

## Locating Multiple Self-Consistent Field Solutions: An Approach Inspired by Metadynamics

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We propose a method to locate the solutions to the self-consistent field (SCF) equations, using an approach based upon metadynamics. We define a distance function between density matrices. Within an SCF calculation, when a solution is found, a biasing potential based on distance from the solution is added to the energy to avoid reconvergence to the same solution. Multiple solutions can therefore be relatively easily found. Using this method we locate all known solutions and one unknown solution of the H4 model. The set of restricted Hartree–Fock (RHF) solutions for the nitrogen molecule is located, and a broken-symmetry solution lower in energy than the symmetric RHF solution is found corresponding to dissociation into doublet fragments.

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Within electronic structure theory, the solution of the self-consistent field (SCF) equations is a crucial matter, both in density functional theory (DFT) and in Hartree–Fock (HF) Theory. The SCF equations are nonlinear in the electron density, and the solutions are given by the stationary points of the energy functional with respect to changes in the density. The well-established methods of solution are based on iterative methods, which have been honed to converge rapidly on a solution via a number of acceleration techniques. The nonlinearity of the equations presents a challenge mathematically, as, for a given system, the number of solutions is not known. Upper and lower bounds have been placed by Fukutome [1], both of which increase exponentially with system size. Furthermore, the space of solutions has no well-defined properties (such as the orthogonality of eigenfunctions of a linear operator) which enable the use of projection methods to solve the equations.

The variational principle places the lowest energy solution as an upper bound to the true energy of the system, but there is no way to guarantee that any solution found is a global rather than a local minimum. However, with a suitable initial guess, most molecular systems will quickly converge to a solution which behaves physically, and is similar to the observed ground state of the molecule. As the use of electronic structure theory has become more widespread, interest has turned to more pathological systems where there is more than one low-lying electronic state. In such cases there may be many low-lying SCF solutions, and the solution found is heavily dependent on both the initial conditions and the convergence method. Consequently, the practice has arisen of using a number of different initial conditions and convergence methods, and selecting the lowest obtained solution.

Recently de Andrade *et al.* [2,3] have used a simulated annealing approach to combat this problem, using it to reliably locate the lowest RHF and Unrestricted Hartree–Fock (UHF) minima in some simple molecules. While this stochastic technique has proved very successful at sampling multidimensional spaces, there is the possibility that the minima found are not the lowest.

We propose an alternative method, inspired by the method of metadynamics [4] which is used to explore energy surfaces in molecular dynamics simulations by adding biasing potentials to “fill in” minima whenever they are found, and thus avoiding the simulations being trapped in any one well. While this still gives no guarantee of locating the lowest solution, it locates a number of solutions by biasing against any previous solutions found to avoid converging to them.

To manipulate the nonorthogonal basis of atomic spin-orbitals,  $|\chi_\mu\rangle$ , we shall use the tensor notation of Head-Gordon *et al.* [5] where subscripts denote covariant quantities, and superscripts contravariant quantities. These may be interconverted by use of the metric, in this case the overlap matrix  $S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle$ , and its inverse,  $S^{\mu\nu} = (S^{-1})_{\mu\nu}$ . The molecular orbitals (MOs),  $|\psi_i\rangle$  are defined in terms of the atomic orbital basis,  $|\psi_i\rangle = |\chi_\mu\rangle C_i^\mu$ . Here and after we have used the Einstein summation convention where repeated indices give rise to an implicit summation over that index. We will use the standard notation  $i, j, \dots$  for occupied orbital indices which we shall here restrict to real orthogonal canonical molecular orbitals. From the occupied MOs, we form the density matrix,  $P^{\mu\nu} = C_i^\mu C_i^{*\nu}$ , which is contravariant. The SCF equations are converged when the energy,  $E$ , is stationary with respect to occupied-virtual orbital rotations,

$$E = (h_{\mu\nu} + \frac{1}{2}(J_{\mu\nu} - K_{\mu\nu}))P^{\nu\mu}, \quad (1)$$

where  $J$  contains Coulomb interactions, and  $K$  the exchange (and correlation in DFT), which both depend on the density. The Fock matrix is the derivative of the energy with respect to the density matrix,

$$F_{\mu\nu} = \frac{\partial E}{\partial P^{\nu\mu}} \quad (2)$$

$$= h_{\mu\nu} + J_{\mu\nu}(P) - K_{\mu\nu}(P). \quad (3)$$

Each SCF solution may be uniquely described by its density matrix,  $P^{\mu\nu}$ , and we will describe a set of such solutions as  ${}^wP^{\mu\nu}$ ,  ${}^xP^{\mu\nu}$ ,  $\dots$ . Considering the space of density matrices as a vector space, we may define an inner product,

$$2\langle {}^wP, {}^xP \rangle = {}^wP^{\mu\nu}S_{\nu\sigma}{}^xP^{\sigma\tau}S_{\tau\mu} \quad (4)$$

$$= {}^wP^{\mu\nu}{}^xP_{\nu\mu}. \quad (5)$$

The square norm may therefore be defined  $\|{}^xP\|^2 = \langle {}^xP, {}^xP \rangle$ . We define the square distance between two solutions,  $d_{wx}^2 = \|{}^wP - {}^xP\|^2 = N - 2\langle {}^wP, {}^xP \rangle$ , as the trace of each density is the number of electrons,  $N$ . This definition is equivalent to the following more intuitive definition,  $d_{wx}^2 = \langle {}^w\Psi | {}^w\rho - {}^x\rho | {}^w\Psi \rangle$ , where  ${}^w\Psi$  is a Slater determinant formed from the orthonormal orbitals,  ${}^w\phi_i$ , of solution  $w$ , and  ${}^w\rho$  is the one-particle density operator for  ${}^w\Psi$ . This may be expanded as

$$d_{wx}^2 = \langle {}^w\Psi | (|{}^w\phi_i\rangle\langle{}^w\phi_i| - |{}^x\phi_i\rangle\langle{}^x\phi_i|) | {}^w\Psi \rangle \quad (6)$$

$$= N - {}^wP^{\mu\nu}{}^xP_{\nu\mu}. \quad (7)$$

Clearly  $d_{ww}^2 = 0$ , and  ${}^wP^{\mu\nu}{}^xP_{\nu\mu} = \langle {}^w\phi_i | {}^x\phi_j \rangle \langle {}^x\phi_j | {}^w\phi_i \rangle$  is bounded by 0 and  $N$ , so the square distance is positive semidefinite, and has as a maximum the number of electrons,  $N$ .  $d_{wx}^2$  gives a very intuitive measure of distance between solutions, the density matrices from two configurations differing by a single spin-orbital have  $d_{wx}^2 = 1$ , while the overlap between the many particle wave functions would vanish and give no information about configurations which differ by more than a single excitation. While  $d_{wx}^2$  has the formal quality of a square distance, its bounds make it naturally have the units of number of electrons, and we shall use it as a distance measure.

This concept of distance in density matrix space proves very useful to characterize and distinguish between solutions. In a manner analogous to classical metadynamics, to bias against the set of previously located solutions,  $x$ , we create a new Lagrangian,

$$\tilde{E} = E + \sum_x N_x e^{-\lambda_x d_{0x}^2}, \quad (8)$$

where 0 represents the present density. From this we may derive a new effective Fock matrix,

$$\tilde{F}_{\mu\nu} = F_{\mu\nu} + \sum_x {}^xP_{\mu\nu} N_x \lambda_x e^{-\lambda_x d_{0x}^2}. \quad (9)$$

This may be used with very little modification within a standard DIIS procedure [6] to locate multiple solutions. When close to a new solution, the biasing potential can be removed so the location of that solution is not affected by it. We have found starting with values  $\lambda_x = N_x = 1$ , with the biasing parameters being automatically increased if the bias proves insufficient to avoid convergence to the same minimum. To perform calculations, we have implemented this method in a modified version of Q-CHEM [7]. Orbital isosurfaces were generated with VMD [8].

To our knowledge, the only complete enumeration of Hartree–Fock states of a system is by Kowalski and Jankowski [9], where the Hartree–Fock equations were parameterized by the coefficients of the density matrix, and homotopy-following used to locate the solutions of the resulting equations. This method was applied to the H4 model [10] (Fig. 1) with parameter  $\alpha = 0.005$ . Without using any information as to their whereabouts, we have located all of their solutions [11], and in addition have located an extra solution [12] of energy  $-0.123495E_h$ . It is possible that this solution was missed because of the finite step size used in the homotopy following method. We have also found a double degeneracy for solutions 3, 7, and 9 (where the solutions differ by only the signs of some coefficients). After locating the solutions, a stability analysis [13,14] was performed, revealing that only the two lowest energy solutions are minima, the remainder having at least one negative orbital Hessian eigenvalue.

In Fig. 2, we plot the set of solutions against quasidegeneracy parameter,  $\alpha$ . Starting at  $\alpha = 0.005$  ( $90.9^\circ$ ), by using a previous geometry’s located solutions’ densities as initial guesses, we have been able to follow the solutions with changing  $\alpha$ . We note that as the quasidegeneracy decreases ( $\alpha$  increases), a number of solutions coalesce and then cannot be located. There also seems to be very little relationship in number or energy between the  ${}^1A_1$  Full CI solutions and the excited state RHF solutions, aside from the FCI lowest and highest solutions being lower and upper bounds for the respective RHF solutions.

The dissociation of the nitrogen molecule has been much studied in quantum chemistry, and the breaking of the triple bond is regarded as a extremely difficult problem, even for the most sophisticated of correlated methods [15–22]. While the RHF solution may appear a poor starting

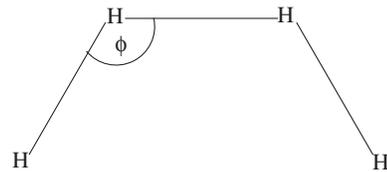


FIG. 1. The geometry of the H4 model. Measured in degrees,  $\phi = 90 + 90\alpha$ . All bond lengths are  $2a_0$ .

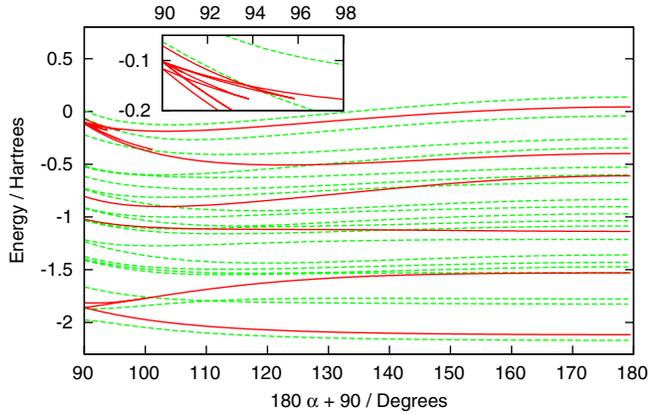


FIG. 2 (color online). The located closed-shell RHF solutions of the H4 model (solid); the  $^1A_1$  Full CI solutions (dotted).

position, the tantalizing simplicity of single-reference methods still make it the first choice to build upon. Unlike the UHF solution, it suffers no spin contamination, giving, like the Full CI solution, a pure singlet throughout the binding curve.

Working in Dunning's cc-pVDZ basis [23], we have applied our method to the nitrogen molecule binding curve. At positions along the binding curve, many RHF solutions were enumerated, and the lowest of them were tracked along the binding curve with steps of 0.05 Å or smaller. These have been plotted in Fig. 3. The curves end where it has not been possible to further follow the solutions. What is commonly regarded as the RHF solution (shown thick solid), is not always the lowest possible RHF solution. While it minimizes the energy when the orbitals are restricted to transform with the point group of the molecule, if no spatial symmetry is taken into account, as the bond is stretched beyond 1.4 Å, it becomes a saddle point with negative orbital Hessian eigenvalues. The lowest overall solution at these distances is a symmetry-broken solution whose orbitals and orbital energies are shown in Fig. 4(b). It is apparent from these plots that the symmetry breaking

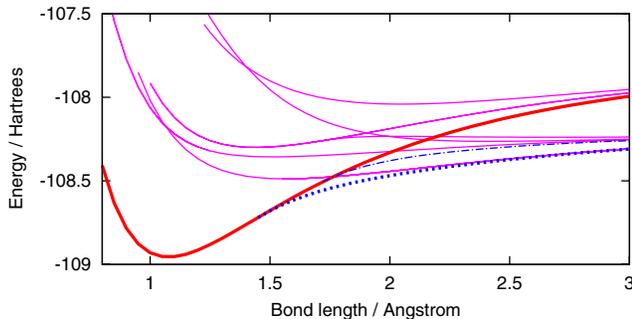


FIG. 3 (color online). Some of the lowest RHF stationary states of the N<sub>2</sub> molecule: the lowest symmetric (thick solid), the lowest broken-symmetry (thick dotted), a third solution breaking off from the RHF (thin dot dash), and others (thin solid).

allows the molecule to localize two electrons in an orbital on each of the nitrogen atoms, leaving only one pair of electrons delocalized in a  $\sigma$ -bond. This reduced electrostatic effects result in a lowering of the overall energy. At separation, it appears the fragments are approaching a singlet coupled pair of doublet nitrogen atoms, rather than the quartet atoms achieved with Full CI. We note that this solution has very recently been used as a starting point in coupled-cluster calculations [21]. In the general case of multiple-bond breaking, it seems likely that such symmetry-broken solutions exist and are of lower energy,

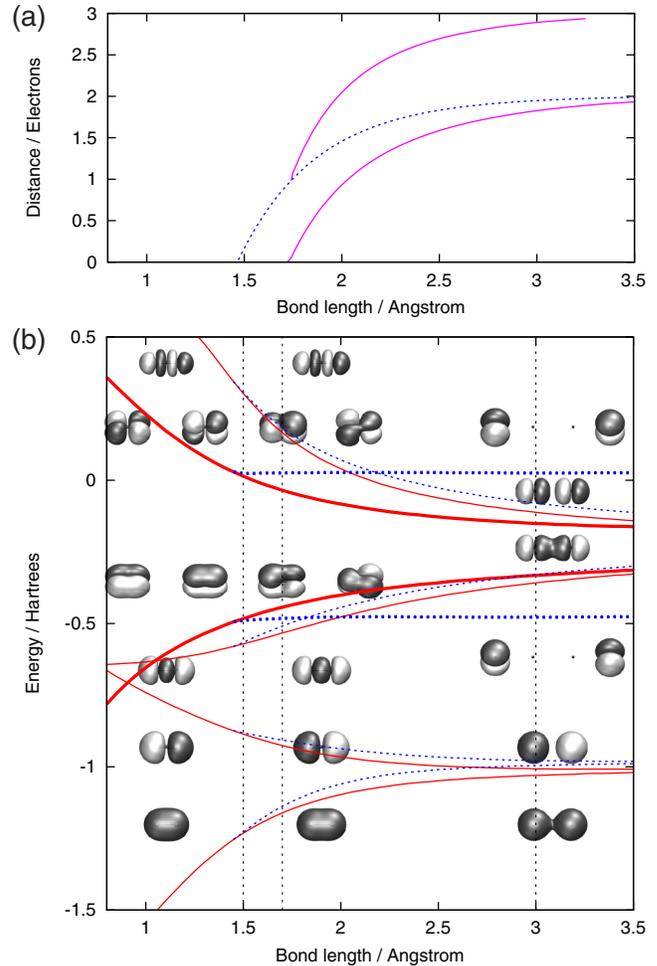


FIG. 4 (color online). The dissociation of N<sub>2</sub> using a cc-pVDZ basis. (a) The distance,  $d^2$ , between minima. The dotted line is the distance between symmetric and broken-symmetry RHF solutions. The solid lines correspond to a third solution which breaks off the symmetric solution at 1.7 Å. The lower line is the distance from the symmetric solution, and the upper the distance from the broken-symmetry solution; (b) the orbital energies. Solid lines represent the symmetric RHF solution, and dotted lines the symmetry-broken solution. Thick lines indicate a double degeneracy. Superimposed on the plot are isosurface plots of the symmetry-broken orbitals at bond lengths 1.5, 1.7, and 3 Å, as indicated by the vertical lines. The symmetric orbitals take forms very close to those at 1.5 Å throughout the binding curve.

(a)  $-0.482$  (b)  $-0.466$  (c)  $-0.299$  (d)  $-0.118$  (e)  $0.013$  (f)  $0.045$ 

FIG. 5. 3 highest occupied and 3 lowest unoccupied MOs for the third minimum found in Fig. 4(a) at bond length 3 Å, labeled by eigenvalue (in Hartrees). The remaining occupied orbitals are very similar to those found in the symmetric RHF solution.

and may be suitable as a starting place for correlation treatments. As the bond length increases, the distance between the symmetric and symmetry-broken solution approaches 2 electrons [Fig. 4(a)]. This may be understood as each  $\pi_u$  orbital creating a linear combination with its  $\pi_g$  counterpart, resulting in a distance of half an electron. As there are two doubly occupied orbitals, the total distance is 2 electrons, as the remaining orbitals are relatively unaffected.

As a further illustration of the distance between solutions, we have also investigated a third solution which breaks off from the symmetric RHF solution at about 1.7 Å. This solution breaks the degeneracy of the  $\pi_u$  orbitals by mixing one in with the  $p\sigma_u$ , and the complementary  $\pi_g$  with the  $p\sigma_g$ . At large separations this results in the orbitals shown in Fig. 5. This similarly reaches a distance of 2 electrons from the symmetry-broken SCF for the same reasons as above, but three electrons from the symmetry-broken solution as the three highest MOs have contributions from both an occupied and a virtual MO from this solution.

In conclusion, we have developed the notion of a distance between density matrices which is a quantity measured in electrons and recovers the intuitive values of the distance between configurations whose orbitals differ. We demonstrated that, with a simple modification of the SCF procedure to include a biasing potential based upon this distance measure, it is possible to enumerate a number of different solutions to the SCF equations. While to locate these solutions requires more steps than an ordinary SCF calculation, confirming their existence and energies can give an increased confidence that a given solution is the required lowest solution, and in the search for reaction intermediates. Owing to the nonlinearity of the Hartree-Fock equations, there is still, however, no guarantee that the lowest solution has been found. While in molecules composed of first row elements it is unlikely that around equilibrium geometries incorrect local minima are being found, we expect this method to be a useful tool in transition metal systems, where there are many states close in energy. In the dissociating nitrogen molecule we have found a lower energy symmetry-broken RHF state corresponding to the dissociation into doublet fragments, at a geometry stretched by only 30% from equilibrium.

Although we have limited this paper to RHF calculations, the method is equally applicable to Unrestricted

calculations as well as to Kohn-Sham theories. In the context of DFT, ensuring that the located state is the global minimum is perhaps more important, as it is upon the variational nature of this state that the Hohenberg-Kohn theorems are based.

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