

Hartree-Fock Stability Theory and its Relation to Strong Correlation

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I. GOALS AND RELEVANCE OF PROPOSED RESEARCH

The goal of electronic structure theory is to solve the electronic Schrödinger equation for a molecule or solid state system. The prevailing approach in *ab initio* quantum chemistry is to first compute a self-consistent single-determinant Hartree-Fock (HF) solution which will serve as a reference for many-body perturbative (MP) or coupled-cluster (CC) approaches. Implicit in these methods is the assumption that the reference wave function will be sufficiently close to the exact solution of the Schrödinger equation to converge to the correct answer in a computationally feasible manner. Both the MP and CC approaches have the attractive quality that they are systematically improvable, i.e. increasing the accuracy of the resulting solution can be done by using a higher order of the theory. These so-called post-Hartree-Fock methods are able to recover more of the total electronic energy by accounting for the *correlation energy* in the system. Traditionally, the correlation energy is defined by the difference between the exact energy and the Hartree-Fock energy [17]

$$E_{corr} = E_{exact} - E_{HF} \quad (1)$$

In many cases the correlation energy is relatively small and the Hartree-Fock reference captures a significant portion of the exact total energy. In such cases, the prevailing approach is usually successful and has only implementation issues for larger systems. On the other hand there are systems which are not well treated by this approach, which are often called “strongly correlated”. Examples of such systems are those with degenerate or near-degenerate HOMO-LUMO gaps, metallic solids or molecules close to breaking bonds. Oftentimes for such systems the traditional Hartree-Fock solutions are not even qualitatively correct, implying inadequacies in either the single-reference or mean-field approach.

It is often neglected, however, that the usual way for computing a Hartree-Fock solution in practice is to use a restricted form of the single determinantal wavefunction. In the Restricted Hartree-Fock (RHF), the wave function is restricted to be an eigenfunction of the \hat{S}^2 and \hat{S}_z operators, while in the Unrestricted variant (UHF), the wave function need only be an eigenfunction of the \hat{S}_z . There is yet another lesser-known variation of the theory, known as General Hartree-Fock (GHF), which assumes no spin-symmetries in the wave function. This allows for greater variational flexibility at the cost of “broken symmetry”. Together these three levels of Hartree-Fock theory form a

heirarchy of increasing parameter space within which to minimize the total energy. Thus the term “Hartree-Fock Energy” is inherently ambiguous; this fact calling into question commonly held ideas about correlation and Hartree-Fock theory. Take for example the dissociation curve of H_2 in the RHF and UHF approximations, compared with the exact solution obtained by full configuration-interaction in the complete basis set limit.

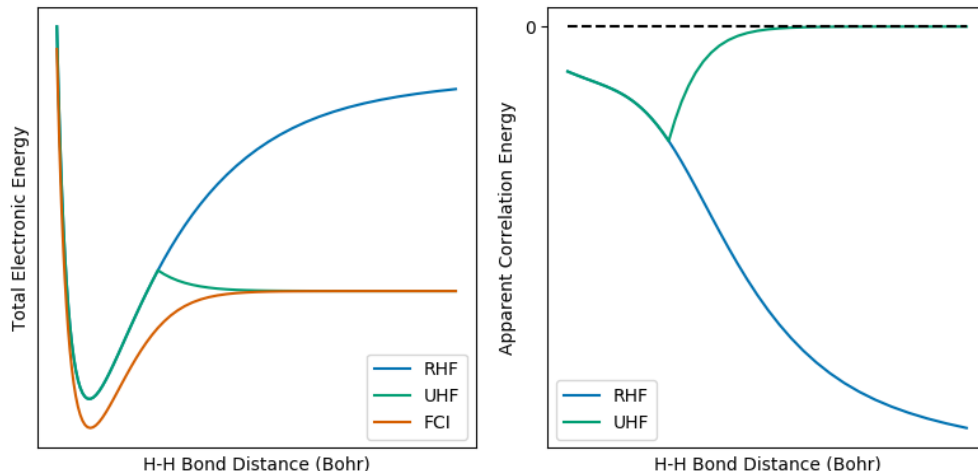


FIG. 1: Dissociation curve of H_2 in the RHF and UHF approximations, compared to the exact limit (FCI). The difference in correlation energies as determined by each reference illustrates the ambiguity of that quantity. In the dissociation limit, the UHF correlation energy vanishes while the RHF correlation energy increases in magnitude.

The correlation energy for the RHF reference case is dramatically larger than that for the UHF reference. In other words, *the correlation energy is, by definition, inherently coupled to the Hartree-Fock reference*. The given example is well understood, but it brings to mind a more general idea that there may be more cases where apparently large correlation energies are due to simply using an inadequate level of Hartree-Fock theory. Scuseria and coworkers have leveraged this idea to create new coupled cluster theories while preserving the symmetry of the reference [18].

Another approach to this problem is to allow breaking of symmetry, and to take the variational principle at face value; lower energy is always better. For predicting certain observables this is not the case, but for energies alone we are free to maintain this mindset. If the HF solution is allowed to relax fully in its most general form, the resulting correlation energy may be reduced dramatically. Therefore the overarching theme of the proposed work is that *many examples of strong correlation may be misleading, and in order to find out we have to find lower energy Hartree-Fock solutions, even at the cost of broken symmetry*.

For some time an approach to find lower energy HF solutions has been known to follow the instability eigenvectors

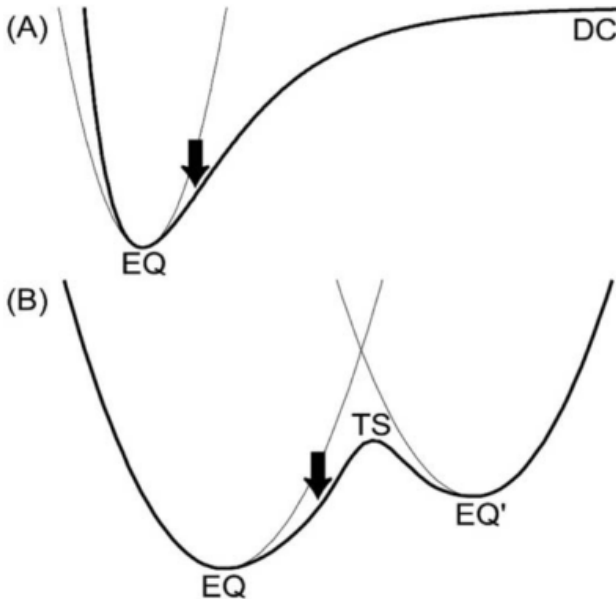


FIG. 2: Example PES illustrating the ADD effect. A) The anharmonicity increases in the direction towards flattening of the PES due to dissociation (DC). B) The anharmonic distortion of the harmonic potential points in the direction from one equilibrium point to another. Taken from Ohno[20].

down in energy to find lower energy solutions [3]. This approach will, by construction, always lead to a lower energy HF solution than the starting point. However, it is important to remember that the instability condition is a local phenomena, and the lower energy solution is not itself guaranteed to be the *lowest* energy solution. The standard approach still suffers from the global optimization problem: whether a solution is a local or global minimum can only be known by comparing it to the other minima of the surface. In fact, the problem of finding the lowest energy HF solution has a direct correspondence to the problem of finding minimum energy points on a potential energy surface of atomic coordinates. It is therefore proposed to adopt approaches from that field to apply to the current problem. An attractive approach is the Global Reaction Route Mapping (GRRM) method with its Anharmonic Downward Distortion (ADD) algorithm [19, 20].

In essence, the algorithm leverages the idea that the presence of a local minimum influences the surrounding energy landscape (in a smooth surface). The minimum will lower the energy pathways leading towards it, and softens the ascent of energy around a transition state. This softening of the PES can be seen by increased anharmonicity in the PES's Taylor expansion (see Fig. 2). Thus a waypoint from one minimum to another can be determined by finding the direction with the highest anharmonicity, and these can be followed to find new solutions. By adopting this approach to use molecular orbital expansion coefficients in place of normal mode coordinates, many minima of the

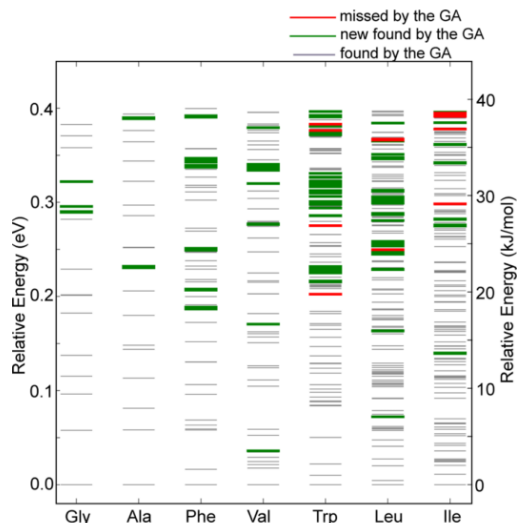


FIG. 3: Conformations of dipeptides found in a search using a Genetic Algorithm. The GA results were compared to a reference data set. Taken from Supady [21]. Note that the only missed conformations are relatively higher-energy.

Hartree-Fock electronic energy surface can be found. The proposed algorithm would have the following steps. First, a HF calculation will be performed and solved self-consistently to find a stationary point. This solution will then be subject to the stability analysis. If the solution is unstable, the instability eigenvector will be followed downhill and a new solution will be found. This will be repeated until a local minimum solution is found. Once this has been completed, the ADD algorithm can be applied to the minimum solution to search for the direction of other minima using the HF stability eigenvectors (the electronic analogue to vibrational modes). We then perturb our solution in that direction and repeat the process to search for all relevant minima.

In the event that the ADD algorithm doesn't perform well, there is another option that requires no assumptions about the underlying potential energy surface. The Genetic Algorithm is a machine learning technique that has been applied to search for minimum energy conformations in peptide dimers [21]. Genetic algorithms have seen use in various global optimization problems, and have been designed via mutation to avoid being stuck in local minima. This makes them well suited for finding a host of high-fitness solutions (see Fig. 3). This approach could be implemented by using the GHF initial guess density matrix as a gene for the algorithm, and a fitness function which prioritizes low-energy HF solutions in a manner similar to the method of Supady [21].

If effective, either the ADD or the Genetic algorithm could then be used to investigate strong correlation of various systems. If it turns out that fully minimizing the HF energy can reproduce a majority of the “correlation energy” in these systems, then using this HF searching method becomes a justified method of solving strongly correlated systems.

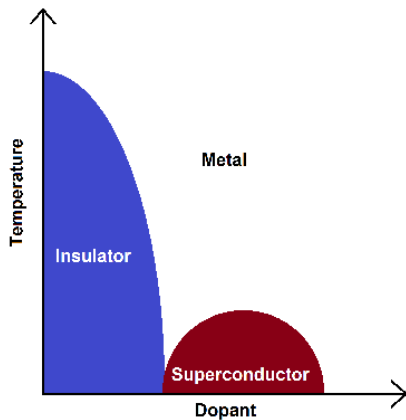


FIG. 4: Cartoon illustration of a phase diagram of superconducting transitions. The insulator (SDW) phase is thought to increase with the superconducting phase.

This would mean that the strong correlation was in fact illusory, and is convertible to a weak correlation problem by means of a more rigorous Hartree-Fock theory.

Another topic of interest is the metal-insulator transition in infinite systems. For a particular type of insulator, the Mott Insulator, the transition from the metallic phase to the insulating phase is due to emergence of a Spin Density Wave (SDW). The SDW is oscillating density of up and down spins throughout space in a checkerboard pattern. The presence of a gapped Mott insulator phase in high- T_c cuprates (which is not predicted by band theory) hints at a connection between Mott insulators and some superconducting materials, but this is not fully understood. Again the finite systems may give clues to explain under what circumstances (Temperature, Pressure, dopant concentration) this transition occurs. Since HOMO-LUMO degeneracy in RHF solutions of finite systems is accompanied by a triplet instability, the emergence of triplet instability can serve as a proxy for an RHF-UHF transition. The corresponding corollary for the solid state case is that triplet instability can signal a paramagnetic-SDW transition. Therefore we can calculate the instability as a function of temperature, pressure and dopant concentration to map out a metallic / insulating phase diagram for infinite systems. A temperature-dependent periodic Hartree-Fock has already been developed and applied to a 2D hydrogen sheet (by other members of the Hirata Lab), a crude but reasonable starting point for testing this approach. By varying the dimensionality, temperature and pressure of the hydrogen sheet, we can monitor the UHF instability and determine under what circumstances the SDW phase becomes present at higher temperatures. In doing so, we hope to be able to understand further how to create new materials with controlled Mott-Insulating transitions, which may be related to increasing the T_c of superconducting materials (See Fig. 4).

II. ACCOMPLISHMENTS

A. Hartree-Fock Stability

Hartree-Fock (HF) Theory has been the foundation for *ab initio* electronic structure theory throughout its history. An often overlooked aspect of the theory is that there are many solutions to the HF equations for a given system, but being a solution to the Hartree-Fock equation ensures only that the solution is stationary with respect to the determined orbitals. If the solution is indeed a minimum, it is called “stable”, while if there is any displacement in the electronic structure which lowers the energy, the solution is “unstable”. A method for determining the stability of a Hartree-Fock solution was proposed by Thouless in 1960[1]. The condition was rederived into the expression familiar to quantum chemists by Cizek and Paldus in 1967[2]. Furthermore, the stability equations factorize depending on the symmetry of the Hartree-Fock eigenfunctions. To this end, Seeger and Pople outlined a hierarchical approach to systematically evaluate the stability of HF states in the restricted, unrestricted and generalized Hartree-Fock procedures[3]. Recently, the method has been used to aid the search for the lowest-energy Unrestricted Hartree-Fock (UHF) solutions in molecules, as well as the General Hartree-Fock (GHF) solutions in geometrically frustrated hydrogen rings which cannot conform even to the UHF scheme[4, 5]. The lower energy HF solutions in these studies were located by first finding the instabilities in the higher spin-symmetry solutions, then using this information to obtain “symmetry breaking” displacements that lower the energy.

To determine if there is indeed a symmetry-broken HF solution of lower energy, the usual method is to determine the stability of a found Hartree-Fock solution. Instabilities are indicated by a negative eigenvalue the Electronic Hessian,

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}, \quad (2)$$

where the matrices \mathbf{A} and \mathbf{B} have dimension $N_{occupied} \times N_{virtual}$ with elements given by

$$A_{i \rightarrow a, j \rightarrow b} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle aj || ib \rangle, \quad (3)$$

$$B_{i \rightarrow a, j \rightarrow b} = \langle ab || ij \rangle. \quad (4)$$

For a paramagnetic HF solution (RHF), the Orbital Hessian factorizes into the matrices known to chemists as the singlet and triplet instability matrices ($^1\mathbf{H}$ and $^3\mathbf{H}$, respectively)[3, 6].

$${}^1A'_{i \rightarrow a, j \rightarrow b} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + 2 \langle aj|ib \rangle - \langle aj|bi \rangle \quad (5a)$$

$${}^3A'_{i \rightarrow a, j \rightarrow b} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} - \langle aj|bi \rangle \quad (5b)$$

$${}^1B'_{i \rightarrow a, j \rightarrow b} = 2 \langle ab|ij \rangle - \langle ab|ji \rangle \quad (5c)$$

$${}^3B'_{i \rightarrow a, j \rightarrow b} = -\langle ab|ji \rangle \quad (5d)$$

The lowest eigenvalue of both of these matrices will reveal the stability of the RHF solution. If ${}^1\mathbf{H}$ has negative eigenvalues, the solution is unstable with respect to changes that preserve singlet character (singlet instability), while if ${}^3\mathbf{H}$ has negative eigenvalues, the solution is unstable towards displacements that would change the wavefunction towards a triplet state (triplet instability). The solution is stable if neither ${}^1\mathbf{H}$ nor ${}^3\mathbf{H}$ has a negative eigenvalue. An eigenvalue of 0 does not indicate instability, and this case is discussed in detail by Cui et al [7].

B. Hartree-Fock Stability of the Homogeneous Electron Gas

Previously it has been shown for finite systems with form-degenerate HOMO-LUMO, there always exists a symmetry-breaking instability[8]. Whether this theorem holds in the infinite case remains to be seen. To investigate HF instabilities in zero band gap solids, a natural starting point is the Homogeneous Electron Gas (HEG, often called Jellium or Uniform Electron Gas) model. The model consists of electrons in a box with periodic boundary conditions and the constraint that the entire system is charge-neutral via a uniform background positive charge. The resulting Coulomb interactions cancel exactly, and the only remaining terms are due to kinetic and exchange energies. Historically it was thought that the plane-wave paramagnetic solution to the HF equations for this model was the “correct” solution. However, in a landmark paper, Overhauser showed that certain symmetry broken solutions *always* have lower-energy than the paramagnetic solutions at all electron densities[9]. This hints at, but does not show, that the analogous triplet instability theorem persists in the infinite case.

Overhausers’ paper sparked new interest in the HEG, and since then Energies of various phases thereof have been computed to great accuracy[10]. More recently, phase diagrams have been determined for the HEG in 2 and 3 dimensions[11–13]. In all cases the phase diagrams are made by computing the energies of the polarized and unpolarized states, and comparing them. This approach necessitates that the form of the solutions is known ahead of time.

The present work focuses on directly calculating the Hartree-Fock stability of the paramagnetic homogeneous

electron gas as a function of electron density. The motivation is two-fold. First, the numerical studies of this model can give computational evidence for or against the ubiquity of symmetry-breaking HF instabilities in metallic solids. Secondly, the instabilities can help in determining lower energy HF solutions of the HEG. This is because the study will reveal where the symmetry broken Hartree-Fock reference is needed. To date, an optimal form (i.e. minimal energy in the HF manifold) of the Hartree-Fock solution to the HEG remains unknown, even though exact energy (including correlation) is essentially known. Therefore determining a lower energy HF solution can yield insight into the effects of correlation of this fundamental physical model.

C. Method

Starting with the Jellium Hamiltonian in atomic units,

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2} + \frac{1}{2} \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}, \quad (6)$$

one solution to the Hartree-Fock equations in D dimensions are plane waves of the form

$$\phi_{\vec{k}} = \frac{1}{\sqrt{L^D}} e^{i\vec{k}\vec{x}}, \quad (7)$$

where L is the length of one side of the direct lattice with cubic symmetry. Using this as the basis for the rest of the analysis, the two electron repulsion integrals are analytic and well-behaved in two and three dimensions[11, 14]

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \stackrel{2D, 3D}{=} \begin{cases} \frac{\pi}{L^D} \frac{2^{D-1}}{|\vec{k} - \vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' + n\vec{G} \text{ and } |\vec{k} - \vec{k}''| \neq 0 \\ 0 & \text{else,} \end{cases} \quad (8)$$

where $n\vec{G}$ is any integer times a reciprocal lattice vector of the system. The orbital energies are

$$\epsilon_{\vec{k}, \sigma} = \frac{\hbar^2 \vec{k}^2}{2m} - \sum_{\vec{k}}^{|k| < k_f} n_{\vec{k}\sigma} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle, \quad (9)$$

where $n_{\vec{k}\sigma}$ is the occupation number of the state with momentum \vec{k} and spin σ [14]. In one dimension, the two electron integral diverges, and it is common to use a delta function interaction,

$$V(r_{12}) = V_0 \delta(r_{12}), \quad (10)$$

and the two electron integral in this case is simply

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \stackrel{1D}{=} \begin{cases} V_0 & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' + n\vec{G} \\ 0 & \text{else.} \end{cases} \quad (11)$$

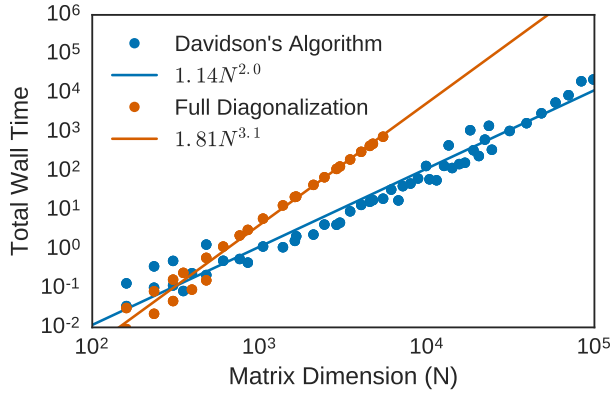


FIG. 5: The asymptotic scaling of both algorithms behaves as expected.

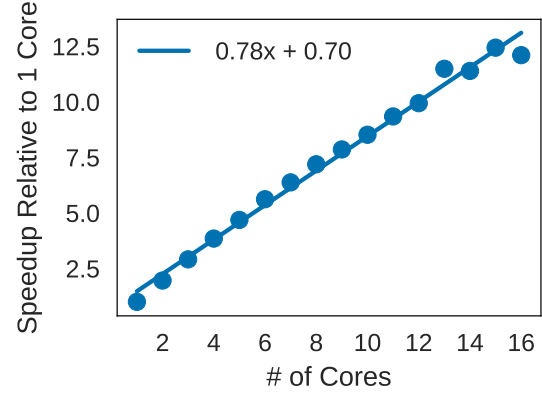


FIG. 6: The speedup of the entire calculation as the number of computer cores is sufficiently linear.

D. Results

Using the equations for energies and two electron integrals, the stability analysis was performed on the paramagnetic HEG model as a function of electron density (or equivalently, the Wigner-Seitz radius, r_s). The naive approach of explicitly constructing and diagonalizing the orbital hessian is intractable both in terms of memory and calculation time requirements. Since the instability condition is that the any eigenvalue is negative, it suffices to calculate the sign of only the lowest eigenvalue. This is a task well suited for an iterative subspace solver. To this end, a parallel version of the Jacobi-Davidson algorithm was implemented by representing the matrix as a matrix-vector product (made possible by the SLEPc library[15]). This allowed for two necessary optimizations. First, the algorithmic change from full diagonalization to a subspace algorithm reduces the memory requirements from $O(N^2)$ to $O(N)$ and the computational scaling from $O(N^3)$ to $O(N^2)$ (See Fig. 5). Secondly, the parallelization of the algorithm allows the program to be run on the Blue Waters supercomputer with about 80% strong parallel scaling efficiency (Fig. 6).

These optimizations allow the calculation to be performed with enough grid points to converge the resulting “transition r_s ”, the Wigner-Seitz radius at which the HF solution transitions from stable to unstable.

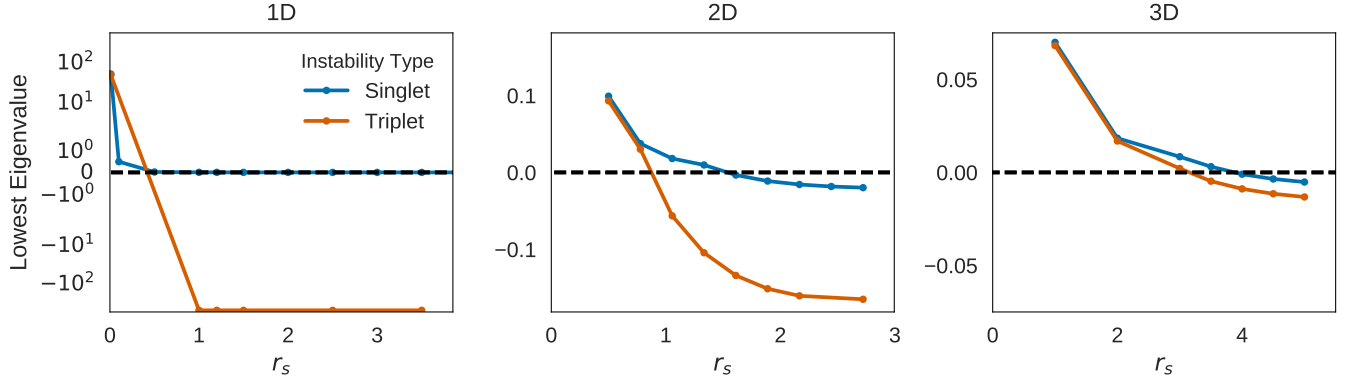


FIG. 7: The Lowest eigenvalues of the triplet and singlet instability matrices in 1, 2 and 3 dimensions.

The transition r_s occurs at $r_s = 1$ in 2D and $r_s = 3$ in 3D (See Fig. 7 and Fig. 8). These results are consistent with those seen by other methods[12, 16]. On the other hand, the transition r_s for one dimension tends towards zero and stays quite close as the number of gridpoints increases. Indeed, numerical issues appear at very high density (low r_s) due to divergence of the two electron integrals in the asymptotic limit. With this in mind, it is clear at least that the instability in the 1D case persists even at very high densities (potentially all finite densities), which is to be expected from Overhauser's proof of instability at all values of r_s in 1D for the delta function potential [9].

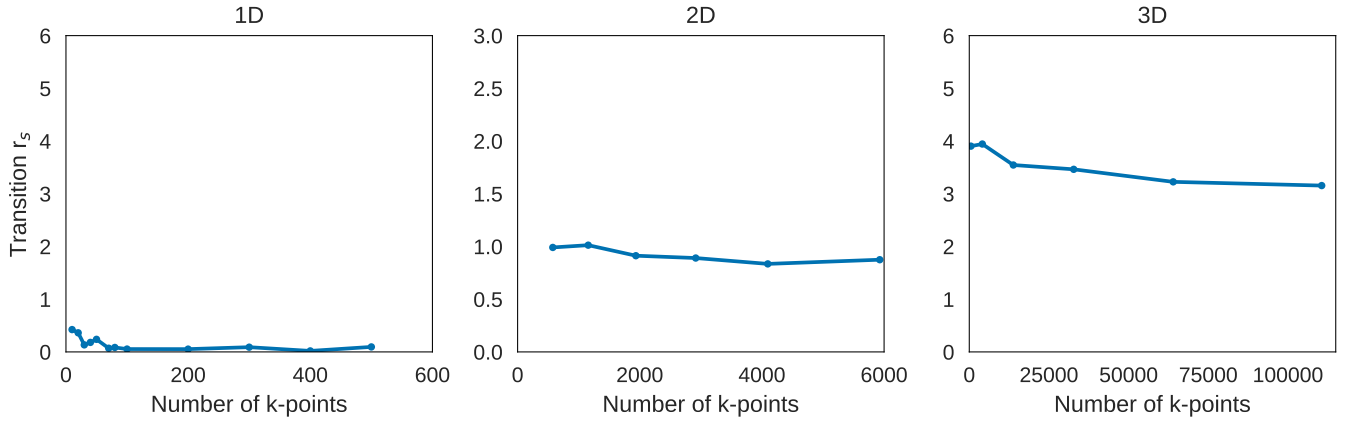


FIG. 8: The value of r_s at which the triplet instability occurs with increasing number of k-points in 1, 2 and 3 dimensions.

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