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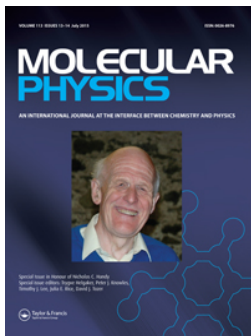
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INVITED ARTICLE

**Wavefunction stability analysis without analytical electronic Hessians:
application to orbital-optimised second-order Møller–Plesset theory and VV10-containing
density functionals**Shaama Mallikarjun Sharada^a, David Stück^{b,c}, Eric J. Sundstrom^{b,c}, Alexis T. Bell^{a,c} and Martin Head-Gordon^{b,c,*}^aDepartment of Chemical and Biomolecular Engineering, University of California, Berkeley, CA, USA; ^bDepartment of Chemistry, University of California, Berkeley, CA, USA; ^cChemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

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Wavefunction stability analysis is commonly applied to converged self-consistent field (SCF) solutions to verify whether the electronic energy is a local minimum with respect to second-order variations in the orbitals. By iterative diagonalisation, the procedure calculates the lowest eigenvalue of the stability matrix or electronic Hessian. However, analytical expressions for the electronic Hessian are unavailable for most advanced post-Hartree–Fock (HF) wave function methods and even some Kohn–Sham (KS) density functionals. To address such cases, we formulate the Hessian-vector product within the iterative diagonalisation procedure as a finite difference of the electronic gradient with respect to orbital perturbations in the direction of the vector. As a model application, following the lowest eigenvalue of the orbital-optimised second-order Møller–Plesset perturbation theory (OOMP2) Hessian during H₂ dissociation reveals the surprising stability of the spin-restricted solution at all separations, with a second independent unrestricted solution. We show that a single stable solution can be recovered by using the regularised OOMP2 method (δ -OOMP2), which contains a level shift. Internal and external stability analyses are also performed for SCF solutions of a recently developed range-separated hybrid density functional, ω B97X-V, for which the analytical Hessian is not yet available due to the complexity of its long-range non-local VV10 correlation functional.

Keywords: quantum chemistry; stability analysis; density functional theory; Brueckner orbitals; orbital optimisation**Introduction**

Self-consistent field (SCF) solutions to wavefunction theory and Kohn–Sham (KS) [1,2] formalism of density functional theory (DFT) are typically determined by imposing constraints on the spin orbitals. These constraints not only lower SCF costs, but also allow the approximate wavefunction to share some properties in common with the exact wavefunction such as spin or spatial symmetry. Variational minimisation ensures that the energy is stationary with respect to first order changes in the spin orbitals. Therefore, second derivatives with respect to spin orbital coefficients must be positive for the energy to be a true local minimum, and the procedure to verify this condition is termed stability analysis.

Thouless [3] originally derived the conditions for stability of HF wavefunctions from second quantisation. This was followed by a density matrix-based approach [4], and a reformulation of the Thouless conditions to treat both closed and open-shell systems [5,6]. Seeger and Pople [7] devised a systematic approach to treat HF instability beginning with real spin-restricted HF orbitals, and progressively removing each of these constraints. For each case, they obtained the conditions for internal stability, where spin orbitals are

varied within the space of defined constraints, as well as external stability where one constraint is removed at a time. Stability analysis for HF involves the calculation of the lowest eigenvalue of a stability matrix (or electronic Hessian). Since diagonalisation of the large stability matrix (whose elements form a fourth rank tensor) may be prohibitive, stability analysis employs iterative diagonalisation techniques such as the Davidson method [8]. Fortunately, the critical step in iterative diagonalisation, which involves contraction of the stability matrix with a trial vector, can be performed in a manner very similar to forming a Fock matrix. Therefore the cost of SCF stability analysis is comparable to SCF costs.

The HF solution is typically used as a reference for advanced methods that incorporate correlation such as second-order Møller–Plesset perturbation theory (MP2) and coupled cluster (CC) theory, although HF orbitals quite commonly suffer from spatial or spin symmetry-breaking. To address these problems, orbital-optimised second-order perturbation theory (OOMP2) [9] distinguishes itself from standard MP2 by optimising the zeroth order orbitals in the presence of correlation in an approach based on approximate Brueckner orbitals [10]. By optimising the single

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reference, artificial spin contamination can be removed [9–12] and energies as well as properties of open shell molecules can be significantly improved [9–11,13–15]. Because the energy is made stationary to changes in the orbitals, a Hellman–Feynman condition applies and all first order properties will be continuous as the orbitals change continuously [16]. Recently, δ -OOMP2 has been developed as a simple way to regularise the method against small HOMO–LUMO gaps as well as removing systematic errors in the method [17]. While approximate forms have been applied in previous studies [11], full analytical expressions for the electronic Hessian are unavailable and finite-difference electronic Hessians are intractable. As a result, the stability of spin-restricted and unrestricted formalisms of OOMP2 has not been properly investigated. For the same reason, stability analysis is not available for size-consistent, Brueckner orbital-based coupled cluster techniques such as Brueckner theory doubles (BD) [18] and optimised-orbital coupled cluster doubles (OD) [10,13,19].

The stability conditions for density functionals are essentially analogous to HF, and have been derived by Bauernschmitt and Ahlrichs [20] for internal (singlet) and external (triplet) stability of restricted KS-DFT. The formalism, however, requires calculation of second derivatives of the exchange-correlation energy. Analytical expressions for the second derivative of the exchange correlation term in KS-DFT are not available for all functionals. ω B97X-V [21], for instance, is a minimally parameterised range-separated hybrid functional that can accurately capture both non-covalent interactions as well as thermochemistry. The functional includes non-local correlation described by VV10 [22], for which an analytical form of the Hessian has not yet been derived. In such cases, stability analysis can prove intractable since calculation and diagonalisation of the full finite-difference electronic Hessian is not feasible.

Our aim is to establish a technique for stability analysis that is readily applicable to any post-HF or KS-DFT method, regardless of the availability of analytical second derivatives of electronic energy. We have previously reported a finite-difference implementation of the Davidson method to calculate the lowest eigenvalue of a nuclear Hessian [23], which can determine whether a stationary point calculated using geometry optimisation is a minimum or saddle point. The same approach can be extended to wavefunction space, where the finite-difference Davidson method is applied to perturbations in the molecular orbitals in order to calculate the lowest eigenvalue of the electronic Hessian. Potential curves for dissociation of H_2 are calculated to analyse the stability of SCF solutions for OOMP2 and δ -OOMP2 theory, with some interesting and in some ways remarkable results. Additionally, finite-difference-based stability analysis is applied to the ω B97X-V functional in order to demonstrate the utility of this technique when second derivatives are unavailable.

Method

The Davidson method is an iterative diagonalisation procedure to determine a few extreme eigenvalues of large symmetric matrices when full diagonalisation is prohibitive. The algorithm is described in detail elsewhere [8,24]. Briefly, the procedure employs a small orthonormal subspace of vectors, $B_k = [b_i]$ at each iteration k , consisting of dominant components of the desired eigenvector of a matrix, A . A smaller interaction matrix, $B_k^T A B_k$, is constructed and diagonalised to obtain the lowest/highest eigenpair, (λ_k, y_k) . The Ritz vector, $x_k = B_k y_k$, is then used to estimate the residual error between the exact and approximate eigenvector, $r_k = -(\lambda_k I - A)x_k$. The initial subspace is augmented with a new vector that contains this information, and the procedure is iterated until convergence.

The Davidson method was originally applied to large-scale configurational interaction (CI) treatment of wavefunctions [8,25]. The finite-difference implementation of the Davidson method can be used when the matrix calculation itself is intractable. For instance, if the matrix A corresponds to the Hessian of the energy with respect to nuclear displacements, the exact matrix–vector product, $A b_1$, is replaced with a finite-difference approximation in terms of the gradient of the energy (∇E) [23]:

$$A b_1 \approx \frac{\nabla E(X_0 + \xi b_1) - \nabla E(X_0 - \xi b_1)}{2\xi}, \quad (1)$$

where b_1 is the subspace guess, X_0 corresponds to nuclear coordinates of a system, and ξ is the finite-difference step. This expression can be used to calculate a few key eigenvectors as inputs to mode-following methods for transition state searches on nuclear potential energy surfaces [26–28]. The same principle can also be applied to selective mode tracking in vibrational analysis [29,30], and characterisation of stationary points [23,31] where the lowest one or two eigenvalues of the nuclear Hessian are sufficient to verify whether a geometry corresponds to a minimum or transition state, respectively.

Wavefunction stability analysis also requires only the lowest eigenvalue of the electronic Hessian. Therefore, the finite-difference Davidson approach can be extended to stability analysis in cases where analytical Hessians are either expensive or unavailable. Since rotations between occupied–occupied or virtual–virtual orbitals do not affect the total energy, stability analysis is carried out in the space of occupied–virtual rotations. The most obvious choice for the initial subspace guess, therefore, corresponds to a HOMO–LUMO rotation. To avoid possible orthogonality between the guess and the exact eigenvector, a small amount of randomness is added in to the subspace guess.

Orbital perturbation in the occupied–virtual space along the subspace guess closely follows the procedure outlined by Van Voorhis and Head-Gordon [32]. A skew-symmetric unitary transformation matrix, $U_{1\pm}$, is determined by first

scaling the guess,

$$\Delta_{1\pm} = \pm\xi b_1, \quad (2)$$

where b_1 is the subspace guess corresponding to HOMO–LUMO rotation, ξ ($= 0.01$) is the finite-difference step, and the number in the subscript corresponds to the iteration. The transformation matrix is then given by

$$U_{1\pm} = e^{\Delta_{1\pm}}. \quad (3)$$

The off-diagonal elements of this matrix correspond to rotations in the occupied–virtual space. The rotated orbitals are given by a unitary transformation of the converged SCF orbital coefficients, C_0^σ , where σ corresponds to α - or β -spin:

$$C_{1\pm}^\sigma = C_0^\sigma U_{1\pm}. \quad (4)$$

Rotations of α -spin and β -spin orbital coefficients are identical during internal stability analysis of restricted or unrestricted spin orbitals. In order to examine external stability of restricted spin orbitals, on the other hand, spin symmetry needs to be broken. Therefore, α -spin and β -spin orbital coefficients are rotated in opposite directions:

$$C_{1+}^\beta = -C_{1+}^\alpha \quad \text{and} \quad C_{1-}^\beta = -C_{1-}^\alpha. \quad (5)$$

The Hessian-vector product Davidson iterations is then calculated similar to (1) using finite differences of gradients with respect to the rotated coefficients:

$$Ab_1 \approx \left[\frac{\nabla E(C_{1+}^\alpha) - \nabla E(C_{1-}^\alpha)}{2\xi}, \frac{\nabla E(C_{1+}^\beta) - \nabla E(C_{1-}^\beta)}{2\xi} \right]^T, \quad (6)$$

where A corresponds to the electronic Hessian. The Davidson algorithm proposed by Sleijpen and van der Vorst [33] is then employed to iteratively calculate the lowest eigenvalue.

Convergence can be accelerated using a good preconditioner for the residual. In the original Davidson algorithm, the preconditioner at the k^{th} iteration, Ξ_k , is given by

$$\Xi_k = (\lambda_k I - D)^{-1}, \quad (7)$$

where D is a matrix consisting of the diagonal elements of A . A reasonable guess for the diagonal Hessian is the difference between orbital eigenvalues, $\{\varepsilon\}$, in the occupied–virtual space [32],

$$D_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab}, \quad (8)$$

where subscripts (i, j) correspond to occupied orbitals and (a, b) to virtual orbitals. In order to ensure the convergence of the method to the lowest eigenvalue, the preconditioner must be negative definite [24]. In cases where preconditioning exceeds a certain cut-off, the cut-off value replaces the difference between the eigenvalue and diagonal element. The chosen value, $\Delta E = -0.1 E_h$, is determined using simple benchmarking of the H_2 molecule at equilibrium separation with B3LYP [34,35] and correlation-consistent basis sets. The technique is implemented in a developmental version of Q-Chem 4.2 [36], in order to examine internal stability of real restricted or unrestricted orbitals, as well as external stability of restricted orbitals for OOMP2 theory and any KS-DFT.

Results

HF versus orbital-optimised MP2 for bond dissociation

Bond dissociation problems are an important application of stability analysis. The reason is that many orbital optimisation methods will not automatically change the character of the orbitals from restricted to unrestricted as the bond is stretched, and therefore stability analysis is needed to detect such a change. Figure 1 illustrates the standard result seen for Hartree-Fock theory for the toy problem of H_2 dissociation. The RHF to UHF instability is detected by a sign change of the smallest eigenvalue, which occurs at a bond-length of about 1.2 Å. Beyond this distance, the UHF solution exhibits an increasing positive smallest eigenvalue and becomes a distinct, lower energy solution, while the

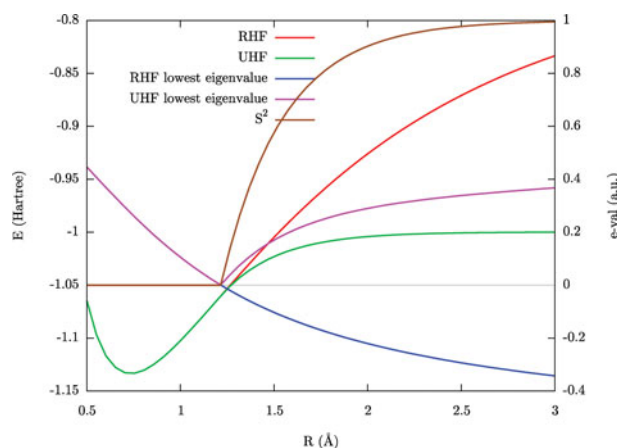


Figure 1. Potential curves (green for unrestricted and red for restricted, where it differs from unrestricted) for the dissociation of H_2 and the associated lowest eigenvalues of the stability matrix (purple for internal stability of the unrestricted solution, blue for external stability of the restricted solution, where it differs from unrestricted) at the Hartree–Fock (HF) level. The lowest energy solution changes character from restricted to unrestricted when the former becomes unstable.

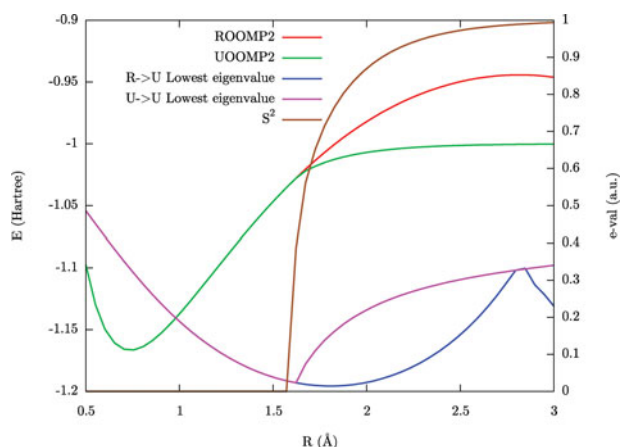


Figure 2. Potential curves for the dissociation of H_2 and the associated lowest eigenvalues of the stability matrix using orbital-optimised MP2 (OOMP2) in the cc-pVDZ basis. The format follows Figure 1. OOMP2 behaves qualitatively differently from HF (see Figure 1). The restricted solution is stable (positive eigenvalue) to spin-polarisation at *all* bond-lengths, and a distinct stable unrestricted solution appears at partially stretched bond-lengths.

smallest eigenvalue of the RHF solution becomes steadily more negative.

How does the inclusion of electron correlation in the OOMP2 method affect this picture? The results are shown in Figure 2, and at first glance the ROOMP2 and UOOMP2 energy curves look qualitatively similar to the RHF and UHF ones. However the ROOMP2 energy reaches a maximum value around 2.8 Å and then begins to turn over, as a result of the HOMO–LUMO gap decreasing. The ROOMP2 and UOOMP2 curves actually cross again at still larger separations than are shown on the figure. What are the implications for orbital stability analysis? Using the finite-difference stability analysis code yields very interesting results. The ROOMP2 and UOOMP2 solutions are in fact both stable when they are distinct solutions. They apparently do not coalesce upon going to shorter bond-lengths.

As a surprising consequence, despite the Hellman–Feynman condition for OOMP2, there are still first derivative discontinuities in the dissociation curve for single bond dissociations such as H_2 . It is scarcely visible in Figure 2, but this is nonetheless a real effect. As a result of the ROOMP2 solution always being a true minimum in orbital space, the UOOMP2 solution must cross it in the energy coordinate without crossing in orbital space.

To better understand the topography of the solutions we look at the UOOMP2 energy for H_2 as a function of spin-polarisation from the ROOMP2 solution in the minimal basis case where there is only a single orbital rotation angle (θ_α and θ_β) in each of the α and β spaces. A spin-polarisation angle, ϕ , can therefore be defined such that $\theta_\alpha = \phi$ and $\theta_\beta = -\phi$. Figure 3 shows the OOMP2 energy as a function of ϕ for a number of bond-lengths close to the crossing, from ROOMP2 being lowest energy to UOOMP2

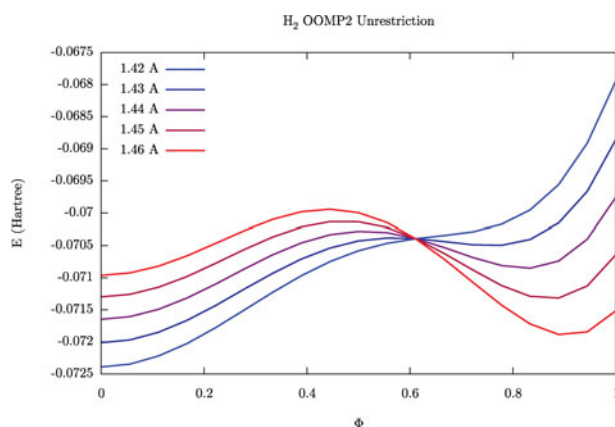


Figure 3. The dependence of the OOMP2 energy of H_2 in a minimal basis on the spin-polarisation angle (see text for definition) at a series of bond-lengths around the critical value at which the character of the lowest energy solution changes. There are two local minima, one restricted and one unrestricted, at these bond-lengths, and at the critical bond-length the nature of the lowest energy solution switches discontinuously.

being lowest. The key observation from Figure 3 is the appearance of a second minimum at non-zero ϕ as the bond is stretched, while the first stationary point ($\phi = 0$) remains a minimum. As the bond-length increases, the second solution eventually becomes the global minimum leading to the discontinuous change in orbitals as we follow the lowest energy orbitals.

While there is no reason to assume that the global minimum of a nonlinear problem will not jump between multiple minima as parameters change, it is still surprising to see it here due to our experience with HF (as exemplified by Figure 1). HF is a diagonalisation-based approach, and so two states with the same energy that can couple through the Hamiltonian should split in energy. OOMP2 on the other hand adds a perturbative correction, which in this case preferentially stabilises the restricted solution and lowers its energy relative to the unrestricted orbitals bringing their energies to coalescence. Similar observations have been made in the context of orbital optimisation in active space methods [37,38]. In cases such as these, as a consequence of the discontinuous change in orbitals, the potential energy surface exhibits a first derivative discontinuity at the point of the jump in orbital solutions (here, the ROOMP2 to UOOMP2 transition).

How might one overcome this unphysical behaviour of OOMP2, and recover smoother potential energy surfaces? We cannot give a complete answer here, but we can apply stability analysis to a modified form of OOMP2 that includes a fixed level shift of 0.4 a.u., termed δ -OOMP2. δ -OOMP2 has been shown to yield systematic improvements relative to OOMP2 across a broad range of properties while being robust to divergences during orbital optimisation [17]. The performance of δ -OOMP2 for the

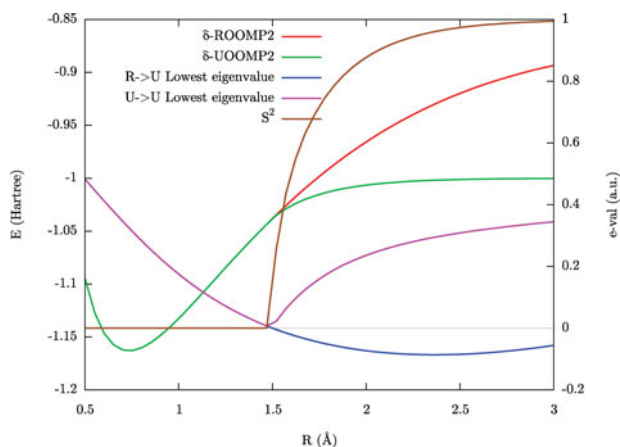


Figure 4. Potential curves for the dissociation of H_2 and the associated lowest eigenvalues of the stability matrix using regularised orbital-optimised MP2 (δ -OOMP2) in the cc-pVDZ basis. The format follows Figure 1. δ -OOMP2 behaves qualitatively differently from OOMP2 (see Figure 2), but is similar to HF (see Figure 1). The restricted solution becomes unstable at a critical bond-length, beyond which the unrestricted solution is lowest in energy.

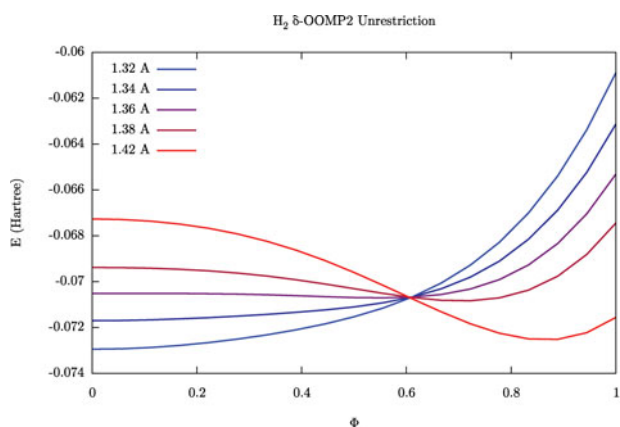


Figure 5. The dependence of the δ -OOMP2 energy of H_2 in a minimal basis on the spin-polarisation angle (see text for definition) at a series of bond-lengths around the critical value at which the character of the lowest energy solution changes. For any given bond-length there is only one local minimum, which changes character from restricted to unrestricted at the critical bond-length.

dissociation of H_2 is shown in Figure 4, and presents a striking contrast with OOMP2 shown in Figure 2. δ -OOMP2 shows only one stable solution at any geometry, like HF, and unlike OOMP2. As a consequence, as shown in Figure 5 for minimal basis H_2 , the optimised orbitals for the global minimum do not change discontinuously as the bond is stretched, and thus the potential energy surface is continuous through first derivatives. Further calculations on a much larger range of molecules are required to test the generality of the present positive result, and the stability analysis method introduced here is a crucial tool for this purpose.

Density functional theory

Using their formulation of stability analysis for KS-DFT, Bauernschmitt and Ahlrichs [20] calculate critical distances for the onset of external instability in dissociating systems. Along similar lines, dissociation calculations are performed on H_2 , and results are compared for restricted HF, B3LYP, and ω B97X-V, and the finite-difference Davidson approach is employed to calculate the lowest eigenvalue for the latter. Since ω B97X-V is trained using very large basis sets in the absence of counterpoise corrections [21], the aug-cc-pVTZ [39] basis set is employed. The critical distances determined with HF, B3LYP and ω B97X-V are 1.21, 1.49 and 1.53 Å, respectively, consistent with the fact that onset of external instability occurs later in density functionals owing to the inclusion of approximate correlation.

In addition to external stability of restricted ω B97X-V, internal stability analysis of the unrestricted formalism is also a useful diagnostic tool since the SCF solution can depend heavily on the quality of the initial guess. For instance, SCF minimisation of singlet methylene [40] (C-H bond distance = 1.11 Å, H-C-H angle = 101.896°) with unrestricted ω B97X-V/aug-cc-pVQZ converges to an unstable solution if the initial SCF guess consists of superposition of atomic densities. The lowest eigenvector corresponding to the unstable solution, calculated either with ω B97X-V or a lower level of theory, can then be used to search for a lower energy solution with ω B97X-V. The resulting orbital coefficients constitute a significantly better SCF guess that converges to the correct singlet ground state, which is 0.004 E_h lower in energy than the unstable solution.

Stability analysis is also essential for molecules containing transition metals, where multiple spin states can emerge from SCF calculations. To illustrate, we examine the stability of an organometallic electrocatalyst for cathodic hydrogen evolution reaction (HER), with potential application in the conversion of solar energy to fuels. The catalyst, shown in Figure 6, is a dimeric cobalt-diaryldithiolene complex with methoxy groups substituted in the aryl *para* positions [41]. The structure is optimised at the BP86

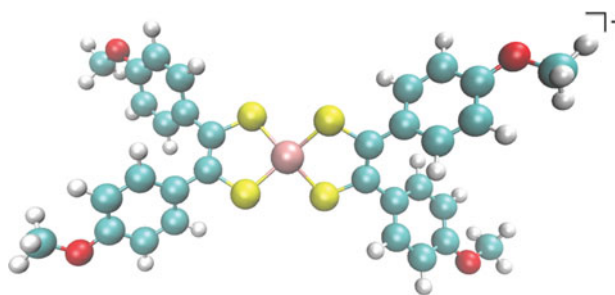


Figure 6. Structure of dimeric cobalt-diaryldithiolene complex, a potential catalyst for electrocatalytic proton reduction in non-aqueous media. Cobalt is in the centre surrounded by sulphur atoms (yellow), and the aryl groups are *para*-substituted with methoxy groups (oxygen atoms in red).

[42,43] /6-31G* level of theory. If the SCF cycles in the subsequent unrestricted single point energy calculation at ω B97X-V/6-31G* converge to a spin singlet, finite-difference stability analysis shows that the solution is internally unstable. The stable solution, with $\langle S^2 \rangle$ of 0.94, is 0.023 E_h lower in energy. While calculation and diagonalisation of the full finite-difference Hessian within the original stability analysis framework can be prohibitive for systems of this size, applying the finite-difference Davidson method to the stable solution costs only about 44 SCF steps. This procedure is therefore not only useful to study bond dissociation characteristics in the absence of analytical electronic Hessians, but is also a practical tool for examining the stability of large, complex systems.

Conclusions

Stability analysis has thus far been limited to formalisms for which analytical second derivatives are available since the cost of full finite-difference Hessian calculation is prohibitive. We describe a Hessian-free approach in which the Hessian-vector product required for iterative diagonalisation within the Davidson method is approximated by finite differences of the gradients with respect to rotation of molecular orbital coefficients in the occupied–virtual space. The procedure is implemented for both orbital-optimised post-HF methods such as OOMP2 as well as DFT, and can successfully examine internal and external stability with respect to spin symmetry constraints. In future, the implementation will also include internal and external stability analysis for complex as well as general spin orbitals. The technique will also be made available for other orbital-optimised methods such as coupled cluster-based BD and OD, for which stability analysis has hitherto not been performed.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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