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Cite as: J. Chem. Phys. **143**, 114112 (2015); <https://doi.org/10.1063/1.4929354>

Submitted: 05 May 2015 . Accepted: 11 August 2015 . Published Online: 18 September 2015

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Singlet and triplet instability theorems

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(Received 5 May 2015; accepted 11 August 2015; published online 18 September 2015)

A useful definition of orbital degeneracy—form-degeneracy—is introduced, which is distinct from the usual energy-degeneracy: Two canonical spatial orbitals are form-degenerate when the energy expectation value in the restricted Hartree–Fock (RHF) wave function is unaltered upon a two-electron excitation from one of these orbitals to the other. Form-degenerate orbitals tend to have isomorphic electron densities and occur in the highest-occupied and lowest-unoccupied molecular orbitals (HOMOs and LUMOs) of strongly correlated systems. Here, we present a mathematical proof of the existence of a triplet instability in a real or complex RHF wave function of a finite system in the space of real or complex unrestricted Hartree–Fock wave functions when HOMO and LUMO are energy- or form-degenerate. We also show that a singlet instability always exists in a real RHF wave function of a finite system in the space of complex RHF wave functions, when HOMO and LUMO are form-degenerate, but have nonidentical electron densities, or are energy-degenerate. These theorems provide Hartree–Fock-theory-based explanations of Hund’s rule, a singlet instability in Jahn–Teller systems, biradicaloid electronic structures, and a triplet instability during some covalent bond breaking. They also suggest (but not guarantee) the spontaneous formation of a spin density wave (SDW) in a metallic solid. The stability theory underlying these theorems extended to a continuous orbital-energy spectrum proves the existence of an oscillating (nonspiral) SDW instability in one- and three-dimensional homogeneous electron gases, but only at low densities or for strong interactions. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929354>]

I. INTRODUCTION

Electronic structures of molecules and solids are unstable when electronic excited and ground states are degenerate or nearly degenerate. Such systems tend to be labile, reactive, and can display colossal response to a minute external perturbation. Such response properties include electrical conductivity, spontaneous symmetry breaking, magnetic orders, electronic phase transitions or crossovers, and superconductivity.^{1,2} Some of these electronic structures are *strongly correlated*³ and not to be described quantitatively by a mean-field theory. Nevertheless, Hartree–Fock (HF) theory seems capable of at least detecting such instabilities under qualitatively correct conditions and is thus potentially useful for some critical issues in chemistry and solid-state physics.

A solution of the HF equation is said to be unstable when the second variation of the associated energy (the stability matrix) is not positive semidefinite.^{1,4–20} This theory was pioneered by Thouless⁴ and fully developed by Čížek and Paldus,⁷ culminating in a comprehensive study by Seeger and Pople,¹¹ who listed 13 types of such instabilities and the corresponding stability matrices. One of the instabilities is that of a real, singlet, restricted Hartree–Fock (RHF) wave function of a closed-shell molecule in the space of real, triplet, unrestricted Hartree–Fock (UHF) wave functions.^{7,9} Another is the instability of a complex, singlet RHF wave function in

the space of complex, triplet UHF wave functions. Together, they may be called the triplet or spin-density-wave (SDW) instabilities.⁷ Yet another is the instability of a real, singlet RHF wave function in the space of complex, singlet RHF wave functions. This is called the singlet or charge-density-wave (CDW) instability.⁷

Here, we introduce the new concept of *form-degeneracy* as a complementary and perhaps more broadly applicable criterion of orbital degeneracy than the usual *energy-degeneracy*. Two canonical spatial molecular orbitals, $\varphi_p(\mathbf{r})$ and $\varphi_q(\mathbf{r})$, of a RHF calculation are considered form-degenerate, when the energy expectation value in the RHF wave function using $\varphi_p(\mathbf{r})$ is unaltered by replacing it by $\varphi_q(\mathbf{r})$. In other words, the excited state in which two electrons are simultaneously promoted from $\varphi_p(\mathbf{r})$ to $\varphi_q(\mathbf{r})$ has the same energy as the ground state. The highest-occupied and lowest-unoccupied molecular orbitals (HOMOs and LUMOs) of the oxygen molecule and collinear methylene (systems that are subject to Hund’s rule and biradicaloids) are form-degenerate. The HOMO and LUMO of a homonuclear diatomic molecule are frequently form-degenerate as its covalent bond is stretched infinitely. On the other hand, HOMO and LUMO of a metal such as a homogeneous electron gas (HEG) are energy-degenerate.

In this article, we present a mathematical proof of the existence of a triplet instability in a real or complex RHF wave function of a finite system with energy- or form-degenerate HOMO and LUMO. The proof provides a basis of Hund’s rule within the framework of HF theory. It explains the propensity of the triplet instabilities in covalent bond breaking. It suggests,

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but not guarantees the spontaneous formation of a SDW in a metallic solid. We furthermore prove the existence of a singlet instability in a real RHF wave function of a finite system in the space of complex RHF wave functions, when HOMO and LUMO are form-degenerate, but have nonidentical electron densities, or are energy-degenerate. An application of this is a CDW formation in the square cyclobutadiene, which is an electronic driving force for its Jahn–Teller distortion.

II. THEOREMS

We use i and j to label occupied spatial orbitals in a RHF wave function Φ_0 of a finite system, a and b virtual orbitals, and p , q , r , and s either type of orbitals. We use I and A to denote HOMO and LUMO, respectively. Φ_{II}^{AA} designates the RHF wave function in which I is replaced by A in Φ_0 , that is, the doubly excited determinant in which two electrons in the I th spatial orbital are promoted to the A th spatial orbital.

Definition. The HOMO and LUMO in a RHF wave function are form-degenerate when

$$0 = \langle \Phi_{II}^{AA} | \hat{H} | \Phi_{II}^{AA} \rangle - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \equiv 2\delta, \quad (1)$$

where \hat{H} is the Hamiltonian.

Remarks. We can express the first integral in the above equation as

$$\langle \Phi_{II}^{AA} | \hat{H} | \Phi_{II}^{AA} \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + 2(\epsilon_A - \epsilon_I) - 4\langle AI|AI \rangle + 2\langle AI|IA \rangle + \langle II|II \rangle + \langle AA|AA \rangle, \quad (2)$$

where ϵ_p is the energy of the p th RHF orbital and

$$\langle pq|rs \rangle = \iint \frac{\varphi_p^*(\mathbf{r}_1)\varphi_q^*(\mathbf{r}_2)\varphi_r(\mathbf{r}_1)\varphi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (3)$$

From Eqs. (1) and (2), we can rewrite the HOMO-LUMO energy difference as

$$\epsilon_A - \epsilon_I = 2\langle AI|AI \rangle - \frac{1}{2}\langle II|II \rangle - \frac{1}{2}\langle AA|AA \rangle - \langle AI|IA \rangle + \delta, \quad (4)$$

with $\delta = 0$ when HOMO and LUMO are form-degenerate.

Form-degenerate orbitals tend to be associated with highly symmetric molecular geometries and to have isomorphic electron densities; $|\varphi_A(\mathbf{r})|^2$ and $|\varphi_I(\mathbf{r})|^2$ may be superimposed exactly onto each other by translation and/or rotation. In spite of this and of the fact that Φ_0 and Φ_{II}^{AA} have the same energy expectation value, form-degenerate ϵ_A and ϵ_I generally differ from each other, i.e., $\epsilon_A > \epsilon_I$. This is because an electron in the I th orbital feels the $(N - 1)$ -electron mean field, whereas an electron in the A th orbital experiences the N -electron mean field, where N is the number of electrons in the molecule.

The usual definition of HOMO-LUMO degeneracy, i.e., energy-degeneracy, is $\epsilon_A = \epsilon_I$. This is a much stronger condition hardly satisfied by any finite system for the aforementioned reasons.²¹

The value of δ may be considered as an unambiguous, quantitative index of strong correlation in the ground state. $\delta = 0$ corresponds to the strongest limit, where there is at

least one excited-state determinant with the same energy as the ground-state determinant, and therefore, a multi-reference wave function is needed to describe the ground state. However, this simple index cannot distinguish a high density of low-lying excited states from a low density, each causing the correspondingly different degree of correlation.

Triplet instability theorem I. A real, singlet RHF wave function of a finite system is always unstable in the space of real, triplet UHF wave functions, when HOMO and LUMO are energy- or form-degenerate.

Proof. In the notation of Seeger and Pople,¹¹ this type of instability exists when the $N_{\text{occ}}N_{\text{vir}}$ -by- $N_{\text{occ}}N_{\text{vir}}$ stability matrix, ${}^3\mathbf{A}' + {}^3\mathbf{B}'$, has at least one negative eigenvalue (the smallest eigenvalue being exactly zero does not imply an instability). Here, N_{occ} (N_{vir}) is the number of occupied (virtual) real spatial orbitals. The matrix elements are given^{7,11} by

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

$${}^3B'_{i \rightarrow a, j \rightarrow b} = -\langle ab|ji \rangle, \quad (6)$$

where δ_{ij} and δ_{ab} are the Kronecker delta. The readers are referred to the original papers^{7,11} for their derivations.

For real spatial orbitals, the stability matrix, ${}^3\mathbf{A}' + {}^3\mathbf{B}'$, is symmetric. Hence, to prove that the lowest eigenvalue is negative, we only need to show that at least one of its diagonal elements is negative. This is because, according to the Hylleraas–Undheim–MacDonald theorem,^{22,23} the former is more negative than the latter.

If the HOMO and LUMO are form-degenerate ($\delta = 0$), the diagonal element corresponding to these orbitals is

$$\begin{aligned} & {}^3A'_{I \rightarrow A, I \rightarrow A} + {}^3B'_{I \rightarrow A, I \rightarrow A} \\ &= \epsilon_A - \epsilon_I - \langle AI|AI \rangle - \langle AA|II \rangle \\ &= \langle AI|AI \rangle - \frac{1}{2}\langle II|II \rangle - \frac{1}{2}\langle AA|AA \rangle \\ &\quad - \langle AI|IA \rangle - \langle AA|II \rangle + \delta, \end{aligned} \quad (7)$$

according to Eq. (4).

As proven in the Appendix, for any locally integrable function, $\xi(\mathbf{r})$, the following inequality holds:

$$\iint \frac{\xi^*(\mathbf{r}_1)\xi(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \geq 0. \quad (9)$$

Substituting $\xi(\mathbf{r}) = |\varphi_I(\mathbf{r})|^2 - |\varphi_A(\mathbf{r})|^2$ in the above, we find

$$\langle AI|AI \rangle - \frac{1}{2}\langle II|II \rangle - \frac{1}{2}\langle AA|AA \rangle \leq 0, \quad (10)$$

where the equality holds if and only if $|\varphi_I(\mathbf{r})|^2 = |\varphi_A(\mathbf{r})|^2$ pointwise.²⁴ An alternative proof of the above can be obtained by using the Cauchy–Schwarz inequality²⁵ and the inequality of arithmetic and geometric means. Equation (10) indicates that the sum of the first three terms of the right-hand side of Eq. (8) is negative.

Exchange integrals such as $\langle AI|IA \rangle$ and $\langle AA|II \rangle$ (in real orbitals) are also shown to be positive by Slater²⁶ and also by Roothaan,²⁴ see the Appendix for yet another proof using Eq. (9). Together, we conclude

$${}^3A'_{I \rightarrow A, I \rightarrow A} + {}^3B'_{I \rightarrow A, I \rightarrow A} < 0, \quad (11)$$

which proves the existence of the instability in the presence of form-degenerate HOMO and LUMO ($\delta = 0$).

If the HOMO and LUMO are energy-degenerate, the corresponding diagonal element is

$${}^3A'_{I \rightarrow A, I \rightarrow A} + {}^3B'_{I \rightarrow A, I \rightarrow A} = -\langle AI|AI \rangle - \langle AA|II \rangle < 0. \quad (12)$$

This proves the instability in the presence of energy-degenerate HOMO and LUMO.

Remarks. This theorem for form-degenerate HOMO and LUMO was implied by Bofill and Pulay.²⁷ It corresponds to the case of $\Delta = 0$ and $|B|^2 = 1/2$ in their notation.

Since the right-hand side of Eq. (8) is strongly negative at $\delta = 0$, it remains negative even with a small positive value of δ , or more precisely, whenever

$$\delta < -\langle AI|AI \rangle + \frac{1}{2}\langle II|II \rangle + \frac{1}{2}\langle AA|AA \rangle + \langle AI|IA \rangle + \langle AA|II \rangle \quad (13)$$

is satisfied. Therefore, the triplet instability exists even when HOMO and LUMO are not strictly form-degenerate but only nearly degenerate. In some cases, the strict energy- or form-degeneracy occurs only asymptotically (such as at infinite bond distances or in the thermodynamic limit), but the theorem suggests that the instability manifests itself before these asymptotic limits are actually reached.

Triplet instability theorem II. A complex, singlet RHF wave function of a finite system is always unstable in the space of complex, triplet UHF wave functions, when HOMO and LUMO are energy- or form-degenerate.

Proof. The pertinent stability matrix is given¹¹ by

$${}^3\mathbf{H}' = \begin{pmatrix} {}^3\mathbf{A}' & {}^3\mathbf{B}' \\ {}^3\mathbf{B}'^* & {}^3\mathbf{A}'^* \end{pmatrix}, \quad (14)$$

of which the submatrices are defined by Eqs. (5) and (6). Here, the orbitals are understood to be complex spatial functions. The diagonal element involving form-degenerate HOMO and LUMO ($\delta = 0$) is

$$\begin{aligned} {}^3A'_{I \rightarrow A, I \rightarrow A} &= \epsilon_A - \epsilon_I - \langle AI|AI \rangle \\ &= \langle AI|AI \rangle - \frac{1}{2}\langle II|II \rangle - \frac{1}{2}\langle AA|AA \rangle \\ &\quad - \langle AI|IA \rangle + \delta < 0. \end{aligned} \quad (15)$$

The inequality follows from Eq. (10) and $\langle AI|IA \rangle > 0$.^{24,26} Likewise, the same element involving energy-degenerate HOMO and LUMO is

$${}^3A'_{I \rightarrow A, I \rightarrow A} = -\langle AI|AI \rangle < 0. \quad (16)$$

Since ${}^3\mathbf{H}'$ is Hermitian, these prove the negativity of its lowest eigenvalue, as per the Hylleraas–Undheim–MacDonald theorem,^{22,23} and thus the existence of the instability.

Remarks. The instability exists for near-degenerate HOMO and LUMO if

$$\delta < -\langle AI|AI \rangle + \frac{1}{2}\langle II|II \rangle + \frac{1}{2}\langle AA|AA \rangle + \langle AI|IA \rangle \quad (17)$$

is satisfied.

Singlet instability theorem. A real, singlet RHF wave function of a finite system is always unstable in the space of complex, singlet RHF wave functions, when HOMO and LUMO are form-degenerate, but have nonidentical electron densities, or are energy-degenerate.

Proof. For form-degenerate HOMO and LUMO ($\delta = 0$), the said instability exists when the following matrix element^{7,11} is negative:

$$\begin{aligned} {}^1A'_{I \rightarrow A, I \rightarrow A} - {}^1B'_{I \rightarrow A, I \rightarrow A} &= \epsilon_A - \epsilon_I + 2\langle AI|IA \rangle - \langle AI|AI \rangle - \langle AA|II \rangle \\ &= \langle AI|AI \rangle - \frac{1}{2}\langle II|II \rangle - \frac{1}{2}\langle AA|AA \rangle \\ &\quad + \langle AI|IA \rangle - \langle AA|II \rangle + \delta. \end{aligned} \quad (18)$$

$$\quad (19)$$

The sum of the first three terms in Eq. (19) is negative because of Eq. (10) unless $|\varphi_I(\mathbf{r})|^2 = |\varphi_A(\mathbf{r})|^2$ pointwise. The sum of the subsequent two terms is zero because orbitals are real. Hence, the right-hand side is always negative unless the HOMO and LUMO have the pointwise identical electron densities. For energy-degenerate HOMO and LUMO, the corresponding element is

$${}^1A'_{I \rightarrow A, I \rightarrow A} - {}^1B'_{I \rightarrow A, I \rightarrow A} = \langle AI|IA \rangle - \langle AI|AI \rangle, \quad (20)$$

where $\langle AI|IA \rangle = \langle AA|II \rangle$ is used. The right-hand side is always negative as per Roothaan.²⁴ These in conjunction with the Hylleraas–Undheim–MacDonald theorem^{22,23} prove this theorem.

Remarks. This theorem and the triplet instability theorem II imply⁹ the existence of another instability, that is, the instability of a real, singlet RHF wave function in the space of complex, triplet UHF wave functions, when HOMO and LUMO are form-degenerate, but have nonidentical electron densities, or are energy-degenerate.

The instability condition for near-degenerate HOMO and LUMO is given by

$$\delta < -\langle AI|AI \rangle + \frac{1}{2}\langle II|II \rangle + \frac{1}{2}\langle AA|AA \rangle. \quad (21)$$

As shown above, the range of δ that satisfies this condition is null when $|\varphi_I(\mathbf{r})|^2 = |\varphi_A(\mathbf{r})|^2$ pointwise and it is generally smaller than those in the case of the triplet instabilities. This indicates that the singlet instability is harder to occur than the triplet instabilities, which is consistent with previous numerical observations.¹

III. DISCUSSION

A. Hund's rule

The HOMO and LUMO are form-degenerate in the singlet RHF wave functions of the oxygen molecule in the minimal

basis set. They are bonding π orbitals perpendicular to each other, which are isomorphic, but not identical in the sense that they are superimposable only upon $\pi/2$ rotation around the molecular axis. Since the rest of the electron density (excluding the density of the HOMO) is axially symmetric, Eq. (1) holds. Thereupon, the triplet instability theorem I states that one can always find a triplet UHF wave function with a lower energy. This can be interpreted as a mathematical basis of Hund's rule within the framework of HF theory.

Comparing the RHF energies of open-shell singlet and triplet states is often used instead to justify Hund's rule.²⁸ However, an open-shell singlet RHF solution is not even a solution of the corresponding UHF equation and has a higher energy than a closed-shell counterpart.¹¹ Therefore, the criterion based on this theorem, which compares the respective minimal energies of singlet and triplet, is more stringent.

With a basis set larger than the minimal one, Coulomb and exchange potentials acting on HOMO and LUMO are different, making them no longer form-degenerate. A triplet instability still tends to occur, as strongly suggested, though not guaranteed by the theorem [cf. Eq. (13)].

The electron densities of the HOMO and LUMO of O₂ are isomorphic, but not identical. This means that the molecule also has the singlet instability according to the eponymous theorem.

B. Biradicaloids

Collinear methylene (CH₂) is another example whose HOMO and LUMO are form-degenerate in the minimal basis set. The triplet instability theorem I dictates that its singlet RHF wave function is unstable in the space of triplet UHF wave functions. It should be cautioned that a "triplet" UHF wave function is not an eigenfunction of the \hat{S}^2 operator and is a mixture of states with different spin multiplicities. These molecules in the UHF description may thus be better characterized as biradicaloids.^{29,30} Biradicaloids are often identified as transition states of radical reactions and associated with small HOMO-LUMO gaps.^{30,31} They are also prime candidates of dyes capable of singlet fission for use in dye-sensitized solar cells.³²

C. Jahn–Teller distortion

The HOMO and LUMO of the singlet RHF solution of square cyclobutadiene in the minimal basis set are form-degenerate. Their electron densities are isomorphic, but not identical. Hence, this solution has both singlet and triplet instabilities as per the respective theorems. In fact, the real singlet RHF solution already displays a "bond" CDW or alternating bond orders, even before molecular orbitals are allowed to be complex-valued; in other words, it has a real singlet instability in addition to a complex singlet instability, with only the latter guaranteed by the theorem. The bond CDW is the electronic driving force of the Jahn–Teller distortion from the square to a rectangular structure.

The triplet instability theorem II furthermore states that it has an even lower-lying UHF solution and is subject to Hund's rule, although the consideration of electron correlation can reverse the conclusion.²⁸

D. Covalent bond breaking

In the limit of an infinite bond length in some homonuclear diatomic molecules with bond order greater than zero, the HOMO and LUMO are symmetric and antisymmetric linear combinations of two atomic orbitals with no overlap. Their electron densities thus become not only isomorphic but also identical asymptotically. All occupied orbitals (excluding the HOMO) then also consist of symmetric and antisymmetric pairs (or axially symmetric π bond pairs, etc.), making Eq. (1) be satisfied. The HOMO and LUMO of infinitely stretched H₂, Li₂, and B₂ (having an odd number of occupied spatial orbitals), for example, display this behavior and are form-degenerate in any basis set, whereas those of He₂, Be₂, and C₂ (having an even number of occupied spatial orbitals) do not. The triplet instability theorem I states that the single RHF wave function of a molecule in the first group is guaranteed to exhibit the triplet instability. The singlet instability theorem does not apply because of the identical HOMO and LUMO electron densities (but does not preclude such an instability, either).

E. Homogeneous electron gas

Overhauser³³ proved that a complex RHF wave function of a HEG is always unstable towards the formation of a "spiral" SDW at any density (see also Refs. 34 and 35). The latter is a general Hartree–Fock (GHF) solution,^{36–43} in which each orbital is a sum of α - and β -spin components. Since the HOMO and LUMO of a HEG are energy-degenerate, the triplet instability theorem II suggests the spontaneous formation of an "oscillating" SDW or a complex UHF solution with a lower energy. However, since every single element of the stability matrix vanishes in the thermodynamic limit [e.g., Eqs. (27) and (34) vanish as $V \rightarrow \infty$ or $\Delta \rightarrow 0$] and the lowest eigenvalue of the stability matrix being zero does not imply an instability, the theorem does not hold. We therefore apply the stability theory underlying the theorems extended to a continuous orbital-energy spectrum (rather than the theorems themselves) to a HEG.

A canonical RHF orbital of a three-dimensional HEG with N electrons in volume V is characterized by its wave vector \mathbf{k} and written as

$$\varphi_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (22)$$

The corresponding orbital energy is

$$\epsilon_{\mathbf{k}} = \frac{k^2}{2} - \frac{V}{(2\pi)^3} \int_{|\mathbf{k}'| \leq k_F} \langle \mathbf{k}, \mathbf{k}' | \mathbf{k}', \mathbf{k} \rangle d\mathbf{k}' \quad (23)$$

$$= \frac{k^2}{2} - \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right), \quad (24)$$

with

$$F(x) = \frac{1}{2} - \frac{1}{4} \left(x - \frac{1}{x}\right) \ln \frac{1+x}{|1-x|}. \quad (25)$$

Here, $k = |\mathbf{k}|$ and k_F is the Fermi wave vector, which corresponds to the HOMO and is related to electron density ρ by

$$\frac{k_F^3}{3\pi^2} = \frac{N}{V} = \rho. \quad (26)$$

A two-electron integral is evaluated analytically as

$$\langle \mathbf{k}, \mathbf{k}' | \mathbf{k}'', \mathbf{k} + \mathbf{k}' - \mathbf{k}'' \rangle = \frac{4\pi}{V|\mathbf{k} - \mathbf{k}''|^2}. \quad (27)$$

The wave vectors of the HOMO and LUMO are designated as \mathbf{k}_I and \mathbf{k}_A , respectively, and $\mathbf{k}_A = \mathbf{k}_I + \Delta$ with $\Delta = |\Delta|$ being a positive infinitesimal.

A RHF wave function composed of the planewaves of Eq. (22) has a triplet instability if the lowest eigenvalue of the stability matrix of Eq. (14) approaches zero from below and is thus always negative until $\Delta = 0$ ($V = \infty$). As per Hylleraas–Undheim–MacDonald theorem,^{22,23} this is implied when ω defined below is negative for one normalized vector, (\mathbf{x}, \mathbf{y}) ,

$$\omega = \begin{pmatrix} \mathbf{x}^* & \mathbf{y}^* \end{pmatrix} \begin{pmatrix} {}^3\mathbf{A}' & {}^3\mathbf{B}' \\ {}^3\mathbf{B}'^* & {}^3\mathbf{A}'^* \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix}, \quad (28)$$

with

$${}^3A'_{\mathbf{k}_i \rightarrow \mathbf{k}_a, \mathbf{k}_j \rightarrow \mathbf{k}_b} = (\epsilon_{\mathbf{k}_a} - \epsilon_{\mathbf{k}_i}) \delta_{\mathbf{k}_i, \mathbf{k}_j} \delta_{\mathbf{k}_a, \mathbf{k}_b} - \langle \mathbf{k}_a, \mathbf{k}_j | \mathbf{k}_b, \mathbf{k}_i \rangle, \quad (29)$$

$${}^3B'_{\mathbf{k}_i \rightarrow \mathbf{k}_a, \mathbf{k}_j \rightarrow \mathbf{k}_b} = -\langle \mathbf{k}_a, \mathbf{k}_b | \mathbf{k}_j, \mathbf{k}_i \rangle, \quad (30)$$

where $|\mathbf{k}_a| > k_F$, $|\mathbf{k}_b| > k_F$, $|\mathbf{k}_i| \leq k_F$, and $|\mathbf{k}_j| \leq k_F$. To establish only the negativity of ω , the vector does not have to be normalized.

For an infinite system, we must switch from the discretized formula given above to its continuous analog, which reads

$$\begin{aligned} \omega &= \frac{V}{(2\pi)^3} \int x^*(\mathbf{k}_i) (\epsilon_{\mathbf{k}_a} - \epsilon_{\mathbf{k}_i}) x(\mathbf{k}_i) d\mathbf{k}_i \\ &+ \frac{V}{(2\pi)^3} \int y^*(-\mathbf{k}_i) (\epsilon_{-\mathbf{k}_a} - \epsilon_{-\mathbf{k}_i}) y(-\mathbf{k}_i) d\mathbf{k}_i \\ &- \frac{V^2}{(2\pi)^6} \iint x^*(\mathbf{k}_i) \langle \mathbf{k}_a, \mathbf{k}_j | \mathbf{k}_b, \mathbf{k}_i \rangle x(\mathbf{k}_j) d\mathbf{k}_i d\mathbf{k}_j \\ &- \frac{V^2}{(2\pi)^6} \iint y^*(-\mathbf{k}_i) \langle -\mathbf{k}_b, -\mathbf{k}_i | -\mathbf{k}_a, -\mathbf{k}_j \rangle y(-\mathbf{k}_j) d\mathbf{k}_i d\mathbf{k}_j \\ &- \frac{V^2}{(2\pi)^6} \iint x^*(\mathbf{k}_i) \langle \mathbf{k}_a, -\mathbf{k}_b | -\mathbf{k}_j, \mathbf{k}_i \rangle y(-\mathbf{k}_j) d\mathbf{k}_i d\mathbf{k}_j \\ &- \frac{V^2}{(2\pi)^6} \iint y^*(-\mathbf{k}_i) \langle -\mathbf{k}_a, \mathbf{k}_b | \mathbf{k}_j, -\mathbf{k}_i \rangle x(\mathbf{k}_j) d\mathbf{k}_i d\mathbf{k}_j. \quad (31) \end{aligned}$$

Each two-electron integral in the above vanishes identically unless the momentum conservation law, $\mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_b - \mathbf{k}_j$, is satisfied. The stability matrix is, therefore, block diagonal with each nonzero block characterized by this momentum transfer. Let us concentrate on the nonzero block whose momentum transfer is Δ , that is, $\Delta = \mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_b - \mathbf{k}_j$, where $\Delta = \mathbf{k}_A - \mathbf{k}_I$. Also, let Δ point in the positive z direction. The volume spanned by \mathbf{k}_i that satisfies this condition is the half-sphere shell of radius k_F and thickness Δ along the z axis (not along the radius). This volume is depicted as domain D_1 in Fig. 1. The volume spanned by $-\mathbf{k}_i$ is designated as D_2 in the same figure.

Using the integration domains defined in Fig. 1, we can write

$$\begin{aligned} \epsilon_{\mathbf{k}_a} &= \frac{|\mathbf{k}_i + \Delta|^2}{2} - \frac{V}{(2\pi)^3} \int_{S_1} \frac{4\pi}{V|\mathbf{k}_i + \Delta - \mathbf{k}_j|^2} d\mathbf{k}_j \\ &= \frac{|\mathbf{k}_i + \Delta|^2}{2} - \frac{V}{(2\pi)^3} \int_{S_2} \frac{4\pi}{V|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_j, \quad (32) \end{aligned}$$

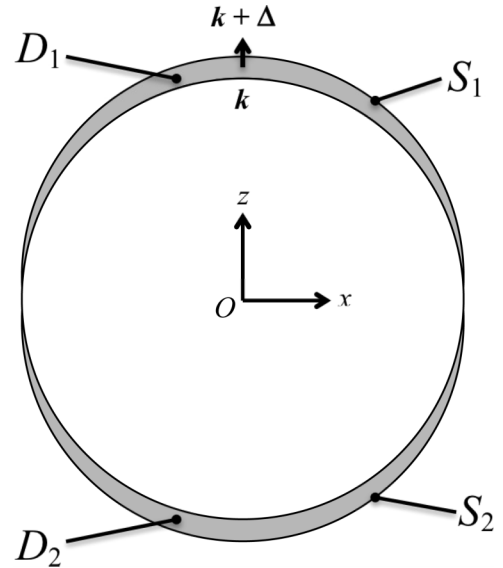


FIG. 1. The xz cross section of the z -axially symmetric integration domains in the k space. Domains S_1 and S_2 are spheres of radius k_F centered at O and $-\Delta$, respectively. Domains D_1 and D_2 are half-sphere shells of radius k_F and thickness Δ along the z axis.

$$\epsilon_{\mathbf{k}_i} = \frac{|\mathbf{k}_i|^2}{2} - \frac{V}{(2\pi)^3} \int_{S_1} \frac{4\pi}{V|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_j, \quad (33)$$

where S_1 and S_2 are the spheres of radius k_F with their centers displaced from each other by Δ . Therefore,

$$\begin{aligned} \epsilon_{\mathbf{k}_a} - \epsilon_{\mathbf{k}_i} &= \mathbf{k}_i \cdot \Delta \\ &+ \frac{V}{(2\pi)^3} \int_{D_1} \frac{4\pi}{V|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_j \\ &- \frac{V}{(2\pi)^3} \int_{D_2} \frac{4\pi}{V|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_j, \quad (34) \end{aligned}$$

in the leading order of Δ at $\Delta \rightarrow 0$.

Letting $x(\mathbf{k}_i) = y(-\mathbf{k}_i) = V^{-1/2}$ for any \mathbf{k}_i within D_1 and $x(\mathbf{k}_i) = y(-\mathbf{k}_i) = 0$ elsewhere, we find

$$\begin{aligned} \omega &= \frac{2}{(2\pi)^3} \int_{D_1} \mathbf{k}_i \cdot \Delta d\mathbf{k}_i \\ &- \frac{4}{(2\pi)^6} \int_{D_1} \int_{D_2} \frac{4\pi}{|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_i d\mathbf{k}_j, \quad (35) \end{aligned}$$

where we have used

$$\int_{D_1} \int_{D_1} \frac{4\pi}{|\mathbf{k}_i + \mathbf{k}_j|^2} d\mathbf{k}_i d\mathbf{k}_j = \int_{D_1} \int_{D_2} \frac{4\pi}{|\mathbf{k}_i - \mathbf{k}_j|^2} d\mathbf{k}_i d\mathbf{k}_j, \quad (36)$$

and so forth. The first (kinetic) term of Eq. (35) is positive and is an $O(\Delta^2 k_F^3)$ quantity, whereas the second (exchange) term is negative and scales as $O(\Delta^2 k_F^2)$. Therefore, when the Fermi wave vector k_F is sufficiently small (i.e., the electron density ρ is sufficiently low), we have an unnormalized vector (\mathbf{x}, \mathbf{y}) that makes the corresponding value of ω negative, dictating the existence of an oscillating SDW instability in the HEG. At a higher density, the same vector (\mathbf{x}, \mathbf{y}) no longer guarantees the negativity of ω or the existence of a SDW instability. This analysis, however, does not preclude an instability of any kind at any density.

It can be seen that the theorems do not apply to an infinite system because its HOMO-LUMO energy-degeneracy occurs

only in the asymptotic limit, at which the kinetic contributions to the stability matrix elements may be comparable in magnitude to the exchange contributions. The foregoing analysis shows that the energy-degeneracy of HOMO and LUMO in a HEG alone may not guarantee the triplet instability; the proof of its existence requires that the Coulomb interaction be strong relative to the kinetic energy.^{44,45}

F. Luttinger liquids

In Ref. 46, Overhauser proved a similar theorem for a one-dimensional metal or the so-called Luttinger liquid with a δ -function interaction. He demonstrated the existence of a spiral or oscillating SDW that has a lower energy than the complex RHF solution at any interaction strength, although an oscillating SDW occurs only for a strong interaction. Here, we apply the stability theory to Luttinger liquids with a δ -function interaction and with the Coulomb interaction.

In a one-dimensional periodic system with N electrons in period L interacting through a δ -function potential, $\gamma\delta(z_i - z_j)$, a canonical RHF orbital is written as

$$\varphi_k(z) = L^{-1/2} \exp(ikz), \quad (37)$$

with the orbital energy being

$$\begin{aligned} \epsilon_k &= \frac{k^2}{2} + \frac{2L}{2\pi} \int_{-k_F}^{k_F} \langle k, k' | k, k' \rangle dk' \\ &\quad - \frac{L}{2\pi} \int_{-k_F}^{k_F} \langle k, k' | k', k \rangle dk' \end{aligned} \quad (38)$$

$$= \frac{k^2}{2} + \frac{\gamma k_F}{\pi}, \quad (39)$$

where $k_F = N\pi/(2L) = \rho\pi/2$ is the Fermi wave vector and

$$\begin{aligned} \langle k, k' | k'', k + k' - k'' \rangle &= \iint L^{-1} \exp\{-ikz_1 - ik'z_2\} \gamma\delta(z_1 - z_2) \\ &\quad \times L^{-1} \exp\{ik''z_1 + i(k + k' - k'')z_2\} dz_1 dz_2 \quad (40) \\ &= \frac{\gamma}{L}. \end{aligned} \quad (41)$$

Let the HOMO and LUMO wave vectors be k_I and k_A , respectively. They are taken to be positive: $k_A - k_I = \Delta > 0$. A triplet instability of the complex RHF wave function is proved to exist if an unnormalized vector, $\{x(k), y(k)\}$, is found that makes ω defined by the continuous analog of Eq. (28) negative. Again, the ${}^3\mathbf{A}'$ and ${}^3\mathbf{B}'$ matrices are block diagonal with each nonzero block associated with the momentum transfer, $k_a - k_i = k_b - k_j$.

Let $x(k_i) = y(-k_i) = L^{-1/2}$ for k_i that satisfies $k_a > k_F \geq k_i > 0$ and $k_a - k_i = \Delta$; they are zero elsewhere. We designate the domain of k_i that satisfies this condition D_1 , whose length is Δ . The corresponding value of ω is

$$\begin{aligned} \omega &= \frac{L}{2\pi} \int_{D_1} x(k_i)^* k_F \Delta x(k_i) dk_i \\ &\quad + \frac{L}{2\pi} \int_{D_1} y(-k_i)^* k_F \Delta y(-k_i) dk_i \\ &\quad - \frac{L^2}{(2\pi)^2} \int_{D_1} \int_{D_1} x(k_i)^* \frac{\gamma}{L} x(k_j) dk_i dk_j \end{aligned}$$

$$\begin{aligned} &- \frac{L^2}{(2\pi)^2} \int_{D_1} \int_{D_1} y(-k_i)^* \frac{\gamma}{L} y(-k_j) dk_i dk_j \\ &- \frac{L^2}{(2\pi)^2} \int_{D_1} \int_{D_1} x(k_i)^* \frac{\gamma}{L} y(-k_j) dk_i dk_j \\ &- \frac{L^2}{(2\pi)^2} \int_{D_1} \int_{D_1} y(-k_i)^* \frac{\gamma}{L} x(k_j) dk_i dk_j \end{aligned} \quad (42)$$

$$= \frac{k_F \Delta^2}{\pi} - \frac{\gamma \Delta^2}{\pi^2}. \quad (43)$$

Hence, only when $\gamma > \pi k_F$ is ω negative. This guarantees the existence of an oscillating SDW only for a strong interaction, but not for a weak interaction, although it does not preclude the instability for the latter. Note that this threshold ($\gamma = \pi k_F$) coincides with the interaction strength at which the ferromagnetic (*fully* spin-polarized) solution begins to have a lower energy than the paramagnetic (RHF) one.⁴⁶ This is unsurprising because the increase in the kinetic energy and the decrease in the interaction energy in Eq. (43) have the same, quadratic dependence on Δ .

Next, we consider the Luttinger liquid with electrons interacting through Coulomb forces in a compensating uniform positive charge. The two-electron integral is defined by

$$\begin{aligned} \langle k, k' | k'', k + k' - k'' \rangle &= \iint L^{-1} \exp\{-ikz_1 - ik'z_2\} \frac{1}{|z_1 - z_2|} \\ &\quad \times L^{-1} \exp\{ik''z_1 + i(k + k' - k'')z_2\} dz_1 dz_2 \end{aligned} \quad (44)$$

$$= -\frac{C}{L} \ln |k - k''|, \quad (45)$$

where C is a positive constant.

Following the same logic leading to Eq. (35), we find the value of ω with $x(k_i) = y(-k_i) = L^{-1/2}$ for k_i in domain D_1 to be

$$\omega = \frac{k_F \Delta^2}{\pi} + \frac{4}{(2\pi)^2} \int_{D_1} \int_{D_2} C \ln |k_i - k_j| dk_i dk_j, \quad (46)$$

where D_2 is the domain of k that satisfies $-k - \Delta < -k_F \leq -k < 0$. The first (kinetic) term is a positive $O(\Delta^2 k_F)$ quantity, whereas the second (exchange) term can be either positive or negative and scales as $O(\Delta^2 \ln k_F)$. Therefore, Eq. (46) guarantees an oscillating SDW instability *only* for a small k_F or at a low density. Again, it does not preclude an instability in other circumstances.

IV. CONCLUSION

It has long been known qualitatively that, as HOMO and LUMO approach near-degeneracy, a triplet instability tends to occur first, often followed by a singlet instability. The three theorems introduced in this study explain this well-known tendency by dictating the existence of the respective instabilities in the limit where HOMO and LUMO are form-degenerate.

Form-degeneracy is a new definition of orbital degeneracy, which is complementary and perhaps more useful than the usual energy-degeneracy because HOMO and LUMO in a finite system are almost never energy-degenerate. On this basis, we have proved the triplet instability theorems I and II and the singlet instability theorem. Whereas the theorems hold

only for finite systems, they suggest (but not dictate) the spontaneous formations of oscillating SDW in a metallic solid such as one- and three-dimensional HEGs. The stability theory underlying these theorems extended to a continuous orbital-energy spectrum shows that one- and three-dimensional HEGs have an oscillating SDW instability at a low density or for strong interactions, although it does not preclude an instability elsewhere.

Examples of strongly correlated systems that are the subject of these theorems are ubiquitous, difficult to characterize otherwise, and crucial in a range of molecular and solid-state problems. They include molecules that are subject to Hund's rule (O_2), biradicaloids (collinear CH_2), Jahn–Teller systems (square cyclobutadiene), and those that are undergoing covalent bond breaking (H_2 , Li_2 , B_2). The theorems suggest the emergence of SDW and, to a lesser extent, CDW in a metal, the former being related to the Mott insulator and antiferromagnetic ordering observed in strongly correlated solids. That HF theory can detect such instabilities in qualitative correct conditions, while most density-functional approximations cannot, may elevate the importance of the former in solid-state applications.

ACKNOWLEDGMENTS

We are indebted to Dr. Paul W. Ayers, Dr. Trygve Helgaker, Dr. Suehiro Iwata, Dr. Josef Paldus, Dr. Peter Pulay, Dr. Kizashi Yamaguchi, and Dr. Shiwei Zhang for insightful discussions. This work has been supported by the SciDAC program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-FG02-12ER46875. S.H. is a Camille Dreyfus Teacher-Scholar and a Scialog Fellow of the Research Corporation for Science Advancement.

APPENDIX: A PROOF OF EQ. (9)

The integral can be transformed as

$$\iint \frac{\xi^*(\mathbf{r}_1)\xi(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \lim_{\eta \rightarrow 0} \frac{1}{2\pi^2} \int \frac{|\zeta(\mathbf{k})|^2}{|\mathbf{k}|^2 + \eta^2} d\mathbf{k} \geq 0, \quad (A1)$$

with

$$\zeta(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \xi(\mathbf{r}) d\mathbf{r}. \quad (A2)$$

In Eq. (A1), a use is made of the three-dimensional Fourier transform of the Coulomb potential,

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \lim_{\eta \rightarrow 0} \frac{e^{-\eta|\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \lim_{\eta \rightarrow 0} \frac{1}{2\pi^2} \int \frac{e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}}{|\mathbf{k}|^2 + \eta^2} d\mathbf{k}. \quad (A3)$$

The inequality in Eq. (A1) follows from the fact that each factor in the integrand is non-negative and the equality holds if and only if $\zeta(\mathbf{r}) = 0$.

That an exchange integral, $\langle pq|qp\rangle$, is always positive can be proven by substituting $\xi(\mathbf{r}) = \varphi_q^*(\mathbf{r})\varphi_p(\mathbf{r})$ in the above.

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