density adiabatic connection path**

The potential $\hat{u}_\lambda(r)$ can be a local potential, chosen so that the density remains constant along the adiabatic connection path, $\rho^0 = \rho^1 = \rho$, as in the formulation by Langreth and Perdew.\(^{14}\) Equations (8) and (9) can then be simplified, because

$$
\text{tr } \mathbf{u}_0 \mathbf{V}^0 + \text{tr } \int_0^1 \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \mathbf{V} \, d\lambda = \text{tr } \mathbf{u}_0 \rho + \text{tr } (\mathbf{u}_1 - \mathbf{u}_0) \rho = 0
$$

(10)

vanishes as $\hat{u}_1 = 0$ to be consistent with the physical Hamiltonian (Eq. (7)). The adiabatic connections (Eqs. (8) and (9)) then reduce to

$$
E^c = \text{tr } \int_0^1 \mathbf{V}(\Gamma^\lambda - \Gamma^0) d\lambda
$$

(11) and

$$
E^c = \text{tr } \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G}^0) d\lambda.
$$

(12)

The G-matrix can be derived from the polarization propagator $\Pi$, which describes density fluctuations

$$
\Pi(E)_{ijkl} = \sum_{n \neq 0} \frac{\langle \Psi^N_n \mid a_i^\dagger a_j \mid \Psi^N_{n'} \rangle \langle \Psi^N_{n'} \mid a_k^\dagger a_l \mid \Psi^N_n \rangle}{E - E_n + i\eta}
$$

$$
- \sum_{n \neq 0} \frac{\langle \Psi^N_n \mid a_i^\dagger a_j \mid \Psi^N_{n'} \rangle \langle \Psi^N_{n'} \mid a_k^\dagger a_l \mid \Psi^N_n \rangle}{E + E_n - i\eta}
$$

resulting in the well-known ACFD theorem

$$
E^c = \text{tr } \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G}^0) d\lambda
$$

$$
= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-E\eta} \text{tr } \mathbf{V}[\Pi^\lambda(E) - \Pi^0(E)] dE d\lambda.
$$

(13)

$$
= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-E\eta} \int dxdx' \times \int \frac{\Pi^\lambda(x, x', E) - \Pi^0(x, x', E)}{|r - r'|} dEd\lambda.
$$

(14)

This equation has been extensively used in conjunction with the ph-RPA, the lowest-order approximation to the polarization propagator $\Pi$. The second-order density matrix can be derived from the pp-propagator (3), resulting in an equivalent adiabatic connection for the correlation energy in terms of pairing matrix fluctuations:

$$
E^c = \text{tr } \int_0^1 \mathbf{V}(\Gamma^\lambda - \Gamma^0) d\lambda
$$

$$
= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{E\eta} \text{tr } \mathbf{V}[\mathbf{K}^\lambda(E) - \mathbf{K}^0(E)] dE d\lambda.
$$

(15)

$$
= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{E\eta} \times \int dxdx' \frac{\mathbf{K}^\lambda(x, x', E) - \mathbf{K}^0(x, x', E)}{|r - r'|} dE.
$$

(16)

This adiabatic connection formulates the correlation energy in terms of dynamic pairing matrix fluctuations and is therefore also a fluctuation-dissipation theorem.

2. **Harris-Jones adiabatic connection path**

The Harris-Jones adiabatic connection provides an alternative to the constant-density adiabatic connection.\(^{36}\) The potential $\hat{u}_\lambda$ is local and linear in lambda, $\hat{u}_\lambda = (1 - \lambda)\hat{u}_0$, such that $H_\lambda = \hat{H} + (1 - \lambda)\hat{u}_0 + \lambda \tilde{V}$. The density is not constrained except at the end points, $\rho^0 = \rho^1$. The one-electron part in Eqs. (8) and (9) is then

$$
\text{tr } \mathbf{u}_0 \mathbf{V}^0 + \text{tr } \int_0^1 \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \mathbf{V} \, d\lambda = -\text{tr } \int_0^1 \mathbf{u}_0 (\rho^\lambda - \rho^0) d\lambda,
$$

so that Eqs. (8) and (9) reduce to

$$
E^c = \text{tr } \int_0^1 \mathbf{V}(\Gamma^\lambda - \Gamma^0) d\lambda - \text{tr } \int_0^1 \mathbf{u}_0 (\rho^\lambda - \rho^0) d\lambda,
$$

(17)

$$
E^c = \text{tr } \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G}^0) d\lambda - \sum_{ij} \int_0^1 \langle \psi^i_k | \psi^j_l \rangle (\gamma^i_{jk} - \gamma^0_{jk}) d\lambda
$$

$$
- \text{tr } \int_0^1 \mathbf{u}_0 (\rho^\lambda - \rho^0) d\lambda,
$$

(18)

where the density changes along the adiabatic connection path.

3. **Linear adiabatic connection path without density constraints**

The linear adiabatic connection path $\hat{u}_\lambda = (1 - \lambda)\hat{u}_0$ can also be used with a – possibly non-local – potential $\hat{u}_0$ for which $\rho^0 \neq \rho^1$. This makes it possible to establish an adiabatic connection between the interacting system and any uncorrelated reference:

$$
E^c = \text{tr } \int_0^1 \mathbf{V}(\Gamma^\lambda - \Gamma^0) d\lambda - \text{tr } \int_0^1 \mathbf{u}_0 (\gamma^\lambda - \gamma^0) d\lambda,
$$

(19)

$$
E^c = \text{tr } \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G}^0) d\lambda - \sum_{ij} \int_0^1 \langle \psi^i_k | \psi^j_l \rangle (\gamma^i_{jk} - \gamma^0_{jk}) d\lambda
$$

$$
- \text{tr } \int_0^1 \mathbf{u}_0 (\gamma^\lambda - \gamma^0) d\lambda.
$$

(20)

In contrast to the constant-density or the Harris-Jones adiabatic connection, which requires the exact KS reference potential to satisfy the density constraint $\rho^0 = \rho^1$, this adiabatic connection is valid for any non-interacting reference.

4. **Generalized adiabatic connection paths**

The linear dependence of the Hamiltonian Eq. (7) on the interaction strength can be further generalized: the electron-electron interaction may have a nonlinear dependence on the interaction strength $\lambda$.\(^{37}\) As long as the end points 0 and $b$ correspond to the non-interacting reference system and the fully interacting system,\(^{37}\) Assuming the form $\hat{H} = \hat{h} + \hat{u}_\lambda$.
5. Numerical illustrations on the adiabatic connection in terms of pairing matrix fluctuations

From a practical point of view, the constant-density adiabatic connection path is most useful as it only requires knowledge of the pp-propagator $K^k$ along the adiabatic connection path. We will use this form of the adiabatic connection in the numerical illustrations of the lowest-order approximation to the pp-propagator, the particle-particle random phase approximation in Sec. IV. We will analyze the pp-RPA energy contribution along the adiabatic connection, given by $U(\lambda)$,

$$U(\lambda)^{pp} = \text{tr} \mathbf{V}(\Gamma^k - \Gamma^0)$$

such that the area under the graph of $U(\lambda)$ represents the correlation energy, $E^c = \int_0^\lambda U(\lambda) d\lambda$. In the above equation $\chi_{ij}^{n,-2} = \langle \Psi_n^N | a_i a_j | \Psi_0^N \rangle$. For comparison, we will show analogous plots for the ph-RPA correlation energy,

$$U(\lambda)^{pb} = \text{tr} \tilde{\mathbf{V}}(\Gamma^k - \mathbf{G}^0)$$

where the density is assumed to be constant, just like in the pp-RPA and ph-RPA calculation, although this assumption is not generally valid. Unless the density is explicitly constrained along the adiabatic connection path, it changes with the interaction strength, and only expression (19) is exact in this case. We therefore also present v2DM reference calculations using expression (19)

$$U(\lambda)^{v2DM} = \text{tr} \mathbf{V}(\Gamma^k - \Gamma^0).$$

Since this adiabatic connection makes no assumption on the density along the path and the two-positivity conditions are exact for two-electron systems, Eq. (28) yields exact reference values for two-electron systems and generally very accurate values for three- and four-electron systems. Note that the exact $U(\lambda)$ along this adiabatic connection path is not necessarily convex, unlike $U(\lambda)$ along the constant-density adiabatic connection path. The pp-RPA adiabatic connection path is illustrated and further discussed in Figures 1–5 and Sec. IV.

C. The particle-particle random phase approximation

The adiabatic connection (16) is in principle exact, but – just like the adiabatic connection in terms of the polarization propagator – it requires an expression for the pp-propagator at each interaction strength. The pp-RPA is the most straightforward approximation to the pp-propagator; it makes the propagator’s dependence on the interaction strength explicit. It approximates the interacting propagator $K$, Eq. (3), in terms of the uncorrelated propagator $K^0$, Eq. (4), in the form of a
Dyson-like equation, similar in form to the ph-RPA,
\[
K^i(E) = K^0(E) + \lambda K^0(E) V K^i(E),
\tag{29}
\]
where all operators are expressed in an anti-symmetrical basis with restricted two-particle indices \(ij\) for which \(i < j\). Since the non-interacting propagator \(K^0\) only has particle-particle and hole-hole terms the dimension of the matrices \(K^0\) and \(K\) in the pp-RPA is \(\frac{N(N-1)}{2}(N-1)\), where \(N\) is the number of holes (occupied orbitals) and \(v\) is the number of particles (virtual orbitals). The Dyson-like approximation (29) makes it possible to carry out the lambda-integration in (16) analytically and write the correlation energy in closed form by recognizing that the Dyson-like equation generates an infinite series equivalent to the Taylor expansion for \(\ln(I - K^0V)\):
\[
E_{pp}^c = -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} \lambda \frac{d}{d\lambda} \left[ \text{tr} \left( K^i(E) V - K^0(E) V K^i(E) \right) \right] d\lambda
= -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} \lambda \frac{d}{d\lambda} \left[ \text{tr} \left( K^0V \right) \right] d\lambda
= -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} \sum_{n=2}^{\infty} \lambda^{n-1} \text{tr} \left[ (K^0V)^n \right] d\lambda
= \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \sum_{n=2}^{\infty} \frac{1}{n} \text{tr} \left[ (K^0V)^n \right] dE
\tag{30}
\]
This is just one way to characterize the pp-RPA correlation energy. The Dyson-like equation can be reformulated as an eigenvalue problem by multiplying each side of the equation by \((E - \omega_n^0)^{-2}\) and subsequently taking the limit \(E \rightarrow \omega_n^0\) to single out the terms that have \((E - \omega_n^0)^{-2}\) in the denominator on each side of the Dyson-like equation. This reveals a symplectic eigenvalue problem in the eigenvalues \(\omega_n\) and the eigenvectors \(\chi^n\),
\[
\sum_{c<d} (V_{abcd} + \delta_{ac}\delta_{bd}\omega^0_{ab}) \chi^c_{ed} + \sum_{h<i} V_{abh}\chi^i_{hi} = \omega_n \chi^n_{ab},
\sum_{c<d} V_{hcd}\chi^c_{ed} + \sum_{k<i} (V_{hijk} - \delta_{jk}\delta_{hi}\omega^0_{hi}) \chi^i_{jk} = -\omega_n \chi^n_{hi},
\]
where \(\omega^0_{pq} = \epsilon_p + \epsilon_q - 2\nu\). The same set of equations emerges for the double electron addition energies \(\omega_n^{N+2}\). These equations can be written in the form \(RX = \omega MX\) with \(M = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\) or
\[
\begin{pmatrix} A & B \\ B^\dagger & C \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}
\tag{32}
\]
when the eigenvectors are divided up into pp-vectors \( x \) and hh-vectors \( y \) and the matrix \( R \) is divided accordingly into submatrices \( A, B, \) and \( C \), defined as

\[
A_{abcd} = \langle ab | cd \rangle + \delta_{ac} \delta_{bd} \omega_{ab}^0,
B_{abij} = \langle ab | ij \rangle ,
C_{ijkl} = (ij | kl) - \delta_{ik} \delta_{jl} \omega_{ij}^0.
\]  

(33)

The indices \( a, b \) are particle indices and \( i, j \) are hole indices restricted to \( a < b \) and \( i < j \), and \( \nu \) is the chemical potential. While the inclusion of the chemical potential is not strictly necessary, it conveniently shifts the double electron addition energies \( \omega_{ab}^{N+2} \) to be positive and the double ionization energies \( \omega_{ab}^{N-2} \) to be negative. Due to the use of an antisymmetrized basis, the dimension of the matrix \( A \) is \( N_{pp} \equiv \frac{3}{2}(N - 1) \) and the dimension of the matrix \( C \) is \( N_{hh} \equiv \frac{3}{2}(o - 1) \). The correlation energy (31) can then be written in terms of the eigenvalues \( \omega_{ab} \) (in a similar fashion to the ph-RPA), see Ref. 28 for a full derivation,

\[
E_{pp}^c = \sum_{ab}^{N_{pp}} \omega_{ab}^{N+2} - tr A - \sum_{ab}^{N_{hh}} \omega_{ab}^{N-2} - tr C.
\]  

(34)

The symplectic eigenvalue problem (32) can also be derived from the equations of motion (EOM) for the \( N + 2 \) (or \( N - 2 \)) electron excited states generated by the operators \( \hat{O}^n = \sum_{ab} X_{ab} a_a^+ a_b^\dagger = \sum_{ij} Y_{ij}^* a_i a_j^\dagger \) (or their Hermitian conjugate). From the Schrödinger equation, an exact double electron addition operator \( \hat{O}^{n+2} = [\Psi^{N+2}_0 | \Psi^{0}_0] \) must satisfy \( [\hat{A}, [\hat{H}, \hat{O}^n]] = (E_{n}^{N+2} - E_0^{N})[\hat{A}, \hat{O}^n] \) for any operator \( \hat{A} \). Projecting onto an uncorrelated reference wavefunction, this leads to

\[
\langle \Phi^N_0 | [a_p a_q, [\hat{H}, \hat{O}^n]] | \Phi^N_0 \rangle = \omega_{pq} [\Phi^N_0 | [a_p a_q, \hat{O}^n] | \Phi^N_0 \rangle]
\]  

(35)

which is completely equivalent to Eq. (32), as the elements \( [\Phi^N_0 | [a_p a_q, [\hat{H}, \hat{a}_i a_i^\dagger]] | \Phi^N_0 \rangle \) in \( \langle \Phi^N_0 | [a_p a_q, [\hat{H}, \hat{O}^n]] | \Phi^N_0 \rangle \) reduce to elements of the pp-RPA matrix \( R \) and the commutators \( [\Phi^N_0 | [a_p a_q, a_i a_i^\dagger]] | \Phi^N_0 \rangle \) in \( \langle \Phi^N_0 | [a_p a_q, \hat{O}^n] | \Phi^N_0 \rangle \) are either zero or one depending on the pp- or hh-nature of the indices

\[
\langle \Phi^N_0 | [a_p a_q, [\hat{H}, a_i a_i^\dagger]] | \Phi^N_0 \rangle = R_{pqrs},
\]  

\[
\langle \Phi^N_0 | [a_p a_q, a_i a_i^\dagger]] | \Phi^N_0 \rangle = M_{pqrs}.
\]

The pp-RPA energy can alternatively be interpreted as the sum of all ladder diagrams: every term of the infinite series in Eq. (30) corresponds to a ladder diagram of increasing order. As the summation of all ladder diagrams, the pp-RPA is equivalent to the CCD restricted to ladder diagrams,\(^{10,30,32}\)

\[
E_{pp}^c = tr[TB],
\]

where the CCD amplitude matrix \( T \) is a solution to the Riccati equation

\[
T^\dagger A + T^\dagger BT^\dagger + B^\dagger + CT^\dagger = 0.
\]  

(36)

The matrices \( A, B, \) and \( C \) are equivalent to those in the symplectic eigenvalue equation (32). This equation can be easily obtained from the eigenvalue equation (32) by identifying \( T = (XY^{-1})^\dagger \).\(^{31,32}\) Since the ladder diagrams summed to obtain the correlation energy are all connected diagrams, the pp-RPA is size-extensive.\(^{35}\)

D. Stability of the particle-particle random phase approximation

The pp-RPA does not suffer from instabilities like the ph-random phase approximation with exchange (RPAX), i.e., the ph-RPA with exchange in the two-electron integrals. The ph-RPA is almost exclusively used in its “direct” formulation, which neglects the exchange terms in the two-electron integrals, within the DFT community. This preference is motivated by the inherent instability of the ph-RPAX, but neglecting exchange terms also makes it easier to reduce its computational cost via resolution-of-the-identity or density-fitting techniques. Even though the pp-RPA fully accounts for the anti-symmetry of the pp-propagator, it does not suffer from such instabilities. In contrast to the ph-RPAX matrix, which determines the stability of the reference wavefunction under orbital rotations and therefore often breaks down in cases with near-degeneracies, the pp-RPA matrix determines the stability of the reference wavefunction under double ionization or electron addition.

The energies for a physical system at integer electron number decrease monotonically in a convex manner:

\[
E_0^{N+2} - E_0^{N+1} \geq E_0^{N+1} - E_0^{N} \geq E_0^{N} - E_0^{N-1} \geq E_0^{N-1} - E_0^{N-2}.
\]  

(37)

This means that the system is stable with respect to the proportionation reaction from two \( N \)-electron systems to an \( N + 2 \) and an \( N - 2 \) electron system. Since the chemical potential can be defined as either the left- or right-derivative of the energy with respect to electron number,

\[
\nu^+ = E_0^{N+1} - E_0^{N},
\]

\[
\nu^- = E_0^{N} - E_0^{N-1},
\]

FIG. 5. The pp-RPA correctly produces a small correlation energy for He\(_2^+\) at 10 Å, given by the area under the curve, while the ph-RPA adds such a large correlation energy to the exact exchange that it fails to bind He\(_2^+\). The area under the v2DM curve shows the exact correlation energy and the v2DM curve shows an approximate constant-density path.
the inequalities (37) can be written as
\[ E^{N+2}_0 - E^N_0 - 2v^+ \geq 0, \]
\[ E^N_0 - E^{N-2}_0 - 2v^- \leq 0, \]
so the double electron addition and removal energies defined before are positive and negative, respectively,
\[ \omega^{N+2}_n = E^{N+2}_n - E^N_n - 2v \geq 0, \]
\[ \omega^{N-2}_n = E^N_n - E^{N-2}_n - 2v \leq 0, \]
where the chemical potential \( v \in [v^+, v^-] \). This physical requirement on the wavefunction implies that the pp-RPA matrix is positive-semidefinite. For any \( c = \sum a_n \chi^i \),
\[ \sum_{ijkl} c^*_{ij} (\Phi^N_0)_{a_i a_j} [H, a_j a_i] [\Phi^N_0] c_{kl} = c^* R c \]
\[ = \sum_{mn} a^n_m (\chi^n)^i \mathbf{R} \chi^m a_m \]
\[ = \sum_{mn} \omega_m a^n_m (\chi^n)^i \mathbf{M} \chi^m a_m \]
\[ = \sum_n \omega_n a^n_\nu (\chi^n)^i \mathbf{M} \chi^n \]
\[ = \sum_n \omega_n a^n_\nu (\chi^n)^i \mathbf{M} \chi^n + \sum_n \omega_n a^n_\nu (\chi^n)^i \mathbf{M} \chi^n \geq 0. \]

Here we have used the orthogonality of the eigenvectors, \( (\chi^n)^i \mathbf{M} \chi^n = 0 \) for \( m \neq n \) and the normalization of the eigenvectors: eigenvectors dominated by pp-elements involve the \( (N+2) \)-electron states, have a positive norm \( (\chi^n)^i \mathbf{M} \chi^n > 0 \) and can thus be normalized to 1, whereas eigenvalues dominated by hh-elements involve the \( (N-2) \)-electron states, have a negative norm \( (\chi^n)^i \mathbf{M} \chi^n < 0 \) and can thus be normalized to \(-1\). So the stability of the state under double ionization and electron addition implies that the pp-RPA matrix is positive semi-definite. Conversely, positive-semidefiniteness of the pp-RPA matrix guarantees that the symplectic eigenvalue problem produces \( N_{pp} \) real positive double electron addition energies and \( N_{hh} \) real negative double ionization energies and therefore assures that the correlation energy Eq. (34) is real.

The Hartree-Fock ground state for systems described by repulsive Coulombic interactions must satisfy the stability requirement. From the EOM perspective, Eq. (35), it is clear that the elements of the pp-RPA matrix (32) are the elements of the double commutator matrix \( R_{kl ij} = (\Phi^N_0)_{[a_i a_j] [H, a_j a_i]} [\Phi^N_0] \) which determines the second derivative of the energy with respect to double ionization or electron removal. Suppose \( e^{i\hat{u}} [\Phi^N_0] \), with \( \hat{u} \) a double ionization/electron addition operator \( \hat{u} = \frac{1}{2} \sum_{ij} u_{ij} a^\dagger_i a^\dagger_j + u^\dagger_{ij} a_i a_j \), represents a small transformation of the uncorrelated wavefunction \( \Phi^N_0 \) that breaks the particle number symmetry, since \( \hat{u} \) does not commute with the electron number operator \( \hat{N} \). The second-order derivative of the energy under such a transformation, evaluated at \( \Phi^N_0 \) is
\[ \frac{\partial^2 E}{\partial u^*_{ij} \partial u_{ij}} \bigg|_{\hat{u}=0} = \frac{\partial^2}{\partial u^*_{ij} \partial u_{ij}} \langle \Phi^N_0 | e^{-i\hat{u}} \hat{H} e^{i\hat{u}} | \Phi^N_0 \rangle \bigg|_{\hat{u}=0} = \langle \Phi^N_0 | [a_k a_l, [\hat{H}, a^\dagger_i a^\dagger_j]] | \Phi^N_0 \rangle. \]

If the double commutator matrix \( \mathbf{R} \) is not positive-semidefinite, the eigenvectors with negative eigenvalue indicate that there exists a Bogoliubov transformation to a superfluid state with \( \langle \hat{N} \rangle^2 \neq \langle \hat{N} \rangle^2 \) and non-vanishing pairing matrix with lower energy. This is impossible: the energy contribution from the non-zero pairing matrix in such a state is of the form \( \sum_{pqrs} \kappa_{pq} V_{pqrs} \kappa_{rs} \) and is manifestly positive for a repulsive interaction \( \hat{V} \). The pp-RPA based on a HF reference must therefore have real eigenvalues and correlation energies.

III. COMPUTATIONAL DETAILS

The numerical illustrations on the pp-RPA in Sec. IV are post-HF or post-KS calculations based on HF or KS reference wavefunctions from Gaussian03\(^{45} \) for the dissociation graphs and HF or KS reference wavefunctions from QM4D\(^{52} \) for the weakly bound dimers. For the subsequent pp-RPA calculations, we used our own implementation. For the discussion of the molecular dissociation graphs and the adiabatic connection, we used the local density approximation (LDA) reference, while for the weakly bonded dimers we used HF references to enable comparison to second-order Möller-Plesset perturbation theory (MP2). For the accurate reference calculations along the adiabatic connection path we used our own semi-definite optimization algorithm to optimize the second-order density matrix under two-positivity conditions.\(^{38} \) We denote this method as “tv2DM.”

We used a cc-pVDZ basis set for the calculations of the dissociation graphs and adiabatic connection graphs, a cartesian d-aug-cc-pVTZ basis sets for the Ar dimer and aug-cc-pVDZ for the other van der Waals systems, both limited to f-angular momentum functions.

IV. NUMERICAL ILLUSTRATIONS ON THE pp-RPA

The adiabatic connection (31) provides a framework for developing density functionals based on pairing matrix fluctuations. The most straightforward functional is perhaps the pp-RPA, the lowest order approximation to the pp-propagator, which may serve as an illustration of this new path for developing density functionals. We therefore examine the pp-RPA in this section with applications to molecular dissociation and thermodynamic properties. We focus in particular on its comparison to the ph-RPA, since the two RPAs can be viewed as representatives of the two different adiabatic connection
perspectives for the exact exchange-correlation energy, Eqs. (14) and (16). The pp-RPA gives the correct dissociation limit for the two paradigmatic cases for strong static correlation and delocalization, H$_2$ and H$_2^+$. The most commonly used functionals today, local density approximations, generalized gradient approximations, and hybrid density functional approximations, fail to describe both dissociation limits well within a restricted framework. The success of these DFAs for many applications relies on error cancellations between the exchange and correlation part of the functionals, so they fail to describe the extremes of the spectrum, where either correlation or exchange dominate. The H$_2$ and H$_2^+$ molecules are paradigmatic examples of these extremes: describing the dissociated H$_2$ correctly requires strong left-right static correlation, which DFAs typically underestimate, while describing the dissociated H$_2^+$ requires exact exchange but no correlation, so even hybrid functionals that mix in a fraction of exact exchange fail to describe the two extremes. The pp-RPA produces the correct dissociation limit for both H$_2$ and H$_2^+$, while the ph-RPA fails to bind the H$_2^+$ ion. At shorter bond lengths, near 10 Å, the pp-RPA energy for H$_2$ shows an unnatural repulsion, which is also present in the ph-RPA energy, albeit to lesser extent. This unphysical barrier for dissociation occurs for different references and its origin in the ph-RPA has been the object of speculation, with some authors attributing it to the lack of self-consistency — although this hypothesis has recently been rejected by actual self-consistent implementations — and others attributing it to the lack of higher order excitations in the ph-RPA. Unlike the pp-RPA, the pp-RPA is self-interaction free: it reduces to the HF functional for one-electron systems. So it has no delocalization error for the dissociated H$_2^+$ molecule and produces equally good potential energy functions for less trivial odd-electron systems. The ph-RPA has large self-interaction errors for these systems; it adds such a large correlation energy to the exact exchange that the H$_2^+$ and He$_2^+$ molecules are not bound.

The adiabatic connection provides an additional perspective on the pp-RPA energy contribution as a function of the interaction strength. Figs. 1–3 illustrate the correlation energy contribution in the pp-RPA along the adiabatic connection path for H$_2$. In the dissociation limit, the pp-RPA energy along the constant-density adiabatic connection path approaches the step function, much like the exact connection. Near equilibrium, the pp-RPA energy along the constant-density adiabatic connection path has the exact initial slope but falls short in the interacting limit and therefore slightly underestimates the correlation energy. Such an energy profile along the adiabatic connection path seems to be typical in molecules near equilibrium geometry. Near 10 Å the pp-RPA and the ph-RPA severely underestimate the correlation energy, resulting in the unphysical barrier in the dissociation of H$_2$. Figs. 4 and 5 illustrate how the pp-RPA has no self-interaction error in H$_2^+$ or He$_2^+$ while the ph-RPA gives a much too large correlation energy at any interaction strength.

The restricted dissociation of the N$_2$ molecule proves an even greater challenge than the dissociation of H$_2$ because it involves a simultaneous stretch of three bonds. The ph-RPA prevails for such cases, as it has no static correlation error for the stretched N$_2$ molecule, while the pp-RPA energy is much too low, similar to truncated coupled cluster methods like coupled-cluster with singles and doubles (CCSD). The failure of the pp-RPA for such cases, however, seems to have little adverse effects on thermodynamic properties — even the reaction energies surveyed in previous work are rather good — perhaps because chemical reactions rarely involve simultaneous multiple bond breaking.

One of the main reasons for the renewed interest in the ph-RPA has been its ability to capture long-range interactions in a seamless manner with the correct $R^{-6}$ asymptotic decay. It has served as a source of inspiration for more empirical density functionals. Can the pp-RPA also describe this type of interactions? Perhaps surprisingly, the pp-RPA gives very good interaction energies for several types of non-bonded interactions, competitive with or even better than the ph-RPA energies: the pp-RPA(PBE) has an overall mean signed error (MSE) and mean unsigned error (MUE) of $-0.28$ and $0.60$ kcal/mol while the ph-RPA(PBE) has an MSE and MUE of $1.86$ and $1.86$ kcal/mol. A possible explanation for these good results is the correct second-order energy term in the pp-RPA: the second-order term in Eq. (30) is exact, equivalent to MP2 correlation energy. The ph-RPA has a similar second-order energy term but neglects the exchange terms. Since the second-order energy term is the predominant term in describing weak interactions, this may explain why the pp-RPA gives surprisingly good non-bonded interaction energies. Figure 6 supports this explanation: upon dissociation, the pp-RPA interaction energy for the weakly interacting noble gas dimer Ar$_2$ nearly equals the MP2 interaction energy, although MP2 binds the Ar dimer more strongly (Fig. 7). Its correct second order energy term also ensures a physically correct $R^{-6}$ asymptotic decay of the interaction energy, as illustrated in Figure 6. Calculations on the van der Waals database explored in previous work also demonstrate that the second-order energy term constitutes the main part of the interaction energy (Figure 8).

The pp-RPA gives much better atomization energies than the ph-RPA and describes reaction barriers with similar accuracy. While the adiabatic connection graphs (Figures 1–5) suggest that the pp-RPA tends to underestimate the correlation energy in the interacting limit, it provides much better interaction energies than ph-RPA for many applications.
better atomization energies – which rely on relative, rather than absolute, energies – than the ph-RPA. The current literature on ph-RPA molecular atomization energies mostly focuses on small molecules.\textsuperscript{12,47,48} The mean signed error in the ph-RPA atomization energies for such few-atomic systems is of the order of $+10$ kcal/mol. This phenomenon of underbinding in the ph-RPA is well-known.\textsuperscript{12,47} The ph-RPA typically overestimates correlation energies, but it over-correlates atoms more strongly than molecules, such that it underestimates atomization energies. For bigger molecules, this problem becomes even more pronounced: the error in the ph-RPA atomization energies continues to grow with the number of atoms in the molecule, which is reflected in its mean signed error of $22.7$ kcal/mol for the whole G2 set, equal to its mean unsigned error. The pp-RPA does not suffer from this problem: its mean signed error for the whole G2 set is a mere $-1.9$ kcal/mol and its mean unsigned error is $8.3$ kcal/mol, much lower than that for the ph-RPA.\textsuperscript{49} The pp-RPA and ph-RPA give rather similar reaction energies. For reaction barriers involving the molecules contained in the G2 set, the pp-RPA and ph-RPA errors are 2.4 and 2.3 kcal/mol, respectively, and for the DBH24 reaction enthalpy set their respective errors are 3.2 and 2.5 kcal/mol. So while the pp-RPA generally seems to underestimate absolute correlation energies, it describes thermodynamic properties well.

The computational cost of the pp-RPA scales as $O(\sigma^2 v^4)$ without making further approximations. While the full diagonalization of the pp-RPA matrix, Eq. (33), may seem to require $O(v^6)$ operations, not all of the eigenvalues are needed to compute the correlation energy $E^c = -\sum \omega_p \sigma^2 - \text{tr } C$; the $O(\sigma^2)$ double ionization energies suffice. The lowest required computational cost is then $O(\sigma^2 v^4)$. This agrees with the cost of the equivalent ladder-CCD formulation, Eq. (36): the term that dominates the floating point operation count for the ladder-CCD formulation of the pp-RPA is the same $O(\sigma^2 v^4)$ term that dominates the operation count for CCSD.\textsuperscript{49}

\section{V. CONCLUSIONS}

We have formulated an adiabatic connection for the correlation energy in terms of pairing matrix fluctuations. This adiabatic connection formalism is in principle exact, but requires an expression for the pp-propagator at each interaction strength. It thus lays the theoretical foundations for approximate density functionals based on pairing matrix fluctuations. The pp-RPA is the lowest-order approximation to the pp-propagator. Judging from the numerical illustrations on the pp-RPA, the adiabatic connection Eq. (16) may lead to interesting new functionals: the pp-RPA captures the strong static correlation in the dissociation limit of H2 and other single bond systems, has no delocalization error and is self-interaction free. Despite its tendency to underestimate correlation energies, the pp-RPA gives good relative energies and thermodynamic data – in fact, it gives much better atomization energies than the ph-RPA because it does not systematically underbind like the ph-RPA. Its exact second-order energy ensures a correct description of non-bonded interactions. It is size-extensive. Nonetheless, it fails for the simultaneous multiple bond-breaking in N2, and even though common chemical reactions rarely involve simultaneous multiple bond breaking, this is an undesirable feature that can perhaps be alleviated in further development of DFAs derived from the pp-RPA or the pp-propagator.

The adiabatic connection allows for a wealth of approximate density functionals based on pairing matrix fluctuations and their computational scaling obviously depends on the nature of the functional. The pp-RPA is, with its $O(\sigma^2 v^4)$ operation count, computationally expensive, especially due to its high dependence on the virtual orbitals. Because of the explicit antisymmetry of the pp-propagator its computational cost is not as straightforwardly reduced by resolution-of-the-identity techniques as the ph-RPA, which neglects the exchange terms in the two-electron integrals. We are currently exploring other approaches to reduce its computational.

\begin{figure}[H]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{The pp-RPA and the ph-RPA describe the van der Waals interactions in the Ar dimer well. MP2 binds the dimer more strongly.}
\end{figure}

\begin{figure}[H]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{The (counter-poise corrected) pp-RPA interaction energies (in kcal/mol) are very similar to the MP2 interaction energies for a set of van de Waals bonded molecules.}
\end{figure}
cost. The adiabatic connection framework opens the way for further approximations to obtain density functionals based on pairing matrix fluctuations with low computational scaling.

ACKNOWLEDGMENTS


M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh, PA, 2004.

Qm4d, a program for qm/mm simulations.


It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.

It can be proven that the eigenvalue problem $R\mathbf{x} = \sigma\mathbf{M}\mathbf{x}$ has real eigenvalues and eigenvectors when $R$ is positive-semidefinite.