Electronic structure of $InP/Ga_{0.47}In_{0.53}As$ interfaces

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The electronic structure of lattice-matched $InP/Ga_{0.47}In_{0.53}As$ heterojunctions has been studied for the three main crystallographic orientations (001), (110), and (111), using state-of-the-art local-density techniques, and treating the $Ga_xIn_{1-x}As$ alloy by the virtual-crystal approximation. The valence-band offset does not depend on the crystallographic orientation within our numerical accuracy (≈ 10 meV). Our results and, in particular, the orientation independence of the band offset are examined within a linear-response approach in which the interface is treated as a perturbation with respect to an average, periodic crystal. This approach also allows us to describe in a physically sound and quantitatively accurate way the effects of interfacial strain. The effects of disorder-induced and electron-correlation-induced self-energies are also briefly discussed.

The ternary alloy $Ga_xIn_{1-x}As$ grown on InP substrates forms at $x=0.47$ a high-quality lattice-matched heterostructure which is intensively studied at present in view of optoelectronic applications.[1,2] Band offsets at this interface have been measured using different techniques, yielding conflicting results. Optical-absorption and photoluminescence measurements[3] have given valence-band offsets (VBO's) ranging from 0.24 to 0.38 eV, whereas values from capacitance-voltage measurements[4] range from 0 to 0.36 eV. Recent experiments based on admittance spectroscopy have provided VBO's of 0.35–0.39 eV.[5]

Contrary to the large amount of experimental data for this system, no theoretical investigations have been performed so far from first principles;[6] the only theoretical prediction is due to Van de Walle[7] who found VBO's=0.35 eV within his model-solid scheme. We present here results of *ab initio* self-consistent-field (SCF) calculations for the VBO's, performed within density-functional theory (DFT) in the local-density approximation (LDA), using the virtual-crystal approximation (VCA) to describe the alloy. When interfacial strain is neglected, we find the same value of the VBO's (0.31 ± 0.01 eV) for the three main crystallographic orientations, i.e., (001), (110), and (111). Our results are then discussed in the framework of linear-response theory (LRT),[8] where the interface is considered as a perturbation with respect to an average, periodic crystal. This approach, which accounts for the above orientation independence, predicts that the VBO's are independent of the abruptness of the interface, and yields a natural partition of the VBO's into cation and anion contributions. When the effects of interfacial strain are then considered, LRT provides a quantitatively accurate and physically sound insight into the relevant mechanisms affecting the VBO's. The effects of alloying on the VBO's are finally discussed both within LRT, and performing SCF calculations for a model system in which the $Ga_xIn_{1-x}As$ alloy is described by a suitable ordered phase, instead of by the VCA.

As usual,[8,9] the VBO is split into two contributions: The first, the *electrostatic-potential lineup* ΔV, arises from the electron-density distribution at the interface and is defined as the difference between the average electrostatic potential on the two sides of the junction; the second, ΔE_v, is the difference between the valence-band edges resulting when the average electrostatic potentials in the two bulks are aligned. Due to the long range of the Coulomb interaction, ΔV depends in principle on the orientation and other geometrical and structural details of the interface, while ΔE_v is by definition a bulk property of the two constituents. The "difficult," interface-sensitive contribution to the VBO, ΔV, is a ground-state property of the interface and hence within the scope of DFT. The bulk contribution ΔE_v is instead a quasiparticle property which requires in principle a many-body calculation for the two bulks. In this paper we focus our attention on the former contribution, and only provide an estimate of the latter.

Our calculations are performed within the pseudopotential method, where the isolated interfaces are simulated using supercells. Plane-wave basis sets corresponding to a kinetic-energy cutoff of 12 Ry have been used; norm-conserving pseudopotentials and other technical details are similar to those used in Ref. 9. We use the virtual-crystal approximation for $Ga_{0.47}In_{0.53}As$ considering the anions and the virtual cations $X=\langle Ga_{0.47}In_{0.53}\rangle$ at their ideal lattice sites.

We start studying the (001) interface with a supercell of three double layers of each material, thus containing twelve atoms: We checked that this size is large enough to recover bulk features in the regions midway adjacent interfaces. We show in the left panels of Fig. 1 the planar and macroscopic[9] averages of the SCF supercell electron density and electrostatic potential; the corresponding value of the potential lineup is $\Delta V=-0.25$ eV. Adding to ΔV the quantity $\Delta E_v=+0.56$ eV obtained from DFT-LDA calculations for the two bulks corrected with experimental spin-orbit data,[10] we obtain $VBO_{(001)}=0.31\pm0.01$ eV. A convergence test performed at 16 Ry gives

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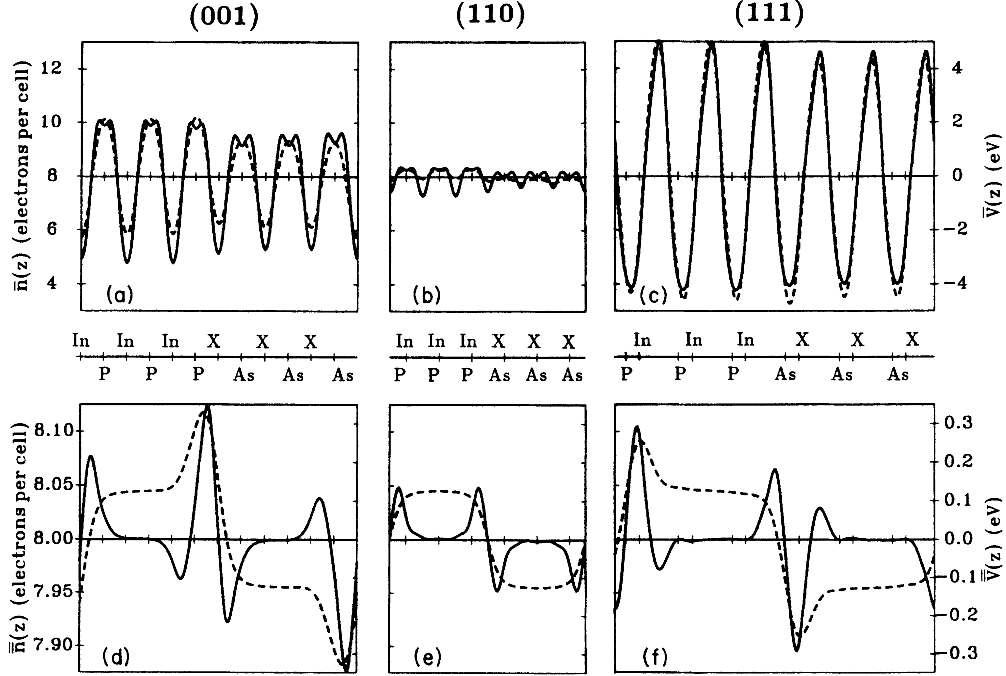

FIG. 1. Supercell electron density (solid line) and electrostatic potential (dashed line): Planar averages for (a) (001), (b) (110), and (c) (111) oriented heterojunctions; macroscopic averages for (d) (001), (e) (110), and (f) (111) oriented heterojunctions.

an equal variation of $+0.02$ eV for both the bulk term and the electrostatic-potential lineup, leaving the resulting calculated VBO unchanged.

In order to investigate the dependence of the VBO on interface orientation, we have also performed SCF calculations for 3+3 supercells oriented along (110) and (111). In the center and right panels of Fig. 1 we report the corresponding electron densities and electrostatic potentials. The different amplitude of the oscillations in the planar averages $\bar{n}(z)$ and $\bar{V}(z)$ reflects the different geometry of the three interfaces. The simple typical dipolar shape already found in other materials[8] can be recognized in the macroscopic average $\bar{\bar{n}}(z)$ for the (110) oriented heterojunction, whereas the charge distribution at (001) and (111) heterojunctions gives rise to more complicated and differently shaped interface dipoles. Despite the strong orientation dependence of the density profiles, their integrals give the same electrostatic-potential lineup within our numerical accuracy, and therefore the same VBO's, for all the three orientations.

The charge rearrangement at a general isovalent heterojunction with no common ions comes from both anionic and cationic contributions which interfere differently for different orientations. In order to isolate the anionic and cationic contributions, we study the two ideal heterojunctions CP/CAs and InA/XA, where "C" is a virtual cation whose pseudopotential is the average between the cationic pseudopotentials of the two bulks, i.e., $C=\langle In_{0.5}X_{0.5}\rangle=\langle In_{0.765}Ga_{0.235}\rangle$, and analogously for the virtual anion $A=\langle P_{0.5}As_{0.5}\rangle$. The results of SCF (001) supercell calculations for these two heterojunctions are reported in Fig. 2. The profiles of the anionic and cationic interface dipoles in CP/CAs and InA/XA heterojunctions have the typical simple dipolar shape, and the contributions to the electrostatic-potential lineup are $\Delta V_A=-0.61$ eV and $\Delta V_C=+0.36$ eV, respectively. Calculations performed for the common-anion and common-cation (110) and (111) heterojunctions show similar macroscopic averages as in (001) direction, and a complete orientation independence for ΔV, within our numerical accuracy.

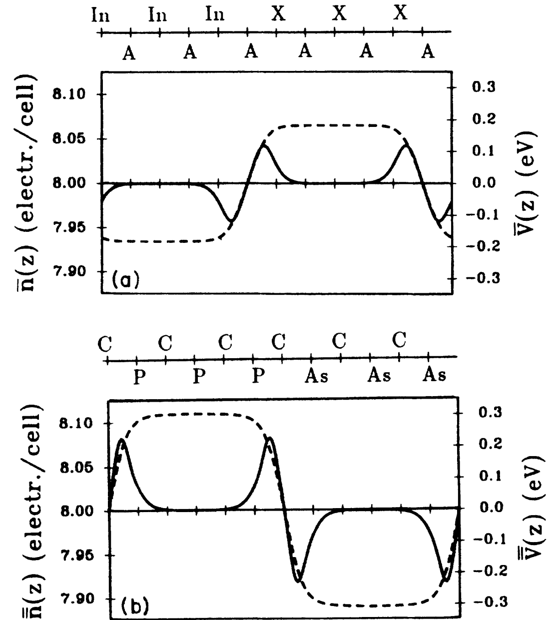

FIG. 2. Macroscopic average of the supercell electron density (solid line) and electrostatic potential (dashed line) of (001) oriented (a) InA/XA and (b) CP/CAs heterojunctions.

The interference of anionic and cationic effects is accurately described assuming linearity: Not only is the total lineup the sum of the anionic and cationic contributions, but even the fine details of the total charge-density profile are closely reproduced by superimposing the density profiles of CP/CAs and InA/XA interfaces centered at the appropriate atomic planes. This explains the different shapes of the macroscopically averaged charge densities obtained for different orientations: The total density profile is the sum of dipoles opposite in sign. These are shifted with respect to each other for (001) and (111) oriented heterojunctions, where anions and cations lie on different planes perpendicular to the growth axis; they are centered instead at the same position for the (110) orientation, where both ionic species lie on the same plane.

The additivity of anionic and cationic effects naturally suggests that this system can be described using linear-response theory. The LRT approach to semiconductor heterojunctions has been extensively discussed in Ref. 8, and we only recall here the relevant points. The real system (bulk, heterostructure, or alloy) is recovered from the virtual crystal CA upon replacement of the virtual cation C with a real one (X or In), and analogously the anion A with P or As. The total bare perturbation which leads from the virtual crystal to the real system is the sum of the localized perturbations which transform the virtual ions into the real ones: $\Delta v_A = \pm \frac{1}{2}(v_{\mathrm{P}} - v_{\mathrm{As}})$, and $\Delta v_C = \pm \frac{1}{2}(v_{\mathrm{In}} - v_X)$, for anions and cations, respectively. Within LRT, the electronic charge induced by a given perturbation is proportional to the charge of the perturbing potential. Hence, the above *isovalent* perturbations do not induce any net charge. Furthermore, because of tetrahedral site symmetry, the electron-density response $\Delta n^{(1)}(\mathbf{r})$ to any of the above perturbations does not carry any net dipole nor quadrupole. Therefore the long-wavelength behavior of the Fourier transform of $\Delta n^{(1)}(\mathbf{r})$ is

$$\Delta n^{(1)}(\mathbf{q}) = Aq^2 + \mathcal{O}(q^3) , \qquad (1)$$

where $A = -\frac{1}{6}\int r^2 \Delta n^{(1)}(\mathbf{r})d\mathbf{r}$ is the second spherical moment of the induced charge. Using the Poisson equation, together with Eq. (1), it is simple to show that—to linear order in the perturbation—the potential lineup at the $\mathrm{InP/Ga}_x\mathrm{In}_{1-x}\mathrm{As}$ interface is

$$\Delta V^{(1)} = \Delta V_A^{(1)} + \Delta V_C^{(1)} = \frac{4\pi e^2}{3\Omega}(A_A + A_C) , \qquad (2)$$

where Ω is the volume of the virtual-crystal unit cell, and A_A and A_C are the second moments of the density responses to anionic and cationic localized perturbations, respectively. The above neutrality and symmetry arguments naturally indicate that the potential lineup is not only independent of the crystallographic orientation of the interface, but even of its abruptness.

This linear-response approach has been pursued by calculating the response of the virtual crystal to a single ionic (anionic or cationic) substitution. This is done again by the supercell technique, considering face-centered cubic (fcc) cells whose linear dimensions are double those of a virtual-crystal unit cell, and therefore containing 16 atoms: out of them only a single virtual cation (or anion) is substituted with a real one. We show in Figs. 3(a) and 3(c) the contour plots of the linear electron-density response to a single $C \rightarrow$ In and $A \rightarrow$ P substitution, and the corresponding spherical averages in Figs. 3(b) and 3(d). The rearrangement of the electron density is almost confined within the primitive Wigner-Seitz fcc cell centered at the substitutional site, but there are also some non-negligible tails spilling out, as it is more perspicuous from the radial spherical averages. We also notice that the quadratic terms are quite small with respect to linear ones, and well confined within the primitive Wigner-Seitz fcc cell; higher-order terms are negligible. We have calculated the second moments of the linear charge-density responses to single cationic and anionic substitutions, obtaining $\Delta V_A^{(1)} = -0.58$ eV and $\Delta V_C^{(1)} = +0.34$ eV, so that the total electrostatic-potential lineup is—to linear order in the perturbation—$\Delta V^{(1)} = -0.24$ eV, in agreement with the value $\Delta V = -0.25$ eV obtained from SCF calculations for the 3+3 superlattices. Notice that quadratic terms do not contribute to the VBO's because they affect the average electrostatic potential by the same quantity on the two sides of the interface: This is due to our particular choice of the reference system.

The lattice-matching condition between InP and XAs arises from a balance between cationic and anionic effects. As a consequence, the PX and InAs bonds present at the interfaces need not be equal to the common bond length of InP and XAs. In fact, recent experimental evidence suggests that the interplanar PX and InAs interfacial spacings are close to what they would be in the corresponding bulk materials.[11] This situation can be described as a kind of *microscopic* strain which is confined in the interface region. Outside this region, the two bulks show a relative displacement with respect to the ideal cubic geometry considered so far. The effect of this *interfacial strain* on the VBO's can be estimated within LRT. The basic ingredients of such an estimate are the dipoles (i.e., Born effective charges, Z^*) and quadrupoles linearly induced by the displacement of a single ion in an otherwise perfect crystal.[12] As an example, we consider the simple case of the (001) interface, where we assume that only the bonds across the interface are strained. In this case, quadrupoles do not affect the VBO's, whereas the dipolar contribution is

$$\Delta V_{\mathrm{strain}} = \frac{4\pi e^2 Z^*}{a\epsilon_\infty}\left[\frac{u}{a}\right] , \qquad (3)$$

where a is the equilibrium lattice spacing of the crystal, ϵ_∞ its electronic static dielectric constant, and u the variation of the interplanar spacing across the interface. A simple proof of Eq. (3) can be given as follows. Consider the displacement of a single ionic plane in an otherwise perfect zinc-blende CA crystal: The induced dipole determines a potential drop between the two sides of the plane equal to $\Delta V_u = (8\pi e^2 Z^*/a\epsilon_\infty)(u/a)$.[13] Such a displacement can be seen as the result of two steps: In the first one ideally stretches a given CA interplanar spacing leaving all the others unchanged; in the second, one squeezes the next AC spacing. Each one of these two steps describes the simplest interface configuration displaying *interfacial strain*. As the anionic and cationic effective

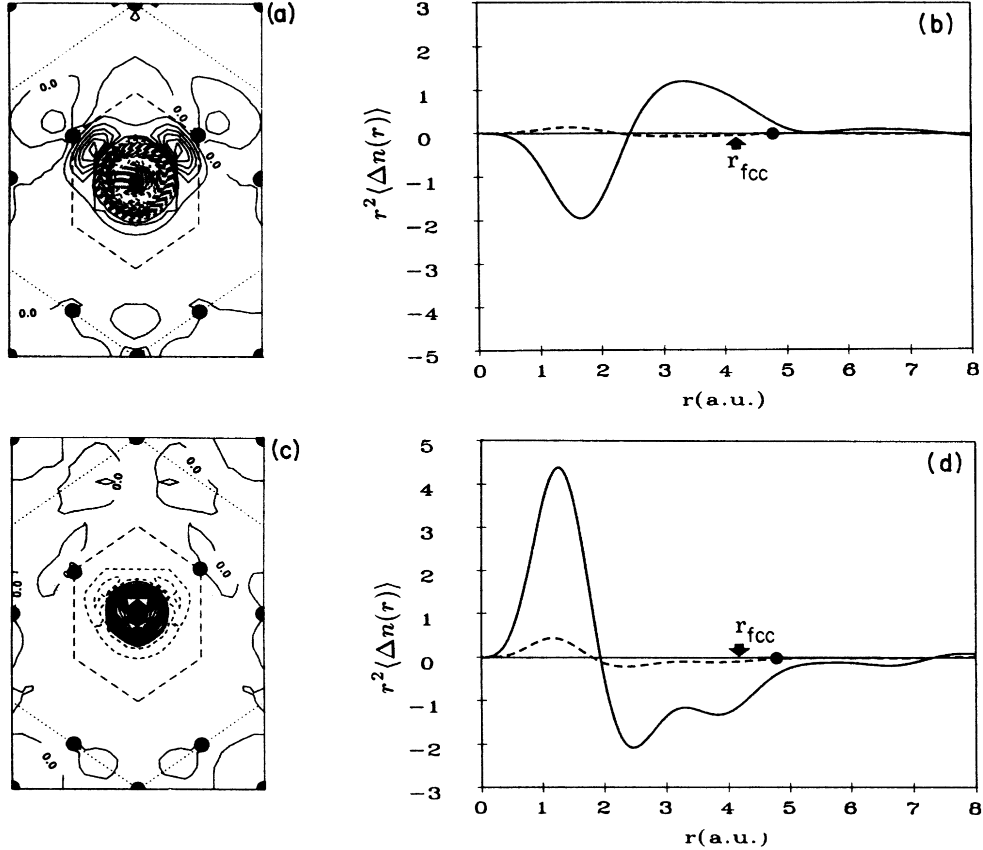

FIG. 3. Electron density response of the *CA* reference crystal to a single ionic substitution $C\rightarrow$ In and $A\rightarrow$ P (units are electrons per fcc unit cells): (a) Contour plots in (110) plane of the linear term $\Delta n_P^{(1)}(\mathbf{r})$ (solid lines indicate positive values, dashed lines negative); the intersection of the plane with a *P*-centered Wigner-Seitz primitive (two-atom) fcc cell (dashed line) and 16-atom fcc cell (dotted line) are also indicated. (b) Radial spherical average of the linear (solid line) and quadratic (dashed line) terms of $\Delta n_P(\mathbf{r})$; the average radii of the bulk Wigner-Seitz fcc cell and the distances of the nearest neighbors from the *P*-site are also indicated. (c) and (d) as (a) and (b), but for the $A\rightarrow$ P substitution.

charges are equal in magnitude and opposite in sign, the two steps must result in the same net potential drop ΔV_{strain}, which equals therefore one-half the drop induced by the displacement of a single plane. Explicit SCF calculations performed for test cases show that Eq. (3) provides a quite accurate estimate of the effect of interfacial strain on the VBO's: $\Delta V_{\text{strain}} \approx 7\times 10^3$ (u/a) meV. The determination of the (meta)stable configuration which actually minimizes the interface energy as a function of the ionic coordinates is deferred to future work; however, a first estimate can be obtained from the experimental data:[11] X-ray-diffraction spectra fitted with a simple model including interfacial strain extending only over one molecular layer suggest $(u/a)=0.009$, which corresponds to $\Delta V_{\text{strain}} \approx 60$ meV as estimated from Eq. (3).

The main sources of inaccuracies of our calculations are the use of the *VCA* for describing the $Ga_xIn_{1-x}As$ alloy, and the neglect of many-body effects in the bulk-band contribution to the offset, ΔE_v. To discuss the former, we consider for simplicity the alloy $Ga_{1/2}In_{1/2}As$. The perturbation leading from the virtual crystal $\langle GaIn\rangle As$ to the real alloy consists of a number of localized perturbations transforming the virtual cation $\langle GaIn\rangle$ into Ga, and in an equal number of *opposite* perturbations transforming it into In. It is evident that—to linear order— the two cancel each other on the average, and thus the *VCA* correctly predicts the potential lineup within LRT. Let us consider then second-order contributions to the lineup. The electrostatic-potential response to a given collection of *localized* perturbations $[\Delta v_i \equiv \Delta v(\mathbf{r}-\mathbf{R}_i)]$ contains both on-site diagonal terms ($\propto \sum_i \Delta v_i^2$), and off-site quadratic terms ($\propto \sum_{i\neq j}\Delta v_i \Delta v_j$). The latter are very complicated quantities because, besides a quadratic response function, they depend on the pair-distribution function of the alloy. Inspection of Fig. 3, however, shows that the quadratic response to a single impurity in the virtual crystal is well localized within an elementary cell, and we can safely assume that off-site quadratic contributions to the lineup are quite small. Corrections to the *VCA* prediction of the lineup due to the former, on-site quadratic terms do not depend on the actual microscopic configuration of the alloy, and they are quite easy to calculate. We have estimated them by calculating the second spherical moment of the quadratic response to the localized perturbations displayed in Fig. 3. The resulting correction to the potential lineup is ≈ 50 meV. In order to test this figure, we have also calculated the lineup between InP and a $(GaAs)_1(InAs)_1$ superlattice which simulates an ordered

phase of the corresponding alloy. The difference between the resulting lineup and that previously calculated by the *VCA* is ≈ 60 meV, in good agreement with the above estimate. A further correction to *VCA* predictions comes from internal distortions present in the $Ga_xIn_{1-x}As$ alloy, where the individual bond lengths are actually intermediate between those of the pure materials (GaAs and InAs) at equilibrium and the ideal ones assumed in this work.[14] To linear order in the displacements, these effects cancel on the average in the bulk random alloy, but not necessarily at the interface. Of course, corrections beyond the *VCA* not only affect the potential lineup ΔV, but also the bulk-band contribution to the offset ΔE_v. A precise estimate of the latter would require the study of disorder-induced self-energy corrections in the bulk alloy, which is beyond the scope of the present paper. A rough estimate of these self-energy corrections is obtained comparing the top of the valence band in the virtual crystal *X*As and in the $(GaAs)_1(InAs)_1$ monolayer superlattice, considered as an extreme case of ordered alloy. The resulting correction amounts to ≈ -40 meV. This partially cancels the correction to the potential lineup, giving a total positive correction of $\approx +20$ meV to the VBO's.

The other important correction to the computed VBO's comes from the inadequate treatment of many-body effects in the LDA.[15] Recent studies for GaAs/AlAs (Ref. 16) have shown that many-body corrections beyond LDA affect the VBO's by 0.12 ± 0.02 eV in this system. No calculations are available for InP, nor for $Ga_xIn_{1-x}As$. Scaling the corrections of Ref. 16 with the difference of the reciprocal dielectric constants of the bulk materials,[17] we estimate many-body corrections to be ≈ 80 meV for the system under consideration here.

We conclude by summarizing the main achievements of the present work. We have successfully applied a new linear-response approach to the study of the electronic structure of $InP/Ga_{0.47}In_{0.53}As$ lattice-matched heterostructure, where the $Ga_xIn_{1-x}As$ alloy is treated within the *VCA*. This approach naturally accounts for the additivity of anionic and cationic effects and for the orientation independence of the VBO's obtained from accurate state-of-the-art DFT calculations. Our LRT approach also gives a simple, sound, and accurate description of the effects of interfacial strain which is present when the two-lattice-matched (pseudo) binary materials have no common ion. Corrections to the *VCA* are then discussed both within our LRT scheme, and also simulating the alloy with an appropriate ordered phase in full SCF calculations.

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