

**Supplementary Material for “Confined helium, density
dependence of the inelastic electron and photon scattering cross
sections and the optical oscillator strength”**

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REMARKS ON MODEL COMPUTATIONS OF THE CORRELATION ENERGY OF THE GROUND STATE OF HELIUM

There is an extensive literature of methods for describing the influence of the environment on an atom or molecule by considering the species to experience a model potential describing its environment. The earliest and simplest model description of a confined mononuclear species was the infinite potential shell model. This describes the environment by adding to the free atom electronic Hamiltonian an additional potential energy which is zero from the nucleus up to a distance R_S beyond which, for all distances, the potential is taken to be infinite. For a system containing only one type of atom, the only reasonable choice for R_S is half of the closest neighbour distance. In Table S1 the Hartree-Fock theory predictions of the energy increases using this potential with $v_0(R_S) = \infty$ for the helium ground state are presented.

	$U_{1g}^{SCF}(R_S)a.u.^{(a)}$		$\Delta U_{1g}^{SCF}(R_S)eV.^{(b)}$			
	$v_0(R_S) = \infty$		$v_0(R_S) = \infty$		$v_0(R_S) = 0$	$v_0(R_S) = -0.2$
$R_S(a.u.)$	from[1]	from[2]	col 1	col 2	from [3]+interpolation ^(d)	
2.0	-2.5594	-2.56253	8.22	8.14	0.99	0.58
2.5		-2.76644		2.59	0.43	0.24
2.8	-2.8057		1.52		0.19	0.097
3.0	-2.8232	-2.83083	1.04	0.84	0.078	0.028
3.785 ^(c)	-2.8471	-2.85257	0.39	0.25	0.021	0.007
4.0	-2.8537	-2.85852	0.21	0.085		
∞	-2.8615	-2.86165				

TABLE S1. Model environment energy increases from Hartree-Fock theory. (a) $U_{1g}^{SCF}(R_S)$ from Table II column 7 of [1] and from Table 2 column 6 of [2]. (b)Results labelled col 1 and col 2 derived from the data in the first [1] and second [2] numerical columns in this table. (c) $U_{1g}^{SCF}(R_S)$ for $R_S=3.785a.u.$ derived by linear interpolation of results for 3.0a.u. and 4.0a.u. (d) $\Delta U_{1g}^{SCF}(R_S)$ for R_S values of 2.0a.u, 3.0a.u and 4.0a.u. directly from Table 1 of [3]. Values for $R=2.5a.u.$ and 2.8a.u. derived by quadratic fits to the results for $R_S =2.0 a.u., 3.0 a.u.$ and 4.0 a.u. For $R_S=3.785,\Delta U_{1g}^{SCF}(R_S)$ prediction derived by linear interpolation between results for 3.0 a.u and 4.0 a.u.

The second and third columns report the results from two independent calculations [1, 2] of the near Hartree-Fock energies $U_{1g}^{SCF}(R_S)$ of the ground state of one Helium atom enclosed in a sphere of infinite potential energy and radius R_S . The corresponding energy increases $\Delta U_{1g}^{SCF}(R_S)$ caused by these confinements are presented in the fourth and fifth columns. These were derived from the data in columns 2 and 3 from

$$\Delta U_{1g}^{SCF}(R_S) = U_{1g}^{SCF}(R_S) - U_{1g}^{SCF}(\infty) \quad (S1)$$

The predicted increases are unreasonably large for the smaller R_S values. This motivated the modification, called the padded box model, in which the infinite potential is replaced by a constant finite value $[v_0(R_S)]$. For the ground state of a helium atom in padded spherical boxes, the last two columns of Table S1 present the respective predictions for $\Delta U_{1g}^{SCF}(R_S)$ for two values (zero and -0.2) of $v_0(R_S)$. The results for the R_S values of 2.0a.u., 3.0a.u. and 4.0a.u. were taken directly from Table 1 of [3] whilst the remainder were derived here from those values by interpolation as described in footnotes (d) and (e). The R_S values of 3.785a.u., 3.0a.u. and 2.8a.u. correspond closely to densities (n) of 0.022 (liquid density), 0.04 and 0.05 atoms \AA^{-3} covering the density range examined in the present computations. The values of $\Delta U_{1g}^{SCF}(R_S)$ produced, are significantly smaller than those resulting from the infinite potential model being not dissimilar to those predicted by the Hartree-Fock computations presented in Table VI of [4] where the largest increase arising from the interaction of a central helium with twelve neighbours is 0.0121eV.

It has been assumed in our calculations that the purely intra-atomic correlation energy of a ground state helium atom in a bulk condensed phase is the same as that of an isolated atom. The only computations probing this assumption are two sets in which the environment is modelled using the infinite potential spherical box model. In this approach, the change ($\Delta U_{1g}^{corr}(R_S)$) in the correlation energy of one such atom on entering the bulk phase from the free atomic state is calculated as the difference between the free atom correlation energy and that predicted with a confining potential of radius R_S .

$$\Delta U_{1g}^{corr}(R_S) = U_{1g}^{corr}(R_S) - U_{1g}^{corr}(\infty) \quad (S2)$$

$R_S(a.u.)$	$U_{1g}^{corr}(R_S)$ a.u.		$\Delta U_{1g}^{corr}(R_S)$ eV. calc from	
	[5]	[1]	[5] data	[1]data
2.0	-0.0401	-0.0383	0.027	0.071
3.0	-0.0402	-0.0420	0.024	-0.030
4.0	-0.0407	-0.0419	0.011	-0.027
∞	-0.04109	-0.0409	0.0	0.0

TABLE S2. Infinite potential box model ground state correlation energies

The $U_{1g}^{corr}(R_S)$ and $U_{1g}^{corr}(\infty)$ from [5] are taken from their Tables III and V respectively with the $U_{1g}^{corr}(R_S)$ originally computed in [6] being taken from the results in Table III of [5]. The reference [1] free atom $U_{1g}^{corr}(R_S)$ presented above is the difference between the “exact” energy in their Table III predicted from their wavefunction ψ_4 and the Hartree-Fock value in Table II from the wavefunction ψ_5 .

For $R = 2.0$ a.u. the $\Delta U_{1g}^{corr}(R_S)$ from the [1] data is smaller than that of [5] because the ‘exact’ energy of [5] is lower than that of [1]. For the two larger R_S values the $U_{1g}^{corr}(R_S)$ of [1] are more negative than those from [5] because the Hartree-Fock values [25] used in [5] are more negative than those reported in [1]. These observations suggest that the results of [5] are more reliable than those of [1]. The result that the infinite box model seriously overestimates the effect of compression on the ground state Hartree-Fock energy indicates that the predictions for $\Delta U_{1g}^{corr}(R_S)$ will be also be very seriously overestimated. Thus it can be concluded that the true $\Delta U_{1g}^{corr}(R_S)$ will be an order of magnitude smaller than even the modest values presented in Table S2 and therefore negligible

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