Breit Interaction, Level Spacing Statistics, and Far-Infrared Absorption in Small Metal Clusters

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Abstract

By considering Coulomb and Breit interactions between the electrons, we derive for the first time the variational Breit-Hartree-Fock (BHF) equation. The Breit interaction has two energy scales; one corresponds with the weak magnetic spin-spin and spin-orbit interactions, and the other corresponds with the tensorial exchange potential, which is on the same order as the Coulomb interaction. For small randomly-shaped jellium clusters with up to 276-electrons, we solved numerically the BHF equation. The calculated level spacing statistics is found to differ qualitatively from the Wigner distribution and better correspond with the Poisson distribution. In particular, the prediction of significantly enhanced far-infrared absorption is in excellent accord with experimental observations. Breit interaction is identified as key to the semi-metallic behavior persistent in small metal clusters at energy scales much lower than the average level spacing.

KeyWords: D. optical properties, D. spin-orbit effects, D. electron-electron interactions, A. nanostructure

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I. INTRODUCTION

Fröhlich was the first to point out that the electronic energy levels in a small cluster must be discrete and separated due to motion quantization [1]. For small metal clusters, the level spacings have long been conjectured to obey the same statistics as the eigenvalues of a random matrix [2-5]. In particular, the probability density of finding a particular nearest level spacing Δ , given the average level spacing $\bar{\Delta}$, has been assumed to follow the “Wigner surmise” [2],

$$P(s) = (\pi s/2) \exp(-\pi s^2/4), \quad (1)$$

where $s = \Delta/\bar{\Delta}$. Recent theoretical developments have linked the level spacing statistics with manifestation of chaos at the quantum energy level [6]. In that context Eq.(1) may be regarded as a signature of quantum chaos arising from the random shapes of the clusters.

Many physical properties of metal clusters, such as the low temperature specific heat, superconductivity, magnetism and far-infrared optics, are controlled by level spacing statistics. *A direct implication of the Wigner distribution is that small metal clusters should affect insulator characteristics at low temperatures or at excitation energies smaller than the average level spacing* [7-11]. In the case of far-infrared absorption, since photons in the far-infrared range have energies comparable to $\bar{\Delta}$ for clusters ranging from 1 to 10 nanometers, they offer a sensitive probe of the level separations. As $\bar{\Delta}$ is a fast-varying function of the cluster size, it is generally expected that the far-infrared absorption should decrease sharply as the cluster size decreases, simply due to the dearth of level spacings for photon excitations in the range of 100 cm^{-1} or less. Calculations based on classical electrodynamics also conform with this general expectation, since the magnetic dipole absorption, dominant for large metal clusters, is known to decrease as the cluster size decreases. Electrical dipole absorption is governed by the imaginary part of the cluster susceptibility, $3(\epsilon_M - 1)/4\pi(\epsilon_M + 2)$. By expressing the metal dielectric function as $\epsilon_M = \kappa + i4\pi\Sigma/\omega$, where Σ denotes the conductivity and ω the angular frequency, it is easy to see that the imaginary part of the cluster

susceptibility is proportional to ω/Σ when $\Sigma \gg \omega$, valids for metallic conductivities and far-infrared frequencies, and to Σ/ω when $\Sigma \ll \omega$. Hence for small metallic clusters the classical electric dipole absorption is small in either the $\Sigma/\omega \rightarrow 0$ limit (insulating, small dissipation) or the $\Sigma/\omega \rightarrow \infty$ limit (perfectly conducting, almost total exclusion of the electromagnetic wave from the clusters interior) but can be large in between, a fact which has been previously noted [9]. *Experimentally, however, the measured far-infrared absorption has shown large discrepancies with the theoretically predicted behavior, both quantitatively and qualitatively* [9-20]. For example, the measured far-infrared absorption by aluminum clusters is orders ($10^3 - 10^4$) of magnitude larger than that predicted theoretically, with a very weak size dependence. A number of mechanisms have been proposed to explain this excess low-frequency absorption. These include absorption due to dielectric losses in their amorphous oxide coatings of the metallic particles [18], and the clumping of the metallic clusters [19]. However, controlled experiments in which these factors were taken into account still indicate intrinsic far-infrared absorption that is significantly larger than the theoretical predictions [20].

In this work, we use the jellium model to study level spacing statistics and the consequent far-infrared absorption in small Al clusters, with particular attention to the effects of the Breit between the electrons. The jellium model treats the metal valence electrons as moving in a uniform positively-charged background; it has enjoyed remarkable success in reproducing many realistic features of metal clusters [21, 22]. In our calculations, cluster shapes are taken to be random perturbations from a sphere; the effects of the Coulomb and Breit interactions are accounted to the accuracy of the Hartree-Fock approximation, iterated to self-consistency. Here by the Breit interaction we mean those pertaining to the electronic spin, such as the spin-spin and spin-orbit interactions between *different electrons* [23, 24]. The Breit interaction is the correction to the instantaneous Coulomb interaction, arising from the exchange of transverse photons between the electrons. The lowest-order Breit correction is easily obtained from quantum electrodynamics by using the second-order perturbation theory. The Breit operator for two electrons is given by

$$V_B = -\frac{e^2}{2r_{12}} \left[\vec{\alpha}_1 \cdot \vec{\alpha}_2 + \frac{(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_1 \cdot \vec{r}_{12})}{|\vec{r}_1 - \vec{r}_2|} \right], \quad (2)$$

where $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$. The operator α_i denotes the 4 by 4 Dirac matrices of the i -th electron. The nonrelativistic reduction of the Breit interaction leads to spin-orbit, spin-other-orbit, and spin-spin corrections to the electron-electron Coulomb interaction. It was derived by Breit and used successfully in his study of the helium far-infrared absorption spectra [25]. The relativistic effects in molecules and solids have been a topic of great interest during the last decade. Recently it has been demonstrated that the basis set expansion method can be applied with success to perform Dirac-Fock Coulomb (DFC) and Dirac-Fock-Breit (DFB) calculations for heavy atoms using spherical Gaussian basis sets in relativistic quantum chemistry [26, 27].

By including both the Coulomb and Breit interactions between the electrons, our results on the electronic energy levels indicate that even in a randomly-shaped cluster, shape quantization can still imply a significant degree of degeneracy. This is in agreement with prior works that show electronic shell structure can be relatively rigid [5]. The addition of the Coulomb and Breit interactions lift most of the degeneracies, but the ensuing level spacing distribution, with the addition of the Coulomb and Breit energy scales, differs qualitatively from the Wigner surmise and is better described by the Poisson distribution, with a predominance of level spacings below the average value $\bar{\Delta} = E_F/N$, where E_F denotes the Fermi energy and N is the number of conduction electrons. This qualitative change in level spacing statistics may be understood as due to the introduction of two successively smaller energy scales (those pertaining to the Coulomb and Breit interactions), with the net result of a Poisson-like distribution arising from the overlap of level spacings associated with shape quantization, Coulomb interaction, and Breit interaction. Our results lead naturally to large far-infrared absorption that is in excellent accord with the experimental observations, as well as to a qualitative understanding of the observed weak size dependence. Taken together, *they imply a persistent semi-metallic behavior in small metal clusters down to energy scales much lower than that anticipated by the average level spacing.* Under the same theoretical

framework we have also calculated the level spacings associated with Coulombic excitations involving the addition or subtraction of electrons from the cluster. The statistics of those level spacings is found to be qualitatively different from that associated with the neutral clusters. These results will be reported elsewhere.

This paper is organized as follows. In Section II, we derive variationally the Breit-Hartree-Fock (BHF) equation by taking into account both the Coulomb and the Breit interactions between the electrons. Solutions of the self-consistent BHF equation for randomly-shaped small metal clusters are discussed in Section III, together with the level spacing statistics for different cases. Results on the electric dipole oscillator strengths and the corresponding sum rule are presented in Section IV, and the electronic susceptibility is evaluated in Section V. The calculated far-infrared absorption coefficients and comparison with experiments are shown in Section VI. We conclude with a few summary remarks in Section VII.

II. DIRAC-BREIT HAMILTONIAN AND THE BREIT-HARTREE-FOCK EQUATION

The starting point of our calculations is the N -electron Dirac-Breit (DB) Hamiltonian [22, 23]

$$H = \sum_{i=1}^N [c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i m_e c^2 + V_O(\vec{r}_i)] + \sum_{j < i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{j < i} \frac{e^2}{2 |\vec{r}_i - \vec{r}_j|} \left(\vec{\alpha}_i \cdot \vec{\alpha}_j + \frac{(\vec{\alpha}_i \cdot \vec{r}_{ij})(\vec{\alpha}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right). \quad (3)$$

where the first summation term represents the Dirac Hamiltonian for N electrons, c denotes the speed of light, m_e the electron mass, $\vec{p}_i = -i\hbar\vec{\nabla}_i$ is the momentum operator for the i th electron, $\vec{\alpha}_i$ and β_i are the 4 by 4 Dirac matrices of the i th electron, and $V_O(\vec{r}_i)$ denotes the jellium potential, defined to be $-(E_F + W)$ inside the cluster boundary and zero otherwise, where W denotes the work function. The second term of the DB Hamiltonian gives the Coulomb interaction between the electrons, with e denoting the electronic charge, and the

third term is the so-called Breit operator, which is the source of the spin-spin interactions. Apart from relativistic effects, the DB Hamiltonian may be regarded as the most complete in terms of describing the various interactions between the electrons [24, 25]. For example, interaction between the electronic magnetic moments may be derived from Eq.(3); not only the spin-orbit interaction for each electron, but also that between the spin of one electron and the orbits of other electrons are noted to be included in DB Hamiltonian.

A relativistic Breit-Hartree-Fock(RBHF) equation can be derived, through tedious algebra, by minimizing the expectation value of the DB Hamiltonian, using as the basis the linear combinations of antisymmetrized Slater determinants product wavefunction. In the non-relativistic limit, by keeping terms up to the square of the expectation value of $\vec{p}/m_e c$, we obtain the non-relativistic Breit-Hartree-Fock(BHF) equation

$$H_O \Phi_{\alpha_i}(\vec{r}_i) - V_F(\vec{r}_i, \vec{r}_j) \Phi_{\alpha_i}(\vec{r}_j) = \varepsilon_{\alpha_i} \Phi_{\alpha_i}(\vec{r}_i), \quad (4)$$

where $\Phi_{\alpha_i}(\vec{r}_j)$ denotes a two (spin)-component i th eigenfunction (here α_i is the quantum number(s) index for the i th single-particle state) for the j th electron, with eigenvalue ε_{α_i} ,

$$H_O = \frac{(\vec{p}_i + \frac{e}{c} \vec{A}_H)^2}{2m_e} + V_O + \frac{e\hbar \vec{\sigma}_i \cdot \vec{B}_H}{2m_e c} + V_H \quad (5)$$

with $\vec{\sigma}_i$ denoting the Pauli spin matrices of the i th electron, $\vec{B}_H = \vec{\nabla} \times \vec{A}_H$,

$$\vec{A}_H(\vec{r}_i) = \frac{1}{c} \sum_{i \neq j} \int d\vec{r}_j \frac{\vec{J}_{\alpha_j}(\vec{r}_j) + c \vec{\nabla} \times \vec{M}_{\alpha_j}^{(i)}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} + \sum_{i \neq j} \oint_s \frac{\vec{M}_{\alpha_j}^{(i)}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} \times d\vec{S}_j, \quad (6)$$

$$V_H = e^2 \sum_{j \neq i} \int d\vec{r}_j \frac{|\Phi_{\alpha_j}(\vec{r}_j)|^2}{|\vec{r}_i - \vec{r}_j|}, \quad (7)$$

and V_F stands for the Fock potential, given by

$$V_F(\vec{r}_i, \vec{r}_j) = \sum_{i \neq j} \int d\vec{r}_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \Phi_{\alpha_j}^+(\vec{r}_j) \left[1 - \frac{1}{2} \left(\vec{\sigma}_i \cdot \vec{\sigma}_j + \frac{(\vec{\sigma}_i \cdot \vec{r}_{ij})(\vec{\sigma}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right) \right] \Phi_{\alpha_j}(\vec{r}_i). \quad (8)$$

In Eq.(6), the “Breit vector potential” $\vec{A}_H$ is put in the physically meaningful form. The current density for the α_j th occupied state below E_F is defined as

$$\vec{J}_{\alpha_j}(\vec{r}_j) = -\frac{e}{2m_e}[\Phi_{\alpha_j}^+(\vec{r}_j)\vec{p}_j\Phi_{\alpha_j}(\vec{r}_j) + h.c.], \quad (9)$$

and the associated magnetization density is

$$\vec{M}_{\alpha_j}^{(i)}(\vec{r}_j) = -\frac{e}{2m_e c}Re\left[\Phi_{\alpha_j}^+(\vec{r}_j)(\vec{r}_{ij} \times \vec{p}_j + \hbar\vec{\sigma}_j)\Phi_{\alpha_j}(\vec{r}_j)\right], \quad (10)$$

with $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. The last term of Eq. (6) gives the surface current contribution. The source of the Breit vector potential for a particular electron comes from the wavefunction-averaged value of the Breit interactions over all the rest $N - 1$. Details of the derivation is given in Appendix A. To our knowledge, the Breit interaction has been generally ignored in prior studies of the energy levels in small metal clusters, and Eqs.(4)-(10) represent the first derivation of the BHF equation. We are also not aware of any local density functional (LDA) calculation which accounts for the Breit interaction between the electrons, together with its vector character. It is expected that the current density functional theory may be extended to treat the interacting electron system including the Breit interaction between electrons [28-31].

Several points are to be noted. First, the effect of the Breit interaction shows up in two places: as the vector potential $\vec{A}_H$ and the magnetic field $\vec{B}_H$, both derived as Hartree terms; and in the exchange-induced Fock term, V_F , given by Eq.(8). Whereas the Hartree terms are small in magnitude and involve the interactions of magnetic moments associated with either the spin or the orbital motion, the exchange-induced Breit contribution to V_F is noted to be on the same order as that for the Coulomb interaction. Second, for small clusters, our numerical results show the Breit vector potential and its related magnetic field to be the source of fine level spacings and the enhanced far-infrared absorption. Indeed, an estimate of the Breit-Hartree energy scale puts it in the far-infrared range as follows. An upper bound to the Breit-Hartree contribution in small clusters may be estimated as the largest possible total energy of N -interacting electronic dipoles [25] : $\Delta E_d \approx N(N - 1)(e^2/4R)(\alpha_f a_B/R)^2$, where R is the average radius of the cluster, $\alpha_f = 1/137$ denotes the fine structure constant. When $N = 276$, we get $\Delta E_d = \pm 90 cm^{-1}$. This ΔE_d should exhibit itself as the (maximum) difference near the Fermi energy level with and without the Breit-Hartree contribution. Its

magnitude implies that the enhanced far-infrared absorption may indeed be achieved through the consideration of the Breit interaction. A more detailed description of the magnitudes for the various interaction terms may be found in Appendix C. Third, since the focus of our work is not on the accurate determination of E_F or the work function W for each cluster, we have simply defined the jellium potential to be its bulk limiting value, $V_0 = -(E_F + W)$, inside the cluster boundary and zero otherwise. The square well approximation is slightly inaccurate at the edge of the potential but will not affect the main thesis of this work.

To carry out numerical calculations, we choose to expand the i th eigenfunction as

$$\Phi_{\alpha_i}(\vec{r}) = \sum_{\alpha} D_{\alpha}^i \psi_{nlm}(\vec{r}) \chi_{m_s}, \quad (11)$$

where $\{\chi_{m_s}\}$ denotes the spin states, and $\{\psi_{nlm}(\vec{r})\}$ is taken to be the set of eigenfunctions of an infinite spherical well with radius $R_O \approx 1.15R$. R_O is taken to be slightly adjustable but larger than the average jellium potential radius of the cluster. In representing the random shapes of the clusters, we let

$$R(\theta, \phi) = R \left[1 + \eta \sum_{l,m} a_{lm} Y_{lm}(\theta, \phi) \right], \quad (12)$$

where the expansion coefficients a_{lm} in the front of the spherical harmonics function $Y_{lm}(\theta, \phi)$ should hold the relation, $a_{lm} = (-1)^m a_{l,-m}$ to ensure that $R(\theta, \phi)$ remains real. Here, the value of a_{lm} is randomly picked but made to satisfy the overall condition of $a_{00} + (\eta/\sqrt{\pi}) \sum_{l,m>0} a_{lm}^2 = 0$ so as to ensure the volume of the cluster remains at $4\pi R^3/3$. Parameters η and $\delta = \sqrt{\oint_s d\Omega [(R(\theta, \phi) - R)/R]^2 / 4\pi} = \eta \sqrt{\sum_{l,m>0} a_{lm}^2 / 2\pi}$ are both small in value and control the amount of deviation from the spherical shape. We have limited the value of l to less than 5 in order to rule out unphysical sharp surface variations, as demonstrated by based on Monte Carlo simulation for small clusters [32, 33]. It should be noted that for clusters with less than few tens of atoms, the equilibrium cluster shapes can deviate significantly from spherical. However, for clusters with more than 50 atoms the equilibrium and metastable shapes are mostly (nearly) spherical [32, 33]. In any case, our assumption of random shapes is consistent with all the previous studies on small metallic particles, as well as with the assumption implicit in the Wigner distribution of level spacings.

By substituting the eigenfunction expansion (11) and Eq.(12) into Eqs.(4)-(10) and carrying out lengthy calculations, Eq.(4) can be rewritten in the following iterative matrix equation form for the solution of the expansion coefficients

$$\left[H_S^{(k-1)} + \delta H_P^{(k-1)} - \varepsilon I \right] D^{(k)} = 0. \quad (13)$$

Here ε is the energy eigenvalue, I the identity matrix, $H_S^{(k-1)}$ denotes the matrix representing the BHF equation at the $(k-1)$ th iteration of the expansion coefficients (i.e., the wavefunctions). The subscript S means the jellium potential is a sphere with radius $R = r_s N^{1/3} a_B$, where $a_B = 0.53 \text{ \AA}$ is the Bohr radius, and r_s is the electron radius parameter determined from the mean electronic density, i.e., $r_s = 2.07$ for aluminum. $H_P^{(k-1)}$ is similar to $H_S^{(k-1)}$ except it refers to perturbations away from the spherical shape. In Appendix B we present the forms of some typical matrix elements of $H_S^{(k-1)}$.

For small deviations, the Hamiltonian matrix element in the noninteracting case may be approximated as

$$\begin{aligned} \langle \alpha' | H_0 | \alpha \rangle &\approx \frac{\hbar^2 x_{nl}^2}{2m_e R_0^2} \delta_{\alpha, \alpha'} + V_0 \delta_{\alpha', \alpha} \\ &\pm \delta V_0 \delta_{m_s m'_s} \sum_{l_1 m_1} \sqrt{\frac{(2l' + 1)(2l_1 + 1)}{\pi(2l + 1)}} C_{l'0, l_1 0}^{l'0} C_{l' m', l_1 m_1}^{lm}. \end{aligned} \quad (14)$$

The notation $C_{l_1 m_1, l_2 m_2}^{lm}$ is the usual Clebsch-Gordan (CG) coefficient, i.e., $l = l_1 + l_2, \dots, |l_1 - l_2|$ and $m = m_1 + m_2$. In particular, the diagonal matrix element may be approximated as

$$\langle \alpha | H_0 | \alpha \rangle \approx \frac{\hbar^2 x_{nl}^2}{2m_e R_0^2} + V_0 \pm \delta V_0 / \sqrt{\pi}. \quad (15)$$

We have chosen $\delta = 3\% \sim 6\%$ in consideration of the fact that except for very small clusters, surface tension of the clusters would prevent large distortions of the cluster shape away from isotropy. Accordingly, shape effects are considered only to the linear order in δ . A plot of the typical cluster cross section is shown in the inset to Fig.1(a). From Eqs.(14) and (15), we can see that the random variation of the Hamiltonian matrix elements due to small shapes is limited to the range $\pm \delta V_0 / \sqrt{\pi}$. The variation of matrix elements in our model is thus not totally random, and therefore do not satisfy the basic RMT assumption [2].

III. LEVEL SPACING STATISTICS

By using parameter values appropriate to bulk Al, i.e., $E_F = 11.7$ eV, $W = 4.25$ eV [34], we have carried out numerical calculations for clusters with up to 276 electrons. The number of basis functions is chosen by requiring the calculated results to reproduce up to $N + 50$ single-electron energy levels (including degeneracies) in a spherical jellium potential, which may be easily obtained separately. Solution iteration is stopped when the root-mean-square deviation of $D^{(k)}$ from $D^{(k-1)}$ is less than one part in 10^6 and the energy levels are consistent to $10^{-6}e^2/2R \sim 10^{-6}eV$. Figure 1 is a plot of three cases of calculated energy levels versus the level number, ordered with 1 denoting the lowest energy level. For visual clarity, we have connected individual points to form three curves, and displaced them vertically from each other. Noninteracting single-electron energy levels for the cluster shown in the inset, with 276 electrons, are delineated by the curve labeled (O). The curve labeled (C) is for the energy levels calculated with the Coulomb interaction added, and that labeled (C+B) is the curve for electrons interacting via both the Coulomb and Breit interactions in the same randomly-shaped jellium cluster. The Breit interaction splits the spin degeneracy usually present in each level. While not shown, the levels in the (C+B) curve alternates between $+1/2$ spin and $-1/2$ as revealed by the eigenfunctions. From the figure it may already be clear that the random shape alone is not sufficient to lift the degeneracies. It is also seen that there are many closely-spaced energy levels for the fully interacting system, occurring in clumps (seen as the nearly horizontal regions), due mainly to the Breit interaction between the electrons. These assertions may be quantified by plotting the distribution of the nearest-level spacings as a function of s . On the $\ln(s)$ scale, there are two well separated groupings. One, centered at $s \sim 10^{-4}$, represents the nearly-degenerate or degenerate levels. Level spacings in this group border on the limit of our calculational accuracy. We will simply denote this group the “degenerate” level spacings and ignore them from our statistical analysis. The second grouping is centered at $s \sim 1-10$, with a tail extending down to $s \sim 10^{-2.5}$. These are shown in Figs. 2(a)-2(c), where the integrated level spacing data from four randomly shaped clusters

are plotted as a function of $\sigma = \Delta/\Delta_0$, with the corresponding distributions shown in the insets. Here Δ_0 denotes the mean level spacing in each case. The exclusion of the group of (nearly) degenerate level spacings means $\Delta_0 > \bar{\Delta}$. The cases of non-interacting electrons (2(a)), with Coulomb interaction (2(b)), and with both Coulomb and Breit interactions (2(c)) are shown. For comparison, we also show the curve representing the integral of the Wigner surmise, with s replaced by σ . The effect of adding interactions is clearly *seen to be a trend of increasing departure from the Wigner distribution*, accompanied by a significant decrease in Δ_0 . It should be noted that in the noninteracting case, the random shapes are not able to destroy the energy shell structure seen in the spherical potential, indicating spectral rigidity. However, the energy shells are found to shift up slightly (in energy), in agreement with the results of Lerme et al. [5]. In Fig.2(c), the data clearly disagree with the Wigner surmise and are better described by the Poisson distribution, the integral of which is shown by the dotted line.

We have noted previously that the elements of our Hamiltonian matrix do not vary randomly. It is thus not surprising that our level spacings do not satisfy the Wigner distribution, which is a direct consequence of the random matrix assumption. However we also like to note that the Wigner distribution is known to be valid in the regime where the electronic kinetic energy is large so that the electron-electron interactions are relatively unimportant. Indeed, it was verified experimentally that the nearest-neighbor statistics of the resonance modes in a stadium shaped cavity, a quantum chaotic system, satisfies the Wigner surmise [35-37]. Extensive theoretical studies also exist for the periodically kicked top [38], nonlinearly coupled oscillators [39], and billiards of different shapes [40, 41], where the Wigner distribution was verified. Therefore, the predictions of the random matrix theory should be viewed as operating in a regime different from that of the small clusters.

Our results imply an abundance of level spacings smaller than the average value Δ_0 due to the small level splittings caused by the Breit interaction. However, *perhaps more important is the fact that the small spacings occur in clumps, which reflects the persistence of the energy shell structure even in the full interaction case*. Within each clump, we predict

the neighboring energy levels to be opposite in their spin states, a potentially verifiable check. Therefore, it is important to emphasize that our Poisson level spacing statistics is due to the existence of multiple energy scales (shape quantization, Coulomb interaction, and Breit interaction). As shown in Fig.3(P) [42], it is clear that the energy levels whose level spacings satisfy the Poisson distribution do not exhibit the shell structures as shown in Fig.3(O) and 3(C+B). *The appearance of clumps of small level spacings is noted to bear a striking resemblance to the recently observed level spacing distribution in small Al clusters* [43].

IV. OSCILLATOR STRENGTHS

Optical properties of jellium metal clusters may be directly evaluated from the knowledge of their energy levels and the associated wavefunctions. The perturbation Hamiltonian is obtained by replacing the term $c\vec{\alpha}_i \cdot \vec{p}_i$ in Eq.(3) by $c\vec{\alpha}_i \cdot (\vec{p}_i + e\vec{A}_0/c)$, where $\vec{A}_0$ denotes the vector potential of the electromagnetic wave field, and retaining the term linear in $\vec{A}_0$ in the BHF formulation. In Figs.4(a)-4(c) we plot the calculated, symmetrized electric-dipole oscillator strength $g_{ij}^e + g_{ji}^e = g_{\{i,j\}}^e$ as a function of the optical transition frequency ν for the three corresponding cases shown in Fig.2. Here the oscillator strength, g_{ij}^e is defined as

$$g_{ij}^e = \frac{2f_j}{m\varepsilon_{ij}} |\langle i | [\vec{p} + \frac{e}{c}\vec{A}_H]_z | j \rangle|^2, \quad (16)$$

with $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$ [44], where the Fermi function $f_j = 1/(\exp[(\varepsilon_i - \varepsilon_F)/k_B T] + 1)$ is evaluated at $T = 300$ K, and $\varepsilon_{i(F)}$ denotes the energy of the i th level (Fermi level). All the (nearly) degenerate states were included and individually accounted for in the calculation. It should be noted that in the present case, the Breit vector potential directly contributes to the oscillator strength, as shown in Eq.(16). Here the results of the four different shaped cluster are plotted together. The symmetrized oscillator strength, $g_{\{i,j\}}^e$, is always positive (nonzero mostly for $\{i,j\}$ pairs straddling the Fermi level) and directly relevant to optical absorption (see Eq. (16)). The Thomas-Reiche-Kuhn sum rule dictates that the sum of $g_{\{i,j\}}^e$ over all

$\{i, j\}$ pairs must be equal to N [9]. Up to $10,000 \text{ cm}^{-1}$ the sum $\sum_{\{i,j\}} g_{\{i,j\}}^e / N$, averaged over *four* randomly-shaped clusters, is noted to vary from 0.80 to 0.87. The magnetic dipole absorption may be similarly treated, where the magnetic oscillator strength may be written as

$$g_{ij}^m = \frac{2\pi^2 f_j}{m \varepsilon_{ij} \lambda^2} |\langle i | [\vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H)]_z | j \rangle|^2,$$

derived in Appendix D. Magnetic dipole absorption is much smaller than the electric dipole absorption in our present calculations. The two absorption components are approximately in the ratio $(R/\lambda)^2 \ll 1$, where λ is the wavelength.

V. ELECTRONIC SUSCEPTIBILITY

To convert the oscillator strengths into an absorption coefficient, we evaluate the electronic susceptibility relevant to the electric dipole transitions [9]:

$$\chi_O^e(\nu) = \frac{3e^2 \hbar^2}{4\pi R^3 m} \sum_{\{i,j\}} g_{\{i,j\}}^e \left\{ \frac{1}{\varepsilon_{ij}^2 - \hbar^2 \nu^2} + i \frac{\pi}{2\hbar \nu} \delta(\hbar \nu - \varepsilon_{ij}) \right\}. \quad (17)$$

We choose to smooth the low frequency susceptibility by requiring the integral of $\text{Im} \chi_O^e = \text{Im}[(\varepsilon_M - 1)/(\varepsilon_M + 2)]$, with $\varepsilon_M = \kappa + i2\Sigma/\nu$, be given by the sum of the (frequency-integrated) discrete (imaginary part) contributions shown in Eq.(17) for up to $\nu = 900 \text{ cm}^{-1}$. The values of κ and Σ are treated as fitting parameters. The result for one of the clusters, with both Coulomb and Breit interactions included, is shown in Fig.5. The ratio Σ/Σ_O obtained from the fit, where Σ_O denotes the surface-scattering-corrected aluminum conductivity, is on the order of 10^{-5} to 10^{-4} , i.e., the effective conductivity is much smaller than the metallic conductivity but still much larger than those of the insulators. *Thus the clusters may be characterized as semi-metallic in nature, which is essential for the enhanced far-infrared absorption as seen below.* For the noninteracting case and the Coulomb interaction (only) case, there are clear gaps ($> 300 \text{ cm}^{-1}$) in the spectrum of $g_{\{i,j\}}^e$, indicating the low frequencies behavior to be insulator-like. We choose to smooth the susceptibilities by

broadening each excitation resonance with a frequency width $\Gamma = k_B T / 2\pi\hbar$. From Eq.(17) and the smoothing procedure(s), the susceptibility of each cluster is obtained by further considering the effect of the depolarizing charges at the cluster surface, which reduces the electric field inside the cluster. $\chi^e(\nu)$ is directly related to χ_O^e by the equation [15]

$$\chi^e(\nu) = \frac{\chi_O^e(\nu)}{1 + (4\pi/3)\chi_O^e}. \quad (18)$$

VI. FAR-INFRARED ABSORPTION

The dielectric constant of the j th randomly-shaped cluster is given by $\epsilon_j = 1 + 4\pi\chi_j^e(\nu)$, where each χ_j^e is evaluated from Eqs.(16)-(18). We wish to compare our calculated results with the far-infrared absorption experiments in which the metal clusters are dispersed in a KCl matrix. For that purpose, it is necessary to evaluate the composite effective dielectric constant $\bar{\epsilon}$ by using the Maxwell-Garnett formula [45]

$$\bar{\epsilon} = \epsilon_m \frac{1 - x + 3 \sum_j x_j \epsilon_j / (\epsilon_j + 2\epsilon_m)}{1 - x + 3 \epsilon_m \sum_j x_j / (\epsilon_j + 2\epsilon_m)}, \quad (19)$$

where $\epsilon_m = 4.85$ is the dielectric constant of KCl, x denotes the volume fraction of the metal clusters, and $x_j = x/4$. The absorption coefficient is directly obtained from $\bar{\epsilon}$ as

$$\alpha = \frac{4\pi}{\lambda} \text{Im}\sqrt{\bar{\epsilon}}. \quad (20)$$

Shown in Fig.6 are the magnitude and frequency dependencies of the absorption coefficient calculated for the three cases. Also shown is the sum of the electric and magnetic dipole absorption coefficients calculated classically [16], $\alpha_{em} = (K_e + K_m)x/\lambda^2$, with $K_e = 9\pi c \epsilon_m^{3/2} m_e / e^2 \tau n$ and $K_m = 8\pi^2 R^2 \epsilon_m^{1/2} e^2 \tau n / 5m_e c$ denoting the respective electric and magnetic dipole contributions. Here $n = (4\pi r_s^3 a_B^3 / 3)^{-1}$ is the electron density, and τ is the effective relaxation time corrected for the surface scattering. Comparison between the different cases clearly demonstrates the effectiveness of the Breit interaction in enhancing the far-infrared absorption of small clusters by three to four orders of magnitude. At low frequencies ($\nu < 50 \text{ cm}^{-1}$) the absorption coefficient is well described by a quadratic frequency

dependence, but at higher frequencies the variation is closer to linear. The magnitude of the calculated far-infrared absorption coefficient compares well with the experimentally measured absorption on samples with larger aluminum clusters. For example, at $\nu = 50 \text{ cm}^{-1}$ the calculated $\alpha = 1.64 \text{ cm}^{-1}$, whereas the measured α is about 5 cm^{-1} for average particle radius down to $40 - 50 \text{ \AA}$, with a drop to $1-2 \text{ cm}^{-1}$ for particle radius of $20 - 30 \text{ \AA}$ [20]. The consideration of the Breit interaction also makes the observed weak cluster size dependence of absorption qualitatively understandable, because as the cluster size decreases, the increasing importance of the Breit vector potential and its associated level spacings tend to counteract the otherwise expected steep drop. As a check, we have calculated the absorption coefficient for a cluster with 108 electrons. At $\nu = 50 \text{ cm}^{-1}$, the value of $\alpha = 0.98 \text{ cm}^{-1}$, which is only somewhat smaller than that for the 276-electron cluster, but still significantly larger than the classical prediction. With the inclusion of the Breit interaction, it would indeed be anomalous if the far-infrared absorption were to be significantly smaller than what have been calculated here, in contrast to the reverse expectation held previously as the norm.

VII. CONCLUDING REMARKS

By considering Coulomb and Breit interactions between electrons, a single-electron Breit-Hartree-Fock (BHF) equation has been derived. For small randomly-shaped jellium clusters with up to 276-electrons, we numerically solved the BHF equation and found the calculated level spacing statistics in randomly-shaped jellium metal clusters to differ qualitatively from the Wigner distribution and better correspond with the Poisson distribution. In particular, the prediction of significantly enhanced far-infrared absorption is in excellent accord with experimental observations. Breit interaction is identified as key to the semi-metallic behavior persistent in small metal clusters at energy scales much lower than the average level spacing.

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APPENDIX A: DERIVATION OF THE BREIT-HARTREE-FOCK EQUATION

Here we present the mathematical details relevant to the derivation of the Breit-Hartree-Fock (BHF) equation. For simplicity, the Hamiltonian in Eq.(3) is rewritten as

$$H = \sum_{i=1}^N [c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i m_e c^2 + V_O(\vec{r}_i)] + \sum_{j < i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + e \sum_{j < i} \vec{\alpha}_i \cdot \vec{B}(\vec{r}_i, \vec{r}_j), \quad (\text{A1})$$

where $\vec{B}(\vec{r}_i, \vec{r}_j)$ is defined as

$$\vec{B}(\vec{r}_i, \vec{r}_j) = -\frac{e}{2|\vec{r}_i - \vec{r}_j|} \left[\vec{\alpha}_j + \frac{\vec{r}_{ij}(\vec{\alpha}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right]. \quad (\text{A2})$$

The Slater determinant of orthonormalized single-particle states $\psi_{\alpha_i}(\vec{r}_i)$ for an N-electron system is $\Psi = \frac{1}{\sqrt{N!}} \det [\psi_{\alpha_i}(\vec{r}_i)]$. The expectation value of the Hamiltonian (A1) is determined by

$$E(\Psi) = \langle \Psi | H | \Psi \rangle. \quad (\text{A3})$$

In the spirit of the Ritz variational principle, minimum $E(\Psi)$ should remain stationary under small variations $\Psi \rightarrow \Psi + \delta\Psi$ of the Slater determinant. The associated differential equation may be expressed formally as

$$\delta E(\Psi) - \sum_i (\varepsilon_i + m_e c^2) \delta \int d\vec{r}_i \psi_{\alpha_i}^+(\vec{r}_i) \psi_{\alpha_i}(\vec{r}_i) = 0. \quad (\text{A4})$$

From Eq.(A4), a relativistics Breit-Hartree-Fock (RBHF) equation may be written as

$$(\varepsilon_i + m_e c^2) \psi_{\alpha_i}(\vec{r}_i) = \left[c\vec{\alpha}_i \cdot \left(\vec{p}_i + \frac{e}{c} \vec{A}_H \right) + \beta_i m_e c^2 + V_O(\vec{r}_i) + V_H(\vec{r}_i) \right] \psi_{\alpha_i}(\vec{r}_i) - V_F(\vec{r}_i, \vec{r}_j) \psi_{\alpha_i}(\vec{r}_j), \quad (\text{A5})$$

where the Fock exchange interaction between the electrons reads

$$V_F(\vec{r}_i, \vec{r}_j) = V_F^c(\vec{r}_i, \vec{r}_j) + V_F^b(\vec{r}_i, \vec{r}_j) = \sum_j \int d\tau_j \psi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \psi_{\alpha_j}(\vec{r}_j) + \sum_j \int d\tau_j \psi_{\alpha_j}^+(\vec{r}_j) e\vec{\alpha}_i \cdot \vec{B}(\vec{r}_i, \vec{r}_j) \psi_{\alpha_j}(\vec{r}_j), \quad (\text{A6})$$

with $V_F^c(\vec{r}_i, \vec{r}_j) = \sum_j \int d\tau_j \psi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \psi_{\alpha_j}(\vec{r}_j)$. The Hartree scalar potential $V_H(\vec{r})$ due to the Coulomb interaction and the vector potential $\vec{A}_H(\vec{r})$ associated with the Breit interaction are expressible as

$$V_H(\vec{r}_i) = \sum_j \int d\tau_j \frac{e^2 \psi_{\alpha_j}^+(\vec{r}_j) \psi_{\alpha_j}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}, \quad (\text{A7})$$

and

$$\vec{A}_H(\vec{r}_i) = \sum_j \int d\tau_j \psi_{\alpha_j}^+(\vec{r}_j) \vec{B}(\vec{r}_i, \vec{r}_j) \psi_{\alpha_j}(\vec{r}_j), \quad (\text{A8})$$

respectively. Equations (A5)-(A8) constitute a set of relativistic Breit-Hartree-Fock equations. Here the four-component wave function $\psi_{\alpha_j}(\vec{r}_j)$ may be decomposed formally as

$$\psi_{\alpha_j}(\vec{r}_j) = \begin{pmatrix} \phi_{\alpha_j}(\vec{r}_j) \\ \chi_{\alpha_j}(\vec{r}_j) \end{pmatrix}, \quad (\text{A9})$$

where $\phi_{\alpha_j}(\vec{r}_j)$ and $\chi_{\alpha_j}(\vec{r}_j)$ denote two different two-component wave functions, respectively. By inserting (A9) into Eq.(A5), Eq.(A5) can be separated into

$$\begin{aligned} c\vec{\sigma}_i \cdot \left[\vec{p}_i + \frac{e}{c} \vec{A}_H(\vec{r}_i) \right] \chi_{\alpha_i}(\vec{r}_i) &= [\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)] \phi_{\alpha_i}(\vec{r}_i) \\ &+ V_F(\vec{r}_i, \vec{r}_j) \phi_{\alpha_i}(\vec{r}_j), \end{aligned} \quad (\text{A10})$$

and

$$\begin{aligned} c\vec{\sigma}_i \cdot \left[\vec{p}_i + \frac{e}{c} \vec{A}_H(\vec{r}_i) \right] \phi_{\alpha_i}(\vec{r}_i) &= [2m_e c^2 + \varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)] \chi_{\alpha_i}(\vec{r}_i) \\ &+ V_F(\vec{r}_i, \vec{r}_j) \chi_{\alpha_i}(\vec{r}_j). \end{aligned} \quad (\text{A11})$$

Solving Eq.(A11) by iteration, one gets

$$\begin{aligned} \chi_{\alpha_i}(\vec{r}_i) &= [2m_e c^2 + \varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)]^{-1} c\vec{\sigma}_i \cdot \left[\vec{p}_i + \frac{e}{c} \vec{A}_H(\vec{r}_i) \right] \phi_{\alpha_i}(\vec{r}_i) \\ &- [2m_e c^2 + \varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)]^{-1} V_F(\vec{r}_i, \vec{r}_j) \\ &\times [2m_e c^2 + \varepsilon_i - V_O(\vec{r}_j) - V_H(\vec{r}_j)]^{-1} c\vec{\sigma}_j \cdot \left[\vec{p}_j + \frac{e}{c} \vec{A}_H(\vec{r}_j) \right] \phi_{\alpha_i}(\vec{r}_j). \end{aligned} \quad (\text{A12})$$

In the non-relativistic limit, we have

$$\left[2m_e c^2 + \varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)\right]^{-1} \approx \frac{1}{2m_e c^2} \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)}{2m_e c^2}\right]. \quad (\text{A13})$$

By inserting Eq.(A13) into Eq.(A12), we have

$$\begin{aligned} \chi_{\alpha_i}(\vec{r}_i) = & \frac{1}{2m_e c} \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)}{2m_e c^2}\right] \vec{\sigma}_i \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H\right] \phi_{\alpha_i}(\vec{r}_i) \\ & - \frac{1}{4m_e^2 c^3} \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)}{2m_e c^2}\right] V_F(\vec{r}_i, \vec{r}_j) \\ & \times \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_j) - V_H(\vec{r}_j)}{2m_e c^2}\right] \vec{\sigma}_j \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H(\vec{r}_j)\right] \phi_{\alpha_i}(\vec{r}_j). \end{aligned} \quad (\text{A14})$$

Substituting Eq.(A14) into Eq.(A10), we obtain

$$\begin{aligned} \varepsilon_i \phi_{\alpha_i}(\vec{r}_i) = & [V_O(\vec{r}_i) + V_H(\vec{r}_i)] \phi_{\alpha_i}(\vec{r}_i) - V_F(\vec{r}_i, \vec{r}_j) \phi_{\alpha_i}(\vec{r}_j) \\ & \times \frac{1}{2m_e} \vec{\sigma}_i \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H(\vec{r}_i)\right] \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)}{2m_e c^2}\right] \\ & \times \vec{\sigma}_i \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H(\vec{r}_i)\right] \phi_{\alpha_i}(\vec{r}_i) \\ & - \frac{1}{4m_e^2 c^2} \vec{\sigma}_i \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H(\vec{r}_i)\right] \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_i) - V_H(\vec{r}_i)}{2m_e c^2}\right] \\ & \times V_F(\vec{r}_i, \vec{r}_j) \left[1 - \frac{\varepsilon_i - V_O(\vec{r}_j) - V_H(\vec{r}_j)}{2m_e c^2}\right] \\ & \times \vec{\sigma}_j \cdot \left[\vec{p} + \frac{e}{c} \vec{A}_H(\vec{r}_j)\right] \phi_{\alpha_i}(\vec{r}_j). \end{aligned} \quad (\text{A15})$$

Furthermore, by using the following identity $(\vec{\sigma} \cdot \vec{C})(\vec{\sigma} \cdot \vec{D}) = \vec{C} \cdot \vec{D} + i\vec{\sigma} \cdot (\vec{C} \times \vec{D})$ and keeping the leading-order Fock term, Eq.(A15) may be simplified as

$$\begin{aligned} \varepsilon_i \phi_{\alpha_i}(\vec{r}_i) = & \frac{1}{2m_e} \left[\vec{p} + \frac{e}{c} \vec{A}_H\right]^2 \phi_{\alpha_i}(\vec{r}_i) + \left[\frac{e\hbar \vec{\sigma}_i \cdot \vec{B}_H}{2m_e c} + V_O(\vec{r}_i) + V_H(\vec{r}_i)\right] \phi_{\alpha_i}(\vec{r}_i) \\ & - V_F(\vec{r}_i, \vec{r}_j) \phi_{\alpha_i}(\vec{r}_j) - \frac{1}{8m_e^3 c^2} \left[\vec{p} + \frac{e}{c} \vec{A}_H\right]^4 \phi_{\alpha_i}(\vec{r}_i) \\ & + \frac{i\hbar}{4m_e^2 c^2} \left[\vec{p} + \frac{e}{c} \vec{A}_H\right] \cdot \vec{\nabla} [V_O(\vec{r}_i) + V_H(\vec{r}_i)] \phi_{\alpha_i}(\vec{r}_i) \\ & - \frac{\hbar}{4m_e^2 c^2} \vec{\sigma}_i \cdot \left[\left(\vec{p} + \frac{e}{c} \vec{A}_H\right) \times \vec{\nabla} [V_O(\vec{r}_i) + V_H(\vec{r}_i)]\right] \phi_{\alpha_i}(\vec{r}_i). \end{aligned} \quad (\text{A16})$$

Here $\vec{B}_H = \vec{\nabla} \times \vec{A}_H$. It should be noted that the wavefunction $\phi_{\alpha_i}(\vec{r}_i)$ is an unrenormalized wave function since $\phi_{\alpha_i}(\vec{r}_i)$ is only the larger component in (A9). In order to make $\langle \phi_{\alpha_i}(\vec{r}_i) | \phi_{\alpha_i}(\vec{r}_i) \rangle = 1$, the wave function in Eq.(A16) should be rewritten as

$$\phi_{\alpha_i}(\vec{r}_i) \rightarrow \left[1 - \frac{(\vec{p} + \frac{e}{c}\vec{A}_H)^2}{8m_e^2c^2} \right] \Phi_{\alpha_i}(\vec{r}_i). \quad (\text{A17})$$

Substituting (A17) into (A16) and combining with the relation

$$\begin{aligned} \left[V(\vec{r}), [\vec{p} + \frac{e}{c}\vec{A}_H]^2 \right] &= 2i\hbar(\vec{p} + \frac{e}{c}\vec{A}_H) \cdot \vec{\nabla} V(\vec{r}) - \hbar^2 \vec{\nabla}^2 V(\vec{r}) \\ &= 2i\hbar \vec{\nabla} V(\vec{r}) \cdot [\vec{p} + \frac{e}{c}\vec{A}_H] + \hbar^2 \vec{\nabla}^2 V(\vec{r}), \end{aligned}$$

a renormalized Breit-Hartree-Fock (BHF) equation is readily obtained:

$$[H_O + H_1 + H_2 + H_3] \Phi_{\alpha_i}(\vec{r}_i) - V_F(\vec{r}_i, \vec{r}_j) \Phi_{\alpha_i}(\vec{r}_j) = \varepsilon_i \Phi_{\alpha_i}(\vec{r}_i), \quad (\text{A18})$$

where

$$H_O = \frac{1}{2m_e} \left[\vec{p} + \frac{e}{c}\vec{A}_H \right]^2 + \frac{e\hbar\vec{\sigma}_i \cdot \vec{B}_H}{2m_e c} + V_O(\vec{r}_i) + V_H(\vec{r}_i)$$

is the Hamiltonian of an electron moving in the mean field;

$$H_1 = -\frac{1}{8m_e^3c^2} \left[\vec{p} + \frac{e}{c}\vec{A}_H \right]^4$$

represents the relativistic correction due to the variation of mass with velocity;

$$H_2 = \frac{\hbar^2}{8m_e^2c^2} \vec{\nabla}^2 [V_O(\vec{r}_i) + V_H(\vec{r}_i)]$$

denotes the so-called Darwin modification; and

$$H_3 = -\frac{\hbar}{4m_e^2c^2} \vec{\sigma}_i \cdot \left[\left(\vec{p} + \frac{e}{c}\vec{A}_H \right) \times \vec{\nabla} [V_O(\vec{r}_i) + V_H(\vec{r}_i)] \right]$$

gives the interaction between the spin moment and its orbital magnetic moment of the spin-orbit coupling .

As the next step, we show that the Breit vector potential and the Hartree-Fock terms may be expressed in the forms of Eqs.(6)-(10). We approximate the wave function $\chi_{\alpha_i}(\vec{r}_i)$ in Eq.(A14) by the leading-order term:

$$\chi_{\alpha_i}(\vec{r}_i) = \frac{1}{2mc} \vec{\sigma}_i \cdot \vec{p} \phi_{\alpha_i}(\vec{r}_i). \quad (\text{A19})$$

Substituting (A9) and (A19) into (A8), with some tedious algebra, we obtain the form of the vector potential in (A8) as

$$\vec{A}_H(\vec{r}_i) = \frac{1}{c} \sum_j \int d\tau_j \frac{\vec{J}_{\alpha_j}(\vec{r}_j) + \vec{J}_s(\vec{r}_j) + \vec{J}_m(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} + \sum_j \oint_{s_j} \frac{\vec{M}_{\alpha_j}^{(i)}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} \times d\vec{S}_j, \quad (\text{A20})$$

where there are three different current densities in Eq.(A20), i.e., the electric current density $\vec{J}_{\alpha_j}$, the spin magnetization current density $\vec{J}_s$ associated with the spin moment, and the magnetic current density $\vec{J}_m$ arising from the second term of the Breit operator in Eq.(A2). The last term in Eq.(A20) is the contribution of the surface current due to the spin moment and the magnetic moment. By using (A9), (A17) and (A19), it is easy to prove that

$$\begin{aligned} -ec\psi_{\alpha_i}^+(\vec{r}_i)\vec{\alpha}_i\psi_{\alpha_i}(\vec{r}_i) &= -\frac{e}{m_e}Re\left[\Phi_{\alpha_i}^+(\vec{r}_i)\vec{p}\Phi_{\alpha_i}(\vec{r}_i)\right] - \frac{e\hbar}{2m_e}Re\vec{\nabla} \times \left[\Phi_{\alpha_i}^+(\vec{r}_i)\vec{\sigma}_i\Phi_{\alpha_i}(\vec{r}_i)\right] \\ &= \vec{J}_{\alpha_i}(\vec{r}_i) + \vec{J}_s(\vec{r}_i), \end{aligned} \quad (\text{A21})$$

where

$$\vec{J}_{\alpha_i}(\vec{r}_i) = -\frac{e}{m_e}Re\left[\Phi_{\alpha_i}^+(\vec{r}_i)\vec{p}\Phi_{\alpha_i}(\vec{r}_i)\right], \quad (\text{A22})$$

and

$$\vec{J}_s(\vec{r}_i) = -\frac{e\hbar}{2m_e}Re\vec{\nabla} \times \left[\Phi_{\alpha_i}^+(\vec{r}_i)\vec{\sigma}_i\Phi_{\alpha_i}(\vec{r}_i)\right]. \quad (\text{A23})$$

The magnetic current density is defined as

$$\vec{J}_m(\vec{r}_i) = \frac{1}{2}\vec{\nabla} \times \left[\vec{r}_{ij} \times \vec{J}_{\alpha_i}(\vec{r}_i)\right]. \quad (\text{A24})$$

The associated magnetization density including the spin moment is

$$\begin{aligned} \vec{M}_{\alpha_j}^{(i)}(\vec{r}_j) &= \frac{1}{2c}\left[\vec{r}_{ij} \times \vec{J}_{\alpha_j}(\vec{r}_j)\right] - \frac{e\hbar}{2m_e c}Re\left[\Phi_{\alpha_j}^+(\vec{r}_j)\vec{\sigma}_j\Phi_{\alpha_j}(\vec{r}_j)\right] \\ &= -\frac{e}{2m_e c}Re\left[\Phi_{\alpha_j}^+(\vec{r}_j)(\vec{r}_{ij} \times \vec{p}_j + \hbar\vec{\sigma}_j)\Phi_{\alpha_j}(\vec{r}_j)\right]. \end{aligned} \quad (\text{A25})$$

Substituting Eqs.(A21)-(A25) into (A20), the vector potential can be rewritten in the form of Eq.(6):

$$\vec{A}_H(\vec{r}_i) = \frac{1}{c} \sum_j \int d\tau_j \frac{\vec{J}_{\alpha_j}(\vec{r}_j) + c\vec{\nabla} \times \vec{M}_{\alpha_j}^{(i)}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} + \sum_j \oint_{s_j} \frac{\vec{M}_{\alpha_j}^{(i)}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} \times d\vec{S}_j. \quad (\text{A26})$$

The Hartree term $V_H(\vec{r}_i)$ is related to the Coulomb interaction:

$$\begin{aligned} V_H(\vec{r}_i) &= \sum_j \int d\tau_j \left[\phi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \phi_{\alpha_j}(\vec{r}_j) + \chi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \chi_{\alpha_j}(\vec{r}_j) \right] \\ &\approx \sum_j \int d\tau_j \frac{e^2 \Phi_{\alpha_j}^+(\vec{r}_j) \Phi_{\alpha_j}(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}, \end{aligned} \quad (\text{A27})$$

where we have neglected a small term associated with the spin magnetic dipole moments of electrons. Similarly, the Coulomb exchange potential $V_F^c(\vec{r}_i, \vec{r}_j)$ in Eq.(A6) may be readily obtained by exchanging the coordinate variables in the wave functions:

$$\begin{aligned} V_F^c(\vec{r}_i, \vec{r}_j) &= \sum_j \int d\tau_j \left[\phi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \phi_{\alpha_j}(\vec{r}_i) + \chi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \chi_{\alpha_j}(\vec{r}_i) \right] \\ &= \sum_j \int d\tau_j \frac{e^2 \Phi_{\alpha_j}^+(\vec{r}_j) \Phi_{\alpha_j}(\vec{r}_i)}{|\vec{r}_i - \vec{r}_j|} \\ &\quad + \sum_j \int d\tau_j \Phi_{\alpha_j}^+(\vec{r}_j) \left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{|\vec{r}_i - \vec{r}_j|^3} - 3 \frac{(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^5} \right] \Phi_{\alpha_j}(\vec{r}_i), \end{aligned} \quad (\text{A28})$$

where the second term represents the interaction between the spin magnetic dipole moments of the electrons, $\vec{\mu}_i = -e\hbar\vec{\sigma}_i/2m_e c$.

Finally, let us derive the Breit-Fock potential $V_F^b(\vec{r}_i, \vec{r}_j)$ in Eq.(A6). By using the matrix algebra

$$\vec{\alpha}_i \psi_{\nu_j}(\vec{r}_i) = \begin{pmatrix} 0 & \vec{\sigma}_i \\ \vec{\sigma}_i & 0 \end{pmatrix} \begin{pmatrix} \phi_{\nu_j}(\vec{r}_i) \\ \chi_{\nu_j}(\vec{r}_i) \end{pmatrix} = \begin{pmatrix} \vec{\sigma}_i \chi_{\nu_j}(\vec{r}_i) \\ \vec{\sigma}_i \phi_{\nu_j}(\vec{r}_i) \end{pmatrix}, \quad (\text{A29})$$

it is obvious that

$$\psi_{\nu_j}^+(\vec{r}_j) \vec{\alpha}_i \cdot \vec{\alpha}_j \psi_{\nu_j}(\vec{r}_i) = \phi_{\nu_j}^+(\vec{r}_j) \vec{\sigma}_i \cdot \vec{\sigma}_j \phi_{\nu_j}(\vec{r}_i) + \chi_{\nu_j}^+(\vec{r}_j) \vec{\sigma}_i \cdot \vec{\sigma}_j \chi_{\nu_j}(\vec{r}_i), \quad (\text{A30})$$

and

$$\begin{aligned} \psi_{\nu_j}^+(\vec{r}_j) (\vec{\alpha}_i \cdot \vec{r}_{ij}) (\vec{\alpha}_j \cdot \vec{r}_{ij}) \psi_{\nu_j}(\vec{r}_i) &= \phi_{\nu_j}^+(\vec{r}_j) (\vec{\sigma}_i \cdot \vec{r}_{ij}) (\vec{\sigma}_j \cdot \vec{r}_{ij}) \phi_{\nu_j}(\vec{r}_i) \\ &\quad + \chi_{\nu_j}^+(\vec{r}_j) (\vec{\sigma}_i \cdot \vec{r}_{ij}) (\vec{\sigma}_j \cdot \vec{r}_{ij}) \chi_{\nu_j}(\vec{r}_i). \end{aligned} \quad (\text{A31})$$

Substituting Eqs.(A19), (A30) and (A31) into Eq.(A6), we obtain $V_F^b(\vec{r}_i, \vec{r}_j)$ as

$$\begin{aligned}
V_F^b(\vec{r}_i, \vec{r}_j) &= - \sum_j \int d\tau_j \phi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{2 |\vec{r}_i - \vec{r}_j|} \left[\vec{\sigma}_i \cdot \vec{\sigma}_j + \frac{(\vec{\sigma}_i \cdot \vec{r}_{ij})(\vec{\sigma}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right] \phi_{\alpha_j}(\vec{r}_i) \\
&\quad - \sum_j \int d\tau_j \chi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{2 |\vec{r}_i - \vec{r}_j|} \left[\vec{\sigma}_i \cdot \vec{\sigma}_j + \frac{(\vec{\sigma}_i \cdot \vec{r}_{ij})(\vec{\sigma}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right] \chi_{\alpha_j}(\vec{r}_i) \\
&\approx - \sum_j \int d\tau_j \Phi_{\alpha_j}^+(\vec{r}_j) \frac{e^2}{2 |\vec{r}_i - \vec{r}_j|} \left[\vec{\sigma}_i \cdot \vec{\sigma}_j + \frac{(\vec{\sigma}_i \cdot \vec{r}_{ij})(\vec{\sigma}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right] \Phi_{\alpha_j}(\vec{r}_i). \quad (\text{A32})
\end{aligned}$$

It should be noted that the tensorial interaction due to the Breit exchange interaction is on the same energy scale as the Coulomb interactions. The sum of the two exchange terms in (A28) and (A32) yields

$$\begin{aligned}
V_F(\vec{r}_i, \vec{r}_j) &= \sum_{i \neq j} \int d\vec{r}_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \Phi_{\alpha_j}^+(\vec{r}_j) \left[1 - \frac{1}{2} \left(\vec{\sigma}_i \cdot \vec{\sigma}_j + \frac{(\vec{\sigma}_i \cdot \vec{r}_{ij})(\vec{\sigma}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^2} \right) \right] \Phi_{\alpha_j}(\vec{r}_i) \\
&\quad + \sum_j \int d\tau_j \Phi_{\alpha_j}^+(\vec{r}_j) \left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{|\vec{r}_i - \vec{r}_j|^3} - 3 \frac{(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{|\vec{r}_i - \vec{r}_j|^5} \right] \Phi_{\alpha_j}(\vec{r}_i). \quad (\text{A33})
\end{aligned}$$

From Eqs.(A18), (A25), (A26) and (A33), we wish to neglect the relativistic correction of the variation of mass with velocity (H_1), the Darwin term (H_2), the spin-orbit coupling term (H_3), and the spin magnetic dipole interaction plus other terms of order higher than $(v_F/c)^2$, where v_F denotes the Fermi velocity of the electron. The resulting BHF equation is thus given by

$$H_O \Phi_{\alpha_i}(\vec{r}_i) - V_F(\vec{r}_i, \vec{r}_j) \Phi_{\alpha_i}(\vec{r}_j) = \varepsilon_i \Phi_{\alpha_i}(\vec{r}_i). \quad (\text{A34})$$

APPENDIX B: CALCULATIONS OF TYPICAL MATRIX ELEMENTS

For small deviations from a sphere, the integral of a matrix element $f(r, \theta, \phi)$ may be approximated as

$$\int_0^{R(\theta, \phi)} r^2 dr \int d\Omega f(r, \theta, \phi) \approx \int_0^R r^2 dr \int d\Omega f(r, \theta, \phi) + \delta \int d\Omega g(R, \theta, \phi), \quad (\text{B1})$$

where $g(R, \theta, \phi) = R^3 \sum_{l,m} a_{l,m} Y_{lm}(\theta, \phi) f(R, \theta, \phi) / \sqrt{\sum_{l,m>0} a_{lm}^2 / 2\pi}$ denotes the matrix elements evaluated with respect to the deviation from the sphere. Below we show the forms of several typical matrix elements in the Breit-Hartree-Fock (BHF) equation for a sphere. We choose the expansion of the i -th eigenfunction in Eq.(4) as

$$\Phi_i^{(k)} = \sum_{\alpha_i} D_{\alpha_i}^{i(k)} \psi_{nlm}(\vec{r}) \chi_{m_s}, \quad (\text{B2})$$

where χ_{m_s} denotes the spin state, the notation $\alpha = \{n, l, m, m_s\}$, k denotes the iteration index, and the basis function ψ_{nlm} is taken to be the set of eigenfunctions of an infinite spherical well with radius R_0 chosen to be slightly larger than the jellium potential radius:

$$\psi_{nlm}(r, \theta, \phi) = \left[\frac{2}{R_0^3 j_{l+1}^2(x_{nl})} \right]^{1/2} j_l(x_{nl}r/R_0) Y_{lm}(\theta, \phi), \quad (\text{B3})$$

where x_{nl} denotes the n -th root of the l -th order spherical Bessel function j_l , and $Y_{lm}(\theta, \phi)$ stands for the spherical Harmonics function. By using (B2), the Hartree matrix element of the Coulomb interaction may be expressed as

$$\begin{aligned} \langle \alpha' | V_H | \alpha \rangle &= \frac{e^2}{R_0} \sum_{j=1} \sum_{\alpha_1, \alpha'_1} B_{nl'n'l_1n'_1l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \delta_{m_s, m'_s} \delta_{m_{s_1}, m'_{s_1}} \\ &\times \int_0^{R/R_0} x^2 dx \int_0^{R/R_0} y^2 dy j_{l'}(x_{n'l'}x) j_l(x_{nl}x) j_{l'_1}(x_{n'_1l'_1}y) j_{l_1}(x_{n_1l_1}y) \\ &\times \int d\Omega \int d\Omega' Y_{l'm'}^+(\theta, \phi) Y_{l'_1m'_1}^+(\theta', \phi') \frac{1}{|\vec{x} - \vec{y}|} Y_{l_1m_1}(\theta', \phi') Y_{lm}(\theta, \phi), \end{aligned} \quad (\text{B4})$$

where the coefficient $B_{nl'n'l_1n'_1l'_1} = 4 / |j_{l+1}(x_{nl}) j_{l'+1}(x_{n'l'}) j_{l_1+1}(x_{n_1l_1}) j_{l'_1+1}(x_{n'_1l'_1})|$. Inserting the identity $1/|\vec{x} - \vec{y}| = \sum_{l=0} \sum_{m=-l}^l [4\pi/(2l+1)] (r_{<}^l/r_{>}^{l+1}) Y_{lm}^+(\theta, \phi) Y_{lm}(\theta', \phi')$, where $r_{<}(r_{>})$ is the smaller (larger) of $|\vec{x}|$ and $|\vec{y}|$, into Eq.(B4) and using the relation

$$\int d\Omega Y_{lm}^+(\theta, \phi) Y_{l_1m_1}(\theta, \phi) Y_{l_2m_2}(\theta, \phi) = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)} \right]^{1/2} C_{l_10, l_20}^{l0} C_{l_1m_1, l_2m_2}^{lm},$$

we simplify Eq.(B3) to the form

$$\begin{aligned}
\langle \alpha' | V_H | \alpha \rangle &= \frac{e^2}{R_0} \sum_{j=1} \sum_{\alpha_1, \alpha'_1} B_{nl n' l' n_1 l_1 n'_1 l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \delta_{m_s, m_{s'}} \delta_{m_{s_1}, m_{s'_1}} \\
&\times \sum_{l_2} \sum_{m_2=-l_2}^{l_2} (-1)^{m_2} \left[\frac{(2l_1+1)(2l+1)}{(2l'_1+1)(2l'+1)} \right]^{1/2} C_{l_2 0, l_1 0}^{l'_1 0} C_{l_2 0, l_0}^{l'_0} C_{l_2 m_2, l_1 m_1}^{l'_1 m'_1} C_{l_2 -m_2, l m}^{l'_1 m'_1} \\
&\times \int_0^{R/R_0} dx j_{l'}(x_{n' l'} x) j_l(x_{n l} x) \left[\int_0^x dy x y^2 \left(\frac{y}{x} \right)^{l_2} j_{l'_1}(x_{n'_1 l'_1} y) j_{l_1}(x_{n_1 l_1} y) \right. \\
&\left. + \int_x^{R/R_0} dy y x^2 \left(\frac{x}{y} \right)^{l_2} j_{l'_1}(x_{n'_1 l'_1} y) j_{l_1}(x_{n_1 l_1} y) \right]. \tag{B5}
\end{aligned}$$

The summation limits for l_2 in Eq.(B5) is easily determined by the nonzero conditions of the CG coefficients. Exchanging the corresponding quantum numbers α_1 and α in Eq.(B5) and combining with Eq.(8), we obtain the Fock matrix element of the Coulomb interactions

$$\begin{aligned}
\langle \alpha' | V_F^c | \alpha \rangle &= \frac{e^2}{R_0} \sum_{j=1} \sum_{\alpha_1, \alpha'_1} B_{nl n' l' n_1 l_1 n'_1 l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \delta_{m_s, m_{s'}} \delta_{m_{s_1}, m_{s'_1}} \\
&\times \sum_{l_2} \sum_{m_2=-l_2}^{l_2} (-1)^{m_2} \left[\frac{(2l_1+1)(2l+1)}{(2l'_1+1)(2l'+1)} \right]^{1/2} C_{l_2 0, l_1 0}^{l'_1 0} C_{l_2 0, l_0}^{l'_0} C_{l_2 m_2, l_1 m_1}^{l'_1 m'_1} C_{l_2 -m_2, l m}^{l'_1 m'_1} \\
&\times \int_0^{R/R_0} dx j_{l'_1}(x_{n'_1 l'_1} x) j_l(x_{n l} x) \left[\int_0^x dy x y^2 \left(\frac{y}{x} \right)^{l_2} j_{l'_1}(x_{n'_1 l'_1} y) j_{l_1}(x_{n_1 l_1} y) \right. \\
&\left. + \int_x^{R/R_0} dy y x^2 \left(\frac{x}{y} \right)^{l_2} j_{l'_1}(x_{n'_1 l'_1} y) j_{l_1}(x_{n_1 l_1} y) \right]. \tag{B6}
\end{aligned}$$

On the other hand, the Fock matrix elements associated with the Breit interaction in Eq.(8) may be expressed as

$$\begin{aligned}
\langle \alpha' | V_F^b | \alpha \rangle &= -\frac{e^2}{2R_0} \sum_{j=1} \sum_{\alpha_1, \alpha'_1} B_{nl n' l' n_1 l_1 n'_1 l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \\
&\times \int_0^{R/R_0} x^2 dx \int_0^{R/R_0} y^2 dy j_{l'_1}(x_{n'_1 l'_1} x) j_l(x_{n l} x) j_{l'_1}(x_{n' l'} y) j_{l_1}(x_{n_1 l_1} y) \\
&\times \int d\Omega \int d\Omega' Y_{l'_1 m'_1}^+(\theta, \phi) Y_{l m}^+(\theta', \phi') \chi_{m'_s}^+(\sigma) \chi_{m'_s}^+(\sigma') \\
&\times \left[\frac{\vec{\sigma} \cdot \vec{\sigma}'}{|\vec{x} - \vec{y}|} + \frac{(\vec{\sigma} \cdot \vec{r})(\vec{\sigma}' \cdot \vec{r})}{|\vec{x} - \vec{y}|^3} \right] \chi_{m_s}(\sigma') \chi_{m_{s_1}}(\sigma) Y_{l_1 m_1}(\theta', \phi') Y_{l m}(\theta, \phi), \tag{B7}
\end{aligned}$$

where $\vec{r} = \vec{x} - \vec{y}$. By using the relation $\sigma_\mu \chi_{1/2 m'_s} = -\sqrt{3} C_{1\mu, 1/2 m'_s}^{1/2 m_s} \chi_{1/2 m_s}$ [46], it is easy to prove two useful identities:

$$\chi_{1/2m'_s}^+(\sigma)\chi_{1/2m'_{s1}}(\sigma')\vec{\sigma}\cdot\vec{\sigma}'\chi_{1/2m_s}(\sigma')\chi_{1/2m_{s1}}(\sigma)=3\sum_{\mu}(-1)^{\mu}C_{1\mu,1/2m_{s1}}^{1/2m'_s}C_{1-\mu,1/2m_s}^{1/2m'_{s1}}, \quad (\text{B8})$$

and

$$\begin{aligned} \chi_{1/2m'_s}^+(\sigma)\chi_{1/2m'_{s1}}(\sigma')(\vec{\sigma}\cdot\vec{r})\times(\vec{\sigma}'\cdot\vec{r})\chi_{1/2m_s}(\sigma')\chi_{1/2m_{s1}}(\sigma) \\ = 3\sum_{\mu\nu}(-1)^{\mu+\nu}C_{1\mu,1/2m_{s1}}^{1/2m'_s}C_{1\nu,1/2m_s}^{1/2m'_{s1}}\vec{r}_{-\mu}\vec{r}_{-\nu}, \end{aligned} \quad (\text{B9})$$

where $\mu, \nu = 0, \pm 1$. By using (B8), the first term in the brackets on the right-hand side of Eq.(B7) can be evaluated directly:

$$\begin{aligned} \langle \alpha' | V_F^{b(1)} | \alpha \rangle = & -\frac{3e^2}{2R_0}\sum_{j=1}\sum_{\alpha_1, \alpha'_1} B_{nl'n'l_1n'_1l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \sum_{\mu} (-1)^{\mu} C_{1\mu,1/2m_{s1}}^{1/2m'_s} C_{1-\mu,1/2m_s}^{1/2m'_{s1}}, \\ & \times \sum_{l_2} \sum_{m_2=-l_2}^{l_2} (-1)^{m_2} \left[\frac{(2l_1+1)(2l+1)}{(2l'_1+1)(2l'+1)} \right]^{1/2} C_{l_2 0, l_1 0}^{l' 0} C_{l_2 0, l 0}^{l'_1 0} C_{l_2 m_2, l_1 m_1}^{l' m'} C_{l_2 -m_2, l m}^{l'_1 m'_1} \\ & \times \int_0^{R/R_0} dx j_{l'_1}(x_{n'_1 l'_1} x) j_l(x_{nl} x) \left[\int_0^x dy y x^2 \left(\frac{y}{x} \right)^{l_2} j_{l'}(x_{n' l' y}) j_{l_1}(x_{n_1 l_1 y}) \right. \\ & \left. + \int_x^{R/R_0} dy y x^2 \left(\frac{x}{y} \right)^{l_2} j_{l'}(x_{n' l' y}) j_{l_1}(x_{n_1 l_1 y}) \right]. \end{aligned} \quad (\text{B10})$$

By using (B9) and the identity [46]

$$\frac{\vec{r}_{\mu}}{r^3} = 4\pi \sum_{l=1} (-1)^l \sqrt{\frac{l}{3}} \frac{r_{<}^{l-1}}{r_{>}^{l+1}} \left[\vec{Y}_{l-1}(\Omega) \otimes \vec{Y}_l(\Omega') \right]_{1\mu}, \quad (\text{B11})$$

the second term in the brackets on the right-hand side of Eq.(B7) can also be evaluated as

$$\begin{aligned} \langle \alpha' | V_F^{b(2)} | \alpha \rangle = & -\frac{e^2}{2R_0}\sum_{j=1}\sum_{\alpha_1, \alpha'_1} B_{nl'n'l_1n'_1l'_1} D_{\alpha_1}^j D_{\alpha'_1}^{j*} \\ & \times \sum_{l_2} \sum_{m_2=-l_2+1}^{l_2-1} \sum_{m'_2=-l_2}^{l_2} \sum_{LM} \sum_{\mu\nu} \left[\frac{(2l_1+1)(2l+1)}{(2l'_1+1)(2l'+1)} \right]^{1/2} \\ & \times (-1)^{l_2+\mu+\nu} \sqrt{3l_2(2l_2-1)(2l_2+1)} C_{1\nu,1/2m_{s1}}^{1/2m'_s} C_{1\mu,1/2m_s}^{1/2m'_{s1}} C_{l_2-1m_2, l_2 m'_2}^{1-\mu} \\ & \times \int_0^{R/R_0} dx x^2 j_{l'}(x_{n' l' x}) j_{l_1}(x_{n_1 l_1 x}) \left[\int_0^x dy y \left(\frac{y}{x} \right)^{l_2+1} j_{l'_1}(x_{n'_1 l'_1 y}) j_l(x_{nl} y) \right. \\ & \left. + \int_x^{R/R_0} dy y \left(\frac{x}{y} \right)^{l_2-1} j_{l'_1}(x_{n'_1 l'_1 y}) j_l(x_{nl} y) \right] \\ & \times \left[\left(\frac{x}{y} \right) C_{l_2 0, l 0}^{l'_1 0} C_{l_2-10, 10}^{L 0} C_{L 0, l_1 0}^{l' 0} C_{l_2 m'_2, l m}^{l'_1 m'_1} C_{l_2-1m_2, 1-\nu}^{LM} C_{LM, l_1 m_1}^{l' m'} \right. \\ & \left. - C_{L 0, l 0}^{l'_1 0} C_{l_2 0, 10}^{L 0} C_{l_2-10, l_1 0}^{l' 0} C_{l_2 m'_2, 1-\nu}^{LM} C_{LM, l m}^{l'_1 m'_1} C_{l_2-1m_2, l_1 m_1}^{l' m'} \right]. \end{aligned} \quad (\text{B12})$$

The total Fock matrix elements is then given by

$$\langle \alpha' | V_F | \alpha \rangle = \langle \alpha' | V_F^c | \alpha \rangle + \langle \alpha' | V_F^{b(1)} | \alpha \rangle + \langle \alpha' | V_F^{b(2)} | \alpha \rangle. \quad (\text{B13})$$

Other matrix elements may be evaluated in the similar manner [47].

APPENDIX C: MAGNITUDES FOR VARIOUS INTERACTION TERMS

In this Appendix, we present a more detailed description of the magnitudes for the various interaction terms. We define contributions of the various interaction terms as follows. For the Coulomb interaction (both the Hartree and Fock contributions),

$$\Delta E_C^i = \varepsilon_C^i - \varepsilon_O^i \quad (C1)$$

denotes the Coulomb interaction contribution to the i th energy level. Here, ε_C^i and ε_O^i represent the i th energy level with and without the Coulomb interaction between the electrons, respectively. The level separation due to the Breit-Fock contribution is given by

$$\Delta E_{BF}^i = \varepsilon_{CBF}^i - \varepsilon_C^i, \quad (C2)$$

where ε_{CBF}^i denotes the i th energy levels with the Coulomb plus the Breit-Fock interactions, where the Breit-Fock exchange interaction between the electrons is given by the second term in the bracket on the right hand side of Eq.(8). Similarly, the level separation associated with the Breit-Hartree term is expressed as

$$\Delta E_{BH}^i = \varepsilon_{CB}^i - \varepsilon_{CBF}^i, \quad (C3)$$

where ε_{CB}^i indicates the i th energy level with both the Coulomb plus the Breit interactions. In general, the magnitudes of ΔE_{BH}^i are smaller than that of either ΔE_C^i or ΔE_{BF}^i . Breit has demonstrated that the contribution of ΔE_{BH}^i is on the same order as the electronic dipole interaction energy [25]. An upper bound to the Breit-Hartree contribution in small clusters may therefore be estimated as the largest possible total energy of N -interacting electronic dipoles:

$$\Delta E_d \approx N(N-1) \left(\frac{e^2}{4R} \right) \left[\frac{\alpha_f a_B}{R} \right]^2, \quad (C4)$$

where R is the average radius of the cluster. Taking the average radius $R = r_s a_B N^{1/3}$, we obtain

$$\Delta E_d \approx (N - 1) \left(\frac{e^2}{4a_B r_s} \right) \left[\frac{\alpha_f}{r_s} \right]^2. \quad (\text{C5})$$

Figure 7 is a plot of three cases of calculated energy level separations for four randomly shaped clusters with 276 electrons. The spread of different ΔE 's are shown in three panels, corresponding to ΔE_C , ΔE_{BF} and ΔE_{BH} . It is found that the magnitudes of ΔE_C and ΔE_{BF} are on the same order, as expected (see Section II). There are very few level splittings in the far-infrared range for ΔE_C . Naturally, ΔE_C alone leads to small far-infrared absorption. The magnitude of the Breit-Hartree term (ΔE_{BH}) is noted to be one order of magnitude smaller than that of either ΔE_C or ΔE_{BF} , and $\Delta E_d = 90 \text{ cm}^{-1}$, which is in the far-infrared range, indeed bounds the spread in ΔE_{BH} . Thus, the level separations near the Breit-Hartree magnitude imply an enhanced far-infrared absorption. To see that ΔE_{BH} can indeed be bound by ΔE_d , we also examine the $(N - 1)$ dependence of ΔE_d as indicated examine in Eq.(C5). To that end we calculate ΔE_{BH} for a spherical jellium cluster with the same electronic density but different electron number N . The results are shown in Fig.8. It is found that the spread of ΔE_{BH} indeed increases with the electron number, in excellent agreement with the prediction of (C5).

APPENDIX D: MAGNETIC SUSCEPTIBILITY

In this appendix we present the derivation of the magnetic susceptibility in the linear response approximation. By considering the Breit interaction in the Hartree approximation, the single-electron Hamiltonian in the presence of a semiclassical electromagnetic field (characterized by the vector potential $\vec{A}_0(\vec{r}, t)$) can be written as

$$\hat{H} = \frac{1}{2m} \left[\vec{p} + \frac{e}{c} (\vec{A}_H + \vec{A}_0) \right]^2 + V_0(\vec{r}), \quad (\text{D1})$$

where $V_0(\vec{r})$ is the potential in the absence of an applied field. For optical properties, we may neglect the term $\vec{A}_0^2$ and treat the terms linear in $\vec{A}_0$ as a perturbation. Thus, Eq.(D1) can be rewritten as

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (\text{D2})$$

with

$$\hat{H}_0 = \frac{1}{2m} \left[\vec{p} + \frac{e}{c} \vec{A}_H \right]^2 + V_0(\vec{r}),$$

and

$$\hat{H}_1 = \frac{e}{2mc} \left[\left(\vec{p} + \frac{e}{c} \vec{A}_H \right) \cdot \vec{A}_0(\vec{r}, t) + \vec{A}_0(\vec{r}, t) \cdot \left(\vec{p} + \frac{e}{c} \vec{A}_H \right) \right]$$

regarded as a small perturbation on the state $|i\rangle$ of H_0 . Next, we calculate the current induced by an applied electromagnetic field. Let $\hat{\rho}$ be the density matrix appropriate to a system described by (D2) in thermal equilibrium: $\hat{\rho} = 1/(\exp[\beta(\hat{H} - \varepsilon_F)] + 1)$, with $\beta = 1/(k_B T)$. For a statistical ensemble, the expectation value of an operator $\hat{Q}$ is

$$\langle \hat{Q} \rangle = \text{Tr}\{\hat{\rho}\hat{Q}\} = \sum_{i,j} \langle i | \hat{\rho} | j \rangle \langle j | \hat{Q} | i \rangle. \quad (\text{D3})$$

To the leading order perturbation [9], we may write

$$\hat{\rho} \approx \hat{\rho}_0 + \hat{\rho}_1, \quad (\text{D4})$$

where $\hat{\rho}_0$ is the density matrix of the system described by $\hat{H}_0$ and $\hat{\rho}_1$ is the perturbation in $\hat{\rho}$ due to $\hat{H}_1$. Note the total density matrix must obey the Liouville equation, i.e., $i\hbar\partial\hat{\rho}/\partial t = [\hat{H}, \hat{\rho}]$. That means

$$i\hbar\frac{\partial\hat{\rho}_1}{\partial t} = [\hat{H}_1, \hat{\rho}_0] + [\hat{H}_0, \hat{\rho}_1]. \quad (\text{D5})$$

Assuming response at the same frequency as the applied perturbation, taken to be of the form $\exp[-i(\omega + i\eta)t]$ (where $\exp(\eta t)$ adiabatically switches on the perturbation from $t = -\infty$), we calculate the matrix element to get

$$\langle i | \hat{\rho}_1 | j \rangle = \frac{e}{2m_e c} \left[\frac{f_i - f_j}{\varepsilon_{ij} - \hbar\omega - i\eta} \right] \vec{B}_0 \cdot \langle i | \vec{r} \times (\vec{p} + \frac{e}{c}\vec{A}_H) | j \rangle, \quad (\text{D6})$$

where $\vec{B}_0$ is the applied magnetic field corresponding to the vector potential $\vec{A}_0$. The current operator in Eq.(9) can be extended directly to the case of an applied field by the transformation of $\vec{p} \rightarrow \vec{p} + \frac{e}{c} [\vec{A}_H + \vec{A}_0]$:

$$\vec{J} = -\frac{e}{m_e} Re \left\{ \Phi^+(\vec{r}) \left[\vec{p} + \frac{e}{c} (\vec{A}_H + \vec{A}_0) \right] \Phi(\vec{r}) \right\} = \vec{J}_0 + \vec{J}_1, \quad (\text{D7})$$

where $\vec{J}_0 = -\frac{e}{m_e} Re [\Phi^+(\vec{r}) (\vec{p} + \frac{e}{c}\vec{A}_H) \Phi(\vec{r})]$, and $\vec{J}_1 = -\frac{e^2}{m_e c} Re [\Phi^+(\vec{r}) \vec{A}_0 \Phi(\vec{r})]$. The density of the magnetic moment reduced by the electronic current density can be expressed as

$$\vec{M} = \frac{1}{2c} \vec{r} \times \vec{J} = \frac{1}{2c} \vec{r} \times [\vec{J}_0 + \vec{J}_1], \quad (\text{D8})$$

with $\vec{M}_0 = (1/2c)\vec{r} \times \vec{J}_0$. Therefore, the expectation value of the magnetic moment density is

$$\langle \vec{M} \rangle = Tr [\rho_0 \vec{M}_0] + Tr [\rho_0 \vec{M}_1] + Tr [\rho_1 \vec{M}_0] + Tr [\rho_1 \vec{M}_1]. \quad (\text{D9})$$

In equilibrium, $Tr [\rho_0 \vec{M}_0] = 0$, while the last term $Tr [\rho_1 \vec{M}_1]$ can be neglected in the linear response limit. Thus, the reduced magnetic moment is determined by

$$\langle \vec{M} \rangle = Tr [(\rho_0 + \rho_1) \vec{M}] = Tr [\rho_0 \vec{M}_1] + Tr [\rho_1 \vec{M}_0]. \quad (\text{D10})$$

The first term and the second term in the right-hand side of Eq.(D10) may be expressed as

$$\text{Tr} [\rho_0 \vec{M}_1] = -\frac{e^2}{2m_e c^2} \sum_i f_i \langle i | \vec{r} \times \vec{A}_0 | i \rangle, \quad (\text{D11})$$

and

$$\text{Tr} [\rho_1 \vec{M}_0] = -\frac{e^2}{4m_e^2 c^2} \sum_{i,j} \frac{f_i - f_j}{\varepsilon_{ij} - \hbar\omega - i\eta} \vec{B}_0 | \langle i | \vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H) | j \rangle_z |^2. \quad (\text{D12})$$

Suppose the applied field is in the z-direction, then by combining (D10) with Eq.(D11) and (D12), the reduced magnetization can be written as

$$M = -\frac{e^2}{2m_e c^2} \left[\sum_i f_i \langle i | z^2 | i \rangle + \frac{1}{2m_e} \sum_{i,j} \frac{f_i - f_j}{\varepsilon_{ij} - \hbar\omega - i\eta} \times | \langle i | \vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H) | j \rangle_z |^2 \right] B_0. \quad (\text{D13})$$

The magnetic susceptibility per volume is defined as $\chi^m(\omega) = |3M/4\pi R^3 B_0|$. Therefore,

$$\chi^m(\nu) = \frac{3e^2}{8\pi R^3 m_e c^2} \left[\sum_i f_i \langle i | z^2 | i \rangle + \frac{1}{m_e} \sum_{i,j} \frac{f_i \varepsilon_{ij}}{\varepsilon_{ij}^2 - \hbar^2 \nu^2} \times | \langle i | \vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H) | j \rangle_z |^2 \right]. \quad (\text{D14})$$

For small clusters, the discreteness of the eigenvalues is important, we perform the low-frequency expansion in Eq.(D14) [9]:

$$\frac{1}{\varepsilon_{ij}^2 - \hbar^2 \nu^2} = \frac{1}{\varepsilon_{ij}^2} + \frac{\hbar^2 \nu^2}{\varepsilon_{ij}^2 [\varepsilon_{ij}^2 - \hbar^2 \nu^2]}$$

to obtain

$$\chi^m(\nu) = \chi^m(0) + \frac{3e^2 \hbar^2}{4\pi m_e R^3} \left[\sum_{\{i,j\}} g_{\{i,j\}}^m \frac{1}{\varepsilon_{ij}^2 - \hbar^2 \nu^2} + i \frac{\pi}{2\hbar\nu} \sum_{\{i,j\}} g_{\{i,j\}}^m \delta(\hbar\nu - \varepsilon_{ij}) \right], \quad (\text{D15})$$

where the symmetrized magnetic dipole oscillator strength is defined as $g_{\{i,j\}}^m = g_{i,j}^m + g_{j,i}^m$.

The magnetic dipole oscillator strength is defined as

$$g_{i,j}^m = \frac{2\pi^2 f_i}{m_e \varepsilon_{ij} \lambda^2} | \langle i | \vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H) | j \rangle_z |^2, \quad (\text{D16})$$

and the real static magnetic susceptibility is given by

$$\chi^m(0) = \frac{3e^2 \hbar^2}{8\pi m_e R^3} \sum_i f_i \left[\langle i | z^2 | i \rangle + \sum_j \frac{| \langle i | \vec{r} \times (\vec{p} + \frac{e}{c} \vec{A}_H) | j \rangle_z |^2}{\varepsilon_{ij} m_e} \right]. \quad (\text{D17})$$

The magnetic permeability follows as $\mu_m(\nu) = 1 + 4\pi\chi^m(\nu)$.

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FIGURE CAPTIONS

Figure 1 Calculated energy levels for one of the clusters whose cross section is shown in the inset. The value of the parameter $\delta = 5.7\%$. The three curves with the same electron number $N=276$, displaced with respect to each other, correspond to the three cases of no interaction between the electrons, labeled by (O), with only Coulomb interaction added, labeled by (C), and Coulomb plus Breit interactions, labeled by (C+B). It is noted that the curves are characterized by many small plateaus. These correspond to either degenerate states or clumps of closely-spaced states.

Figure 2 Integrated level spacing distribution from four randomly-shaped clusters with the same electron number $N=276$ plotted as a function of the normalized level spacing variable $\sigma = \Delta/\Delta_O$, where Δ_O is the mean value of the plotted data. The associated distribution are shown as insets. The integral of the Wigner distribution is denoted by the dash-dotted line. The integral of the Poisson distribution, shown only in (c), is given by the dotted line. Here (a) corresponds to noninteracting electrons, $\Delta_O = 0.34$ eV, (b) corresponds to the case with Coulomb interaction between the electrons, $\Delta_O = 0.176$ eV; (c) corresponds to the case with both the Coulomb and Breit interactions between the electrons, $\Delta_O = 0.081$ eV. The degenerate or nearly degenerate level spacings have been excluded. It is seen that the data in (c) are better described by the Poisson distribution.

Figure 3 Calculated energy levels for one of the clusters with 276 electrons and the parameter $\delta = 3.5\%$. The two panels correspond to the case of no interaction between the electrons, labeled by (O), and the case where both Coulomb and Breit interactions are taken into account, labeled by (C+B). For comparison, the simulated energy levels associated with a true Poisson distribution of level spacing are plotted and labeled by (P).

Figure 4 Symmetrized oscillator strength plotted as a function of the transition frequency. The height of each vertical line gives the magnitude of $g_{\{i,j\}}^e$, which is always positive. The Fermi function in the oscillator strength is evaluated at $T = 300$ K. The data are from the four randomly shaped clusters whose level distributions are shown in Figure 2. The case of noninteracting electrons is shown in (a). There are essentially no transition in the far-

infrared range, due to the dearth of corresponding level spacings. (b) corresponds to the case with added Coulomb interaction between the electrons. There are slightly more transitions in the lower frequency regime. (c) corresponds to the case with added Coulomb and Breit interactions between the electrons. This is the most physically realistic case, and here one sees many transitions in the far-infrared range, implying a significantly enhanced far-infrared absorption as compared with (a) and (b). All the degenerate or nearly degenerate levels have been included in the calculation. The sum of $g_{\{i,j\}}^e/N$ from $\nu=0$, to $10,000 \text{ cm}^{-1}$, averaged over the four randomly-shaped clusters, is 0.85 in (a), 0.80 in (b), and 0.87 in (c), where $N=276$.

Figure 5 Frequency-integrated imaginary part of the susceptibility data for one of the clusters, shown as a staircase, fitted by a two-parameter function derived from the classical dipole susceptibility expression, shown by the smooth solid line. The data is from the case of Coulomb plus Breit interactions between the electrons. One of the fitting parameters, the effective conductivity, is 6×10^{-5} that of the surface-corrected bulk conductivity of Al. It implies a semi-metallic nature for the cluster. The other fitting parameter $\kappa = -2.3$. Since the fitting requires the integrated imaginary part of the susceptibility to be given by that of the data up to $\nu=900 \text{ cm}^{-1}$, the two curves are seen to meet at exactly that point.

Figure 6 Frequency dependence of the calculated absorption coefficient for a sample of KCl with 0.8 volume-percent of dispersed 276-electron Al clusters, assumed to consist of four different random shapes with equal probability. The case of noninteracting electrons is denoted by solid triangles (labeled by O), the classical prediction with surface-corrected conductivity by the solid line, electrons with the Coulomb interaction by solid circles (labeled by C), and electrons with Coulomb plus Breit interactions by solid diamonds (labeled by C+B). The arrow indicates the experimentally measured absorption coefficient, $\alpha(100 \text{ cm}^{-1}) \approx 10 \text{ cm}^{-1}$, for samples of 0.8% Al clusters (with radii ranging from 40 nm down to 4 nm) dispersed in KCl [Refs.14, 20]. The measured absorption coefficient $\alpha(100 \text{ cm}^{-1})$ drops to about 3-5 cm^{-1} at the radius of 2-3 nm. The calculated coefficient shows similar weak dependence on cluster size.

Figure 7 Calculated electron-electron interaction contributions for four randomly shaped clusters with 276 electrons. The first panel corresponds to ΔE_C , the second panel is for ΔE_{BF} , and the third panel is for ΔE_{BH} . The inset displays an enlarged ΔE_{BH} . The arrows indicate the estimated $\Delta E_d = \pm 90 cm^{-1}$. Definitions of the various terms are given in the text.

Figure 8 Variation of ΔE_{BH} with the electron number in a spherical cluster. The arrows indicate the positions of ΔE_d calculated by using Eq.(C5).

Figure 1. Yi & Sheng

Figure 2. Yi & Sheng

Figure 3. Yi & Sheng

Figure 4. Yi & Sheng

Figure 5. Yi & Sheng

Figure 6. Yi & Sheng

Figure 7. Yi & Sheng

Figure 8. Yi & Sheng